**SYMPOSIUM BI01**

*Materials Research by the LGBTQIA+ Community and a Vision for Inclusivity*

April 23 - April 24, 2024

**Symposium Organizers**

Andrew Cairns, Imperial College London
Brett Helms, Lawrence Berkeley National Lab
Amanda Morris, Virginia Polytechnic Institute
Julia Ortony, University of California, San Diego

**Symposium Support**

Bronze
JEOL USA

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* invited paper

** MRS Communications Early Career Distinguished Presenter

** Keynote Speaker

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10:30 AM *BI01.01.01*

**Materials Discovery One Standard Deviation from The Mean: Finding Avalanches in Nanoparticles**

Bruce E. Cohen; Lawrence Berkeley National Laboratory, United States

The first applications of luminescent nanocrystals to bioimaging were semiconductor quantum dots with optoelectronic properties that largely mirrored those of organic compounds, but with substantially increased stability and brightness that have enabled single molecule and other challenging imaging applications. Building on this success, newer nanocrystals have been engineered with optical properties unlike anything found in traditional probes, including perfect photostability, anti-Stokes emission a billion-fold more efficient than 2-photon excitation, and most recently, photon avalanches hosted within nanostructures. Avalanches are steeply nonlinear events in which outsized responses arise from a series of minute inputs. With light, photon avalanching (PA) had been observed only in bulk materials and aggregates, often at cryogenic temperatures, preventing its application to bioimaging. In two recent studies, we describe the engineering and imaging of avalanching nanoparticles (ANPs), which are ~25-nm Tm3+-doped NaYF4 upconverting nanoparticles that efficiently convert near infrared excitation to higher energy emission. Avalanches are steeply nonlinear events in which outsized responses arise from a series of minute inputs and, with light, photon avalanching had been observed only in bulk materials, often at cryogenic temperatures. The extreme nonlinearity of ANP emission enables sub-70 nm spatial resolution using only simple scanning confocal microscopy and before any computational analysis. Two-way NIR photoswitching of ANPs enables full optical control of photodarkening and photobrightening, and we find indefinite photoswitching of individual nanoparticles in ambient or aqueous conditions without measurable photodegradation. This enables unlimited photon collection for calculation of sub-Ångstrom localization accuracies, and we can distinguish individual ANPs within tightly packed clusters. For application of ANPs to live-cell imaging, we have developed synthetic chemistry-free methods for conjugating engineered antibodies to NP-surface SpyCatcher proteins, which bind and spontaneously form covalent isopeptide bonds with cognate SpyTag peptides. This enables controlled and irreversible attachment of antibodies to nanoparticle surfaces, for specific targeting of cell-surface receptors in quantitative live-cell study of their distribution, trafficking, and physiology.


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11:00 AM *BI01.01.02*

**Design of Iron Oxide Nanocatalysts for The Magnetic Induction-Assisted Degradation of Emergent Contaminants**

Alvaro Gallo Cordova, Belen Corrales-Perez, Jesus G. Ovejero and M. Puerto Morales; Instituto de Ciencia de Materiales de Madrid, Spain

The application of nanomaterials in environmental remediation is of utmost importance in addressing the pressing ecological challenges of our time. Nanomaterials offer unique advantages, such as their high surface area and reactivity, which make them exceptionally effective in adsorbing, degrading, and immobilizing various pollutants in air, water, and soil. Within these nanomaterials, iron oxide nanoparticles (IONPs) stand out as great alternatives due to their low price, biodegradability and magnetic properties. Specifically, IONPs when subjected to alternating magnetic fields (AMF), generate localized heat through their physical motion or rotation of their magnetic moments [1]. This controlled heating can be harnessed to accelerate the degradation of various pollutants, including emerging contaminants (e.g. microplastics, antibiotics, cosmetics, etc.). Furthermore, the ability to manipulate the nanoparticles’ movement through the application of external magnetic fields enables reduced operational costs for separation processes, while minimizing ecological disruption.

In this study, we developed a catalytic system via the polyol process, designed specifically for the magnetic induction-assisted degradation of organic matter. The resulting nanocatalyst (NC) displayed a multi-core structure measuring 40 nm, comprising small magnetic cores of 12 nm each [2]. These magnetic cores exhibited a well-ordered crystalline aggregation, which contributed to a collective magnetic behavior, enhancing magnetic induction heating and facilitating efficient separation due to the substantial magnetic moment per particle. To assess the industrial applicability of this approach, we successfully scaled up the production of NCs to a gram-level with remarkable reproducibility in terms of both structure and magnetic properties.

The scaled NCs were used for the magnetic induction-assisted degradation of microplastics (MPs). For this purpose, polyethylene MPs were extracted from a commercial facial scrub and we investigated a combined treatment approach for their degradation. Initially, we subjected the MPs to a hydrolysis process at 150 °C, breaking them down into monomers. Subsequently, we conducted a Fenton-like reaction, employing the as-prepared NCs in the presence of hydrogen peroxide, to degrade the hydrolyzed molecules via highly oxidative species. To assess the efficacy of this process, we monitored the changes in the Total Organic Carbon (TOC) content of the supernatant before and after each stage, which provided insights into the MPs’ degradation.

Notably, we observed that the mineralization of TOC was temperature-dependent, increasing from 20 to 65% at room temperature (RT) and 90 °C. This yield saw a further boost when employing IONPs as a heat source under the influence of an alternating magnetic field, likely attributable to the creation of hot spots on the surface at temperatures exceeding 80 °C.

In general, the use of magnetic nanoparticles in environmental remediation processes brings the advantages of magnetic induction heating, which can significantly reduce energy consumption and enhance the overall catalytic efficiency. As we continue to tackle the challenges of diminishing contamination and advancing sustainable energy solutions, magnetic nanoparticles represent a compelling avenue for achieving environmental remediation, making them a promising technology with the potential to reshape our approach to mitigate climate change.

**Acknowledgements**
The Future of Industrial Decarbonization and Nanotechnology through Atomic Layer Processing

David S. Bergman; University of Washington, United States

Recent years have seen a surge of interest in the development of scalable tools for nanomaterials synthesis. Many emerging technologies, like solar cells, batteries, catalysts, and membranes, rely on atomically-precise materials design to operate effectively. Tools for creating these materials with increased scalability and decreased costs are thus required to enable the widespread adoption of these technologies. One suite of tools, known collectively as atomic layer processing (ALP), is particularly interesting for nanomaterials synthesis, due to its ability to create ultrathin films with sub-nanometer thickness and compositional control. ALP has also been used in the semiconductor industry over several decades, making it easy to deploy in other manufacturing processes. Commercial solar panels and battery electrodes have already started to incorporate ALP-deposited films as passivation layers. However, as demand for nanotechnology increases, there is a continued need to expand the library of materials that can be made with these tools and to accelerate the pace with which these materials are deployed.

In this presentation, in addition to highlighting my journey navigating the academic job search as a gay scientist, I will highlight how my research group at the University of Washington is expanding the applicability of ALP to create new technologies in sustainability. First, the use of vapor phase infiltration (VPI) to modify polymers will be discussed, highlighting our work to make polymer membranes conductive and to upgrade their chemical and thermal stability. Next, I will describe how molecular layer deposition (MLD) can be used to create hybrid organic-inorganic thin films, exploring our work to make atomically precise catalysts for improved electrochemical stability and activity. Last, I will describe how high-throughput materials testing is needed for rapid materials deployment, exploring our group’s work to construct a high-throughput deposition system and to collect data on processing conditions into a database for additional analysis. Through these projects, our group expects to greatly expand the library of materials accessible to ALP and improve the speed with which these new materials can be translated into commercial technologies.

Materials Science Challenges in Ocean-Based Carbon Removal Solutions

Kristin M. Poduska; Memorial University, Canada

There is a critical knowledge gap in understanding the kinetics and mechanisms of mineral formation and degradation in the context of potential technologies that are targeted for carbon capture, utilization, and storage [1]. Both crystallization and dissolution of carbonate minerals figure prominently in many such climate-change-mitigation strategies that aim for carbon dioxide removal. For example, different approaches to ocean-based alkalinity enhancement involve processes that depend on mineral surface and interfacial chemistry in order to increase water pH with concomitant atmospheric carbon removal. In this context, I will describe my team’s work related to tracking changes in carbonate mineral phases, including surfaces and bulk structures, due to dissolution and recrystallization processes. In doing so, I will emphasize the urgent need for collaborations between researchers who do foundational materials science with those involved in developing monitoring, reporting, and verification protocols for potential carbon dioxide removal strategies.


3:45 AM A510.01.01

Exploring the Effects of Neutron Activation on Noble Metal Nanoparticles

Simon Scheid; Liane M. Moreau and Debashree Roy; Washington State University, United States

Gold nanoparticles are widely explored for applications in energy and medicine. One potential application of gold nanoparticles is the use of Au-198 nanoparticles as effective agents in prostate cancer therapy. One challenge to the synthesis of such nanoparticles is the high radioactivity and short half-life of beta-emitting Au-198 as a radiotherapeutic isotope. One solution towards generating Au-198-containing nanoparticles would be to use in-situ neutron activation of Au-197 nanoparticles. This would reduce the need to handle active material and open up options for the wide library of Au nanoparticle morphologies and ligand chemistries that have been developed. Unfortunately, to date, there is not a comprehensive understanding of how Au nanoparticles would behave in the high temperature high-neutron-flux environment of a nuclear reactor. In our studies, we are looking at Au nanoparticle structure pre- and post-irradiation within a nuclear reactor. We are using both morphology and local-structure techniques to evaluate the change in chemistry that occurs upon irradiation. In particular, SAXS and TEM will be used to analyze nanoparticle size and shape changes and XAFS and gamma spectroscopy will be used to characterize composition and local structure changes upon irradiation and beta decay of Au-196 into Hg-198.

As an LGBTQ-identifying researcher, I am deeply committed to fostering an inclusive and diverse environment within the STEM research community. It is crucial to acknowledge that embracing a broad spectrum of identities not only enriches the fabric of our scientific endeavors but also serves as a cornerstone for dismantling the challenges faced by LGBTQ+ scholars and other marginalized groups within this field. In the past, my identity has often led me feeling alienated and unwelcome in academic spaces. In primary and high school, I had to hide who I am and who I like. The schools were filled with bigotry towards the LGBTQ+ community, which led me not knowing if I was “normal” in comparison to others. This along with my parents being unsupportive of who I am made it hard for me to be excited about academia and STEM even though it’s a passion of mine. In college, I have had to actively search for spaces that are explicitly LGBTQ+ friendly, which has allowed me to discover more about myself due to being able to be the true me in these situations. Luckily, in the Moreau group, I have found a scholarly space that is exceedingly accepting and inclusive of all identities. Inclusivity is more than a mere act of acceptance; it is the active cultivation of an environment where everyone can engage in their scholarly pursuits without fear of prejudice or discrimination. When the research community honors and respects the identities and experiences of all its members, it not only amplifies creativity and innovation but also empowers individuals to bring their authentic selves to their work. This authenticity, in turn, drives excellence and propels scientific progress.

8:45 AM A510.02.02

Modeling Small Polaron-Induced Ultrafast Ferroelectric Relaxation in BiFeO₃

Xiaoxiao Li¹ and Wei Xiong²; ¹University of Washington, United States; ²University of California, San Diego, United States

In this report, we employed a combination of ultrafast spectroscopic techniques and high-level calculations to uncover the complex interplay between electronic lattice degrees of freedom in a class of strongly correlated materials. Our observations revealed a transient reduction in the electronic dipole upon optical excitation, which then recovers on 0.5 and 10 ps timescales. Time-dependent density functional theory calculations show that both ligand-to-metal charge transfer and local excitation transitions can be excited. The transient UV dynamics captured both ultrafast free carrier relaxation toward excitation and polaron formation. Multiphase configuration interaction calculations suggest that only polaron formation is associated with the 0.5 ps electronic dipole relaxation, while the faster electronic relaxation does not contribute to changes in ferroelectric properties. Our results decode the multi-dimensions of freedom associated with this ultrafast ferroelectric relaxation and pinpoint the critical motion—local polaron formation—essential for rapid ferroelectric relaxation. These findings offer crucial insights into the specific relaxation dynamics of modulating the properties or phase transitions of strongly correlated materials.

1:15 AM A510.03.03

Elimination of Tg-Confinement Effects and a Recently Revealed, Technologically Important Interfacial Phenomenon in Styrene-Based Random Copolymers Containing 2-Ethyl Hexyl Acrylate

John M. Torkelson; Northwestern University, United States

For two decades, i.e., slightly more than half of my professorial career, my research group has been interested in nanoscale confinement effects and the important roles of polymer interfaces, including the polymer-air interface or free surface, polymer-substrate interface, and polymer-polymer interface, on polymer dynamics. Much of this work has concerned confinement effects on the glass transition temperature (Tg) and physical aging. With ultrathin polystyrene (PS) films, the free surface plays a significant role in perturbing polymer chain dynamics, with Tg decreasing significantly with decreasing thickness below ~100 nm. Past studies by my research group have shown that changes to the PS chain architecture, from linear PS coils to cyclic PS chains with no chain ends, dense PS brushes, or PS bottlebrushes eliminate the Tg-confinement effect in PS films as thin as ~15 nm. However, such unusual polymer architectures are unlikely to be mass produced or adopted at large scale because of complex syntheses and purification steps. Recently, we have demonstrated that such Tg-confinement effects can be eliminated in simple styrene (S)-based random copolymers containing very low levels (2 mol%, 6 mol%) of 2-ethyl hexyl acrylate (EHA). Related results are obtained with ultrathin films of 4-methyl...
The valorization of lignin-derivable (LD) small molecules to polymeric materials offers a promising avenue to reduce dependencies on petrochemical feedstocks in material design. However, challenges in achieving semicrystallinity and material circularity of chain-growth, LD macromolecules have limited the practical application of lignin-based polymers. Here, we describe strategies to address these through considerations in LD monomer design. First, we demonstrate the development of LD vinyl monomers that can undergo living polymerizations to yield stereoregular, semicrystalline macromolecules. Tailored monomer design enabled polymerization under mild synthesis conditions and gave rise to desirable crystallinities and thermal properties in the resulting macromolecules. Then, we detail the development of advanced recycling methods to thermally deconstruct high-glass-transition temperature (> 100 °C) LD polymethacrylates and their constituent monomers in high yields and purities. Understandings of the polymethacrylate surfactants underlying depolymerization enabled bulk chemical recycling to monomers that were then upcycled to value-added polymers. The discoveries described herein offer pathways to broaden the application potential of LD macromolecules and design circular LD polymeric materials.

10:00 AM BREAK

10:30 AM *B101.02.05
Superconducting Thin-Films for Quantum Devices with Off-Line Quality Assessment 
Clara M. Barker, Finn Squires and Susannah C. Speller; University of Oxford, United Kingdom
Quantum computers are capable of high-speed calculations, far superior to modern supercomputers. The data of each strand of the calculation does not need to be stored permanently, but challenges include maintaining the integrity of the data (coherence) for long enough for calculations to be performed with a low error rate. To increase coherence times to useful values for multi-qubit systems, research has focused on the design of resonators and qubits, often overlooking the design of the materials used [1]. Smart materials selection and control of the chemistry and microstructure to optimise the Q-factor of the resonators (ratio of stored energy to input energy) and increase coherence times can help make superconductor-based quantum computers more viable.

Most materials used in quantum circuitry are selected for ease and reliability of deposition of multi-layered JJ structures with reasonable superconducting properties. However, it is known that other materials may have better properties if they could be optimised. For example, control of deposition flux can affect the surface roughness of a material, a parameter that can increase surface resistance and reduce the Q-factor of a quantum resonator. The structure and chemistry of the material can also impact superconducting properties. For example, changes in crystal structure, degree of crystallinity, crystallographic texture and chemical composition can affect the critical temperature of the superconductor of the film. A systematic study of carefully controlled deposition properties, linking film growth and superconducting properties, would be invaluable for assessing alternative materials for quantum resonators.

In this presentation, the results of a thorough, systematic study of the growth of superconducting materials of merit for use in quantum circuits will be reported. This study links growth parameters, material properties and superconducting performance. Initially, metal thin films- specifically niobium and molybdenum - have been deposited using magnetron sputtering, with the aim of fully understanding the deposition window before moving on to more complex materials, such as alloys and nitrides. These thin films have been analysed using SEM, XRD, XPS and AFM to determine microstructural and crystallographic properties. Electrical transport measurements have been performed to determine room temperature resitivity, transition temperature and transition width, critical field and critical current. We also aim to present preliminary low temperature temperature measurements on resonators devices.

Conditions for the growth of high-quality superconducting films will be identified and this presentation will explore any links between deposition properties and material properties, to assess whether high quality room temperature and low temperature properties can be used to predict ultra-low temperature performance of materials for quantum devices.


11:00 AM B101.02.06
Modification of Perovskite Solar Cell Architecture to Increase Thermal and Mechanical Resilience 
Melissa Davis, Kelly Schutt, Duong Nguyen-Minh, Kaitlyn VanSant, Axel F. Palmstrom and Joseph Luther; National Renewable Energy Laboratory, United States
On the cusp of commercialization and market breakthrough, perovskite solar cells have emerged as a competitor to silicon technology. Their efficiency rivals commercial products and the decreased energy for production and overall cost give perovskite solar cells an edge. However, parts of this technology still require improvement, in particular addressing their thermal and mechanical instability. These instabilities can give rise to device degradation. Comprehensive knowledge of these degradation mechanisms is required to address and solve these downfalls. In this research, we present the results of a myriad of tests, including water contact angle, kelvin probe, and double cantilever pull apart tests, designed to address these issues. As a result of the connection between instability and decreased performance, we have correspondingly altered the device architecture of standard p-i-n perovskite solar cells to improve performance. More specifically, thermal stability of devices was studied with the use of water contact angle and kelvin probe tests. Modified hole transport layers, or HTLs, were developed to ease delamination seen during tests due to thermal stress. The mechanical stability of devices was tested with double cantilever beam tests to determine mechanical weak layers. Additional modifications were added to the electron transport layers, or ETLs, to address the mechanical instability. With the adoption of these modifications within the HTL and ETL weak layers, this research introduces perovskite solar cells with improved thermal and mechanical resilience. These improvements will aid in this technology’s path to commercialization.

11:15 AM B101.02.08
Teaching Density Functional Theory to Students of Art Conservation 
Joseph W. Bennett; University of Maryland Baltimore County, United States
As an assistant professor at the University of Maryland, I have been teaching density functional theory (DFT) to students of art conservation and am aware of the multitude of issues surrounding diversity, equity, inclusion, and the university level. My chosen field in STEM is computational materials chemistry and an aim that plagues this field is diversity in students, specifically their identities and backgrounds. This is why I’ve spent 3 summers as an instructor for the Baltimore SCIART program, teaching computational methods to students interested in art conservation science. While many of the students in the program identify as LGBTQIA+, the majority of students that have learned to compute surface interactions are women. Funded by the Andrew W. Mellon Foundation, the Baltimore SCIART Consortium offers a 10-week summer research experience for undergraduate students at the interface between science and art and has been developed for students from Baltimore area academic institutions with a diverse background and strong interest in art conservation science and engineering. The development of density functional methods as a nondestructive probe to study works of art is still in its infancy and here, I will discuss aspects of our inclusive teaching pedagogy and our recent successes both computing surface interactions of objects important to cultural heritage and student outcomes.

SESSION B101.03: Materials Research by the LGBTQA+ Community and a Vision for Inclusivity III
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**Session Chairs:** Ty Christoff-Tempesta and Alvaro Gallo Cordova
**Wednesday Afternoon, April 24, 2024**
**Room 326, Level 3, Summit**

1:30 PM B101.03.01
A Tale from The Queer Resistance: Activism from with(in) Materials Science 
Jeremy A. Yang and Eric Pop; Stanford University, United States
Broader sociopolitical movements toward inclusivity and belonging have brought attention to LGBTQA+ issues in materials science, including the marginalization of LGBTQA+ materials scientists and their views within the field. Previous work on LGBTQA+ students in engineering disciplines highlights the continued struggles for non-straight, non-cisgender people in STEM [1]. In this talk, I [JAY] present my current research in both materials science and engineering education while navigating my interdisciplinary journey straddling two vastly different fields of study. As a cisgender, gay, Asian-American man, my dual existence within both the materials science and engineering education research disciplines has given me unique insights into the nature of science and has substantially informed how I conceptualize equity and inclusivity in materials science.
The "Materiality" of Sexual Orientation and Gender Identity to Materials Science: Exploring LGBTQ Participation in the Sciences

2:00 PM

et al., 33, 314 (1986).


References:

2:00 PM *BIO1.03.03

The "Materiality" of Sexual Orientation and Gender Identity to Materials Science: Exploring LGBTQ Participation in the Sciences

During the AIDS crisis and messages of moral urgency from climate justice groups today. The theory of change of these groups will also be discussed, with the presenter drawing from personal experience envisioning alternative futures, and the willingness to engage in transformative change. This talk will draw parallels between the messages of moral urgency from groups like Act Up during the AIDS crisis and messages of moral urgency from climate justice groups today. The theory of change of these groups will also be discussed, with the presenter drawing from personal experience as a queer scientist engaging in activism.

I contribute my work and my story to argue for two key elements in a vision for inclusivity in materials science: first, to look beyond quantitative metrics for "diversity" and uplift the work that marginalized people are doing to resist systemic inequities, and second, to spark conversations with (queer) social justice scholars outside of materials science, who can provide valuable insight into the equity challenges facing the discipline. Inclusivity rests on recognizing both the existing climate and the agency that queer people hold in materials science and centering marginalized voices in materials science policy. I acknowledge support from the National Science Foundation Graduate Research Fellowship for this work.

In the second part of this work, the development of these new family of materials will be compared, as an example, with my career in the materials science world, where being different has approached. The versatility and adaptability of this family of materials will be described, as an example of how the diversity in materials science is very relevant for progressing in this field.

In this presentation, I will summarize my research on LGBTQ participation within undergraduate STEM (Science, Technology, Engineering, and Mathematics) majors. My research delves into various facets of this phenomenon, shedding light on how LGBTQ undergraduates find a sense of belonging within the heteronormative landscape of STEM disciplines. Additionally, my research investigates the influence of LGBTQ students' social networks on their commitment to pursuing STEM majors as well as how identifying as LGBTQ shapes students' perceptions of future prospects within STEM careers. Collectively, these findings emphatically affirm that LGBTQ identities do, indeed, matter within the sphere of scientific endeavors. Moreover, this research underscores how the intricate interplay between different forms of privilege and oppression continues to structure participation in STEM fields in ways that impede the overarching goals of broadening participation in STEM. My talk will then conclude with concrete recommendations and take-aways to improve the climate within materials science as well as STEM broadly.

2:30 PM BREAK

The design of new materials for energy applications, is a fascinating field that combines in equal parts knowledge in materials science, imagination, risk, and openness to accept and adapt non-conventional ideas. In the first part of this work, a complete novel family of van der Waals materials based on pnictogen chalc-halides (Sb,Bi)(S,Se)(Br,I) will be presented, as an example of out-of-the-box compounds that in principle, does not fulfill the requisites to be excellent semiconductors for energy applications, but that in real are being revealed as very promising compounds. The most relevant non-standard properties of these materials will be presented for the first time, showing that non-conventional ideas can be widely accepted with the right approach. The versatility and adaptability of this family of materials will be described, as an example of how the diversity in materials science is very relevant for progressing in this field.

In the second part of this work, the development of these new family of materials will be compared, as an example, with my career in the materials science world, where being different has always been an extra motivation. I will explain how to be part of the LGBTQIA+ community has impacting in my research career from the very beginning, starting with my PhD, my postdoctoral experience abroad, and my consolidation as independent researcher, giving me an open mind character that I have also applied in my day-to-day work through the development of new materials. Currently, I'm leading a group of 20 very diverse scientists in Barcelona, working in the development of materials and devices for energy applications, from where I'm always very committed and proactive with the visibility of the LGBTQIA+ community, and where I have created a very safe space for the diversity. I will explain how I manage my visibility as a LGBTQIA+ community member, considering that I have coordinated several big European Projects with consortiums including the most relevant academic institutions, and I'm granted with a European Research Council (ERC) Consolidator Grant, which has help me to consolidate my position as Group Leader. I will also explain my interaction with my students, my colleagues in my Institution, and with collaborators worldwide, and how I apply my commitment with the diversity and visibility of the LGBTQIA+ community in my life, helping me to progress as researcher, but more important, as human being.

3:45 PM ROUNDTABLE DISCUSSION

SYMPOSIUM BIO2
Broadening Participation in Materials Research and STEM
April 22 - May 9, 2024

Symposium Organizers
Chartanay Bonner, The Joint School of Nanoscience and Nanoengineering
Lisa Neshyba, University of Washington, Chemistry Department
Kristen Rahilly, Oregon State University
Michael Scheibner, University of California, Merced

* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION BI02.01: Broadening Participation in Materials Research and STEM I
Session Chairs: Chartanay Bonner, Lisa Neshyba, Kristen Rahilly and Michael Scheibner
Thursday Morning, April 25, 2024
Room 326, Level 3, Summit

8:15 AM *BI02.01.01
Best Practices for Engaging HBCUs: Increasing URM Engagement in Materials Research Michael L. Curry1 and Michael Schwartz2; 1North Carolina Agricultural and Technical State University, United States; 2University of Wisconsin–Madison, United States

Only 7.7% of Chemists and 4.4% of Engineers in the US are Black, even though greater workforce diversity drives innovation and contributes to America's economic power. This warrants the exploration of new partnerships and approaches to maintain our competitiveness in the marketplace. Since its inception, Historically Black Colleges and Universities (HBCUs) have contributed to the nation's scientific and technological dominance by producing exceptional talent and cutting-edge research. HBCUs have had an unparalleled impact on the education and professional development of underrepresented minorities in chemistry, engineering, and related fields. While African Americans comprise 9% of the STEM workforce, HBCUs produce more than 24% of Black STEM undergraduates & 30% of Black science/engineering doctorates. Hence, finding new and innovative ways to tap into the human potential of the nation’s 101 Historically Black Colleges and Universities for mining and investment purposes is critical. In this discussion, we will explore best practices for partnering with HBCUs as a promising approach to increase broad participation in the Materials Research community.

8:45 AM BI02.01.02
When The University and City Hall Join Forces: The STEAM BSM_UPC Project Luis Carlos Pardo Soto1, Artur Paz1 and Alba Feria2; 1Universitat Politècnica de Catalunya, Spain; 2Barcelona de Serveis Municipals, Spain

Barcelona's iconic landmarks, including the Olympic Stadium, Gaudi’s Park Güell, the Zoo, and the amusement park Tibidabo, serve as the backdrop for a series of STEAM activities that bring together 6,500 students from across the Barcelona metropolitan area every year. This ambitious project is made possible by the collaboration between the academic expertise of a public university like the Polytechnic University of Catalonia and the public enterprise B:SM, which oversees from Barcelona's parking system to the Zoo or the amusement park. During these events, students aged 10 to 18 engage in a range of experiments and scientific shows tailored to the unique characteristics of each location.

For example, at the Zoo, students explore life and the materials that constitute it, such as DNA and the energy-giving substances essential for life. At the Olympic Stadium, chemistry concepts are taught through an interactive show, and physics is demonstrated through a blend of a contemporary dance quartet and a scientist. In the amusement park, mobile phone sensors are utilized to investigate the movements and forces behind the rides. At the world-renowned Park Güell, we investigate how Gaudi used materials inspired by nature.

However, the project doesn't end with students. Every year, we organize training courses for teachers and public shows designed for a broader audience. These shows feature unique presentations, such as one conducted by a physicist and a violinist or a jazz band exploring the connection between music and mathematics.

Overall, this highly successful project is the result of researchers stepping out of their labs and engaging with a broad audience, and the willingness of the town hall to organize and support such impactful scientific activities.

9:00 AM BI02.01.03
Utilizing Cross-Program Collaboration to Sustain & Enhance STEM Outreach Portfolios Mark Licurse, Ashley Wallace and Eric A. Stach; University of Pennsylvania, United States

Effective management and growth of STEM outreach programs remains an ongoing challenge for many organizations and institutions. While the goals of broadening participation are clear and commonly shared, there is little established guidance on how to build and sustain a successful portfolio of programs. Newly funded initiatives, especially, face pressure to quickly establish programs to compete with more experienced organizations and centers but can often overwhelm limited staff. We have recently implemented an innovative model that engages participants as active contributors to improving and sustaining our portfolio of outreach programs. Rather than treating each program in isolation, this approach specifically utilizes the diverse experiences and skill sets of program participants to enhance the activities and objectives of other programs within the same portfolio. In doing so, we believe this allows for a more robust set of programs to be created and supported. We highlight how this model was implemented for three of our core programs: a summer research experience for undergraduates, a research experience for high school teachers, and a summer camp for high school students focused on materials science and engineering. The integration and exchange across programs provides benefits and extends beyond the sharing of resources. It fosters an inclusive community in which participants contributions matter beyond just their own experience. While tested on materials research education and outreach programs, we believe this approach of utilizing participants' strengths to enhance a portfolio of programs could be applied to STEM outreach broadly across disciplines. Crucially, the model can be integrated into existing outreach efforts, leading to continuous improvement and increased impact over time.

9:15 AM BI02.01.04
The Emergence of Transdisciplinary Material Science in Diverse Applications: Towards The Development of Frameworks for Inclusive and Diverse Perspectives of Material Science Research and Education David Ryman1, Saquib Ahmed2,2 and Sankha Banerjee1,3; 1California State University, Fresno, United States; 2Buffalo State College, United States; 3University of California, Davis, United States

The field of material science is undergoing a transformative shift towards transdisciplinary approaches, demonstrating its relevance in a variety of applications. This shift is paving the way for the creation of comprehensive frameworks that foster inclusivity and diverse perspectives in material science research and education. By embracing a transdisciplinary perspective, material science is adapting to the complex and interconnected challenges of our time, promoting innovation and sustainability in a broader range of applications. This abstract provides an overview of the evolving landscape of material science, highlighting the importance of inclusive and diverse frameworks to advance the field and meet the evolving demands of modern society. The following work focuses on the transdisciplinary aspects of material science research and education in the areas spanning materials fabrication and their application in water treatment, biomedical devices, environmental impact, and economic assessment. It delves into the intersections of material science with these critical fields, emphasizing the need for a holistic
understanding of materials' roles in addressing contemporary challenges. By examining materials science through the lenses of water treatment, biomedical devices, environmental sustainability, and economic evaluation, this work contributes to a more inclusive and diversified approach, fostering a more profound comprehension of the pivotal role materials play in our interconnected world.

Moreover, this work extends its examination to the implementation of these approaches within the semiconductor industry. It sheds light on how these methodologies are being employed to enhance research, development, and education within this industry, ensuring the widespread dissemination of innovations and their potential to drive advancements in material science. By exploring the intersections of material science, using machine learning-based approaches, and diversity-related issues within the context of the semiconductor industry, this research contributes to a more inclusive, sustainable, and technologically advanced future.

9:30 AM BI02.01.05
How can TA Meetings Effectively Prepare TA Instruction? Eugenia S. Vasileiadou; Northwestern University, United States

A General Chemistry course consists of multiple components, amongst these are recitation and office hour sections. These sections are centered on enhancing students’ conceptual understanding and honing their problem-solving skills. Even without the current realization of online teaching, these objectives require a skillful synthesis of technical and pedagogical planning. The goal of this project was to examine how teaching assistant (TA) meetings can effectively prepare TA instruction in General Chemistry discussion sections with inclusive practices, considering an online teaching environment. Firstly, the challenging areas of virtual TA instruction were probed. Subsequently, five quarterly objectives for the TA meetings were determined related to the pedagogical and learning needs TAs reported. Accordingly, biweekly presentations serving the quarterly objectives were developed, containing pedagogical strategies and resources to aid TAs’ preparation for effective and inclusive instruction. Following the biweekly presentations, TAs completed a reflection journal based on a survey format, where overall 4 journal entries were requested. The TA reflection journal inquired if TAs accomplished the learning objectives of the biweekly presentation, as well as it included space for TAs to generate prompts and questions for the next presentation. Importantly, the TA reflection journal incorporated demographic information of TAs, where no corresponding demographics of graduate students had been collected in our Chemistry department prior. Altogether, utilizing the collaborative and informative nature of the TA meetings to the highest extent, serves as a vehicle for the pedagogical development of TAs to make effective instructional decisions that result in enhancing student learning.

9:45 AM BREAK

10:15 AM ROUNDTABLE DISCUSSION

10:45 AM BI02.01.06
Overcoming Technology Barriers and Incorporating Culturally Responsive Outreach in Materials Research Kyle Johnson,1,2 and Ngozi Ezeokeko,1; 1AVELA - A Vision for Engineering Literacy & Access, United States; 2University of Washington, United States

In 2020, 11% of undergraduate students in the University of Washington’s Materials Science and Engineering (MSE) department were from underrepresented minority (URM) backgrounds, with only 8% of graduate students in the department identifying as URM. In contrast, the URM population in Washington State was 21% in 2017, and 34% nationwide. High barriers of entry to the field of materials research limits who is learning about and gets involved in the field. For primary and secondary school students, these barriers include limited access to the expensive technologies required to perform materials research such as load frames, high magnification microscopes, and autoclaves. Not only is it difficult to have K-14 students engage with or research-based material science lessons in primary or secondary school, but inequitable access to technology for Black and Latine communities are compounded by persistent economic challenges, social injustices, and human rights issues. We present sociotechnical access inequalities for Black and Latine urban communities, and our findings show that many students are hesitant to engage with already available technologies due to a lack of enticing support systems. We analyze the AVELA (A Vision for Engineering Literacy & Access) nonprofit’s holistic student-lead STEM engagement model leveraging near-peer mentorship, experiential learning, mentor embodied community representation, and culturally responsive lessons. Through 24 semi-structured interviews with college AVELA members, an analysis of 171 survey responses from AVELA's secondary school class participants, and an autoethnographic analysis we evaluate the model's impact on decreasing sociotechnical access inequalities. Using data from AVELA’s 4 years of operation, where more than 200 university student instructors have taught to 2,500+ secondary school students in 110+ classrooms, we identify access barriers and provide principled recommendations for designing STEM education programs with a focus on material science lessons and activities.

11:15 AM BI02.01.07
Experimenta con PREM: Outcomes and Best Practices from a Two-Decade Materials Research Summer Program for Underrepresented High School Students Idalia Ramos,1 Jose O. Soto Esteva,1 Vibha Bansal2; Francisco Bezares3; Ezio Fasoli4; Mark Licurse5; Rolando Oyola1; Nicholas Pinto1; Juan Santana1; Eric A. Stach2 and Ashley Wallace3; 1University of Puerto Rico at Humacao, United States; 2University of Puerto Rico at Cayey, United States; 3University of Puerto Rico at Mayaguez, United States; 4University of Pennsylvania, United States

A long-standing partnership between the University of Puerto Rico (UPR) and the University of Pennsylvania (PENN) Laboratory for Research on the Structure of Matter aims at diversifying the materials research community by identifying and guiding students through a pathway from high school (and K-8) to STEM undergraduate programs, and then onto graduate school. The program is supported by the National Science Foundation Partnerships for Research and Education in Materials (PREM) program. The UPR-PENN PREM program targets women and students from disadvantaged backgrounds, such as low-income families, first-generation college students, and those living in geographically isolated areas in Puerto Rico, where the student population is approximately 99% Hispanic. The Experimenta con PREM (ECP) summer program for high school (HS) students is a highlight of the UPR-PENN PREM. Since 2005, this two-week research experience has attracted talented students to materials research. The program started at the Humacao campus of UPR and extended to the Cayey campus in 2016. To date, approximately 400 students (68% women), from 34 towns and 59 public schools in Puerto Rico have taken part in ECP. All of them graduated from high school, with 78% pursuing STEM fields. ECP aims to foster scientific literacy and inquiry skills among students and inspire them to pursue research-oriented careers. The experience is expected to be like what they would face in a Research Experience for Undergraduates (REU), from the application process to presenting their findings. The program introduces materials science as a field that welcomes diverse interests and skills, such as materials characterization, devices, soft matter, crystals, and experimental and theoretical-computational methods. Nine UPR faculty mentors create laboratory experiences that are closely aligned with their own PREM research and that incorporate, within the time constraints, the relevant aspects of conducting research such as literature review, data collection and analysis, report, and final oral presentation. In the laboratories, HS students work in groups of up to 4 members with constant guidance from the faculty researcher and undergraduate PREM students.

Before the research experiences, the students participate in a series of workshops that help them develop soft skills that are essential for scientific research, such as diversity awareness, public communication, and laboratory safety. Additional training includes hands-on workshops on scientific writing, programming, and spreadsheet skills. The PENN partners actively contribute to the learning experience. Graduate students, post-docs and faculty members from PENN give talks, workshops and interact with the students on various topics related to materials science. This presentation will cover the goals, components, and achievements of ECP, along with the challenges and lessons learned. We will discuss some of the best practices that emerged from our experience and how they can inform future initiatives in science education.

11:30 AM BI02.01.08
AfterSchool Academy and Teachers Camp for a Diverse Undergraduate Population Andre Schleife and Cecilia Leal; University of Illinois at Urbana-Champaign, United States

It is our goal to broaden participation in materials research starting from the undergraduate level and we particularly focus on increasing our number of students from all underrepresented groups. We find it challenging to accomplish this goal through traditional recruitment practices, including social media, email, and mail-based approaches. Our hypothesis is that we do not effectively reach our target population or reach them too late when they either have decided against college or for a different major. To mitigate this, we started pursuing a two-pronged approach reaching out to (i) high-school students directly through a newly established AfterSchool Academy and to (ii) high-school teachers by organizing a teacher’s camp every summer, together with the ASM Materials Education Foundation. If successful, we envision to advertise materials research to a population of students that is still considering their college career and a population of high-school teachers that can inform students about materials research much earlier and more efficiently and deeply than mail or online campaigns. Our early success indicators are that participating students and teachers were very excited and engaged in the experimental activities and we envision to turn this into better, more diverse undergraduate enrollment over the next years. In this presentation details about both activities and their implementation from scratch will be discussed.

SESSION BI02.02: Broadening Participation in Materials Research and STEM II

Session Chairs: Chartanya Bonner, Lisa Neshyba, Kristen Rahilly and Michael Scheibner
Thursday Afternoon, April 25, 2024
Room 326, Level 3, Summit
BI02.02.01
Materials Science and Engineering Program Needs: Students! Thomas Stoopes; University of Washington, United States

Materials Science and Engineering is a multidisciplinary field that works between the physical and biological sciences, engineering and medicine. Engineering students sometimes have difficulty determining the difference between the many opportunities in MSE and the more well defined opportunities in other engineering areas. In particular, entering undergraduate students who see themselves focused on industrial jobs often choose other engineering departments over MSE because of perceived potential future jobs. Materials engineering, which applies the principles of materials science to practical systems, devices and processes, is an area that Materials Science can be used to attract interest among students. This has been shown based on enhanced interest in both applied experiments and demonstrations used in high school classrooms, and in special programs and camp projects in many locales. These programs include

1. Technology education workshops for teachers
2. Science and technology curriculum development based on material science and engineering, and
3. After school activities such as designing and building a guitar

The National Resource Center for Materials Technology Education (MatEdU) has collected and developed resources that provided means for materials concepts to impact areas as diverse as electronics education and advanced manufacturing, energy and critical materials utilization. Such areas can be used to inform students of their prospects in MSE. These opportunities will be developed in this presentation. General reference www.materialseducation.org.

BI02.02.02
Design and Delivery of Low-Cost Science Laboratory Kits for Primary- and Secondary-Level Classrooms in Eastern Africa Jill Wenderoth1, Joyce Elisadiik2, Julie Formanicki3, Danielle Butts4, Cecilia China5, Gloriana Monko2 and Sossina M. Haile6, 1Drexel University, United States; 2University of Dodoma, Tanzania, United Republic of; 3University of California, Berkeley, United States; 4University of California, Los Angeles, United States; 5Nelson Mandela African Institution of Science and Technology, Tanzania, United Republic of; 6Northwestern University, United States

Only about 30% of women students in higher education globally select science, technology, engineering, and mathematics (STEM)-related subjects, with particularly low enrollment in engineering, manufacturing, and construction (8%) and in natural science, mathematics, and statistics (5%). Improving this representation is a multi-faceted challenge. Women Supporting Women in the Sciences (WS2)3 is an international organization unifying and supporting graduate and professional-level women and allies in STEM.

WS2 spearheaded the Lab Kit Initiative during which low-cost materials science and physics laboratory kits for K-12 students were designed and distributed to schools in eastern Africa. During the design phase, seven international teams composed of 59 volunteers (over 70% women) created 3 lab kits for primary level students and 4 lab kits for secondary level students on the topics of food science, electrostatics, light and color, and energy transfer. A key feature of the lab kits is the use of easy-to-source supplies to ensure low-cost and wide accessibility. Working with eleven partners in Ethiopia, Kenya, Rwanda, Tanzania, and Uganda, WS2 provided lab kits that engaged over 5100 students at over 40 school sites in hands-on science learning, with 62% being girls. This talk will discuss the outcomes of the Lab Kit initiative which concluded in early 2023 and future endeavors in which WS2 has been involved that are broadening the reach of our lab kits.

Women Supporting Women in the Sciences (WS2)3 is an international organization unifying and supporting graduate and professional-level women and allies in STEM.

More Inclusive Q&A Sessions Will Lead to Better Science Christopher Rom; National Renewable Energy Laboratory, United States

Traditional question and answer (Q&A) sessions are a sub-optimal use of conference time because they do not engage the full audience. Since 2017, several studies in a range of academic disciplines have identified that women are under-represented among question-askers after scientific talks. Insufficiently inclusive Q&As leave thought-provoking questions un-asked, meaning our communities miss out on ideas worth hearing. Throughout my PhD and into my postdoc, I have collected data on question asking behavior at the conference talks I attended (ceramics, materials, and solid-state chemistry, broadly speaking), revealing that this disparity is present in our community too. Fortunately, prior research shows that merely discussing this trend can help balance Q&A sessions. In this presentation, I will summarize existing research on gender equity in Q&A sessions, present my own data relevant to the MRS community, and describe preliminary results from possible alternative Q&A formats. This work will spark conversations around how to structure our scientific talks to better foster learning and collaboration, boosting our ability to conduct cutting edge science.

Computational Course-Based Undergraduate Research Experience (CURE) for Condensed Matter Physics David A. Strubbe1 and Enrique Guerrero1,2; 1University of California, Merced, United States; 2California State Polytechnic University, Humboldt, United States

Course-based Undergraduate Research Experiences (CUREs) are a way of bringing the excitement of research into the classroom and potentially reaching more students and reaching them earlier in their studies than would happen with the typical summer research experience or senior thesis project. Key aspects are of a CURE are: students learn and use research methods, give input into the project, generate new research data, and analyze it to draw conclusions that are not known beforehand. I will show a paradigm for a computational CURE in an undergraduate/graduate condensed matter physics class at the University of California, Merced. It is based on computational studies with density functional theory, provided by a convenient GUI tool on nanoHUB (https://nanohub.org/tools/ucb_companion) that we co-developed which requires minimal computational skills. After preparatory exercises, students calculated structures, energies, and Raman spectra of different structures and compositions of a monolayer alloy MoS2xSe2(1-x). They followed a defined protocol to contribute to a novel class dataset which they analyzed, and also calculated an additional property of their choice in consultation with the instructor. Studies show that CUREs improve learning, foster a sense of belonging in the field, increase retention of students in science (including going on to do summer research), and are especially beneficial for minoritized/underrepresented students such as at a Hispanic Serving Institution like UC Merced.

Designing Inclusive Research Experiences for Undergraduates Raajan Kumar; Northwestern University, United States

Research Experiences for Undergraduates (REU) programs are a key driver for broadening participation in materials research. Every year, over 100 REU sites offer essential opportunities for students to gain hands-on exposure to materials research and develop technical skills that extend beyond the classroom. Furthermore, several of these programs aim to increase access to materials research for underrepresented students in order to help diversify academia and other research disciplines. But with increasing participation, how do we tailor REU programs to benefit students from all backgrounds? And how can we provide research opportunities that actually promote continued interest in STEM careers? In order for REU programs to have an even greater impact, we need to focus on designing inclusive research experiences that support all students and foster a sense of belonging in materials science and engineering.

In this talk, I will introduce a template for designing inclusive undergraduate research experiences as demonstrated through the Stanford Materials Science and Engineering REU Program. Overall, our goal is to help undergraduates self-identify as materials scientists and engineers in order to encourage broader participation in STEM careers. Several important components of the REU Program will be described to identify best practices that promote positive outcomes in undergraduate research experiences, regardless of student background or preparation level. These components include program recruitment and selection, research project design, mentorship training, student programming, and program evaluation. Specific efforts related to research and communication skill development, career guidance, and community-based mentorship will also be discussed along with key outcomes from these initiatives.

Empowering Diversity: Inclusive Strategies in STEM Education Debora Monego1,2,1Heidelberg Institute for Theoretical Studies, Germany; 2Heidelberg University, Germany

Empowering Diversity: Inclusive Strategies in STEM Education

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We introduced an innovative interdisciplinary STEAM course for undergraduates in collaboration with the College of Fine Arts, titled “Metal Craft for Engineering Students.” Designed for freshmen, this course enables students to create their own metal crafts under the guidance of Fine Arts professors. Although most participants were new to hands-on activities, they engaged in metalcraft such as casting, hammering, and polishing, all while utilizing CAD/CAM programs for design. In conjunction with the practical craftsmanship, introductory lectures on physical metallurgy topics like hardening, annealing, and dislocation were delivered, contextualizing the applied theories. This hands-on approach allowed students to directly observe material thermodynamic and deformation phenomena. By melding fabrication techniques with scientific principles, the course offers a comprehensive understanding of materials science. Feedback has shown high student satisfaction, underscoring our belief that the course not only broadens perspectives but also ignites an interest in multidisciplinary research. Notably, it fills a critical void for materials science students who typically lack hands-on fabrication experience due to a curriculum predominantly focused on analysis, characterization, and theoretical modeling.

Science/STEM identity is the sense of who students are, what they believe they are capable of, and what they want to accomplish with respect to science by interacting with others in the field. This requires intervention to help the “socializers” (i.e., STEM faculty and UGs) better understand the value and purpose of science literacy themselves so as to encourage students to appreciate science, be aware of possible career options in science, and enjoy learning and doing science. The project involves building “science identity” via the active involvement of Towson University’s (TU) undergraduate student researchers (UGs) in 1) engagement in research with the high school (HS) recruits through the apprenticeship model, 2) outreach activities in local high schools. This results in science identity among undergraduate and high school students as they assist in workshops and internships (where they carry out authentic research) involving synthesis and characterization of nanoparticles. Through surveys collected, we show that we have built science identity and broadened the participation in student participants and in the near-peer mentors. The retention of students in STEM using this method will be discussed.

Elementary Arts Lab is a group of artists, scientists, and educators who are passionate about cultivating enthusiasm and curiosity for how we explore and interact with the world around us. We work with K-12 schools to develop and deliver curriculum that integrates movement, art, and music with the physical sciences. We aim to educate and inspire children and ourselves while challenging the stereotypes of scientists and artists. Our approach uses the concept of integrated learning, or the process of making connections between multiple concepts and topics and using experience-based learning [1]. Integrated learning plays on the idea that when you experience something you are more likely to internalize the concepts you were aiming to learn [1]. Our primary aim is to create a long-term network between educators, scientists, and artists and through this network create arts-based science resources for elementary school teachers and their students.

We began our journey in 2020 at the height of the pandemic, working virtually with University Hill Elementary School in Boulder. We started with eight CU Boulder graduate students, a post-doc, and two elementary school educators, an art and music teacher, in our first phase. Together, we built science lessons for third graders that we communicated through art, dance, and music. Our initial endeavor demonstrated that students were learning and starting to internalize the science concepts we were communicating [2]. Our first expansion included building off the fourth-grade curriculum in the Boulder Valley School District (BVSD) and implementing our work at a larger scale by making lesson plans that were available to all BVSD school teachers [2]. We also worked with a class at Heather Wood Elementary School during this time and doubled our CU Boulder student involvement as well as started to incorporate undergraduate students in both science and arts. Our current phase implements continuing education for current Denver Public Schools (DPS) elementary school teachers. We work directly with DPS teachers throughout a full school year in multidisciplinary diverse teams to build integrated learning lesson plans based on class curriculum. By supporting this approach and maintaining a long-term relationship with these teachers we can indirectly impact all the students that they teach throughout their career. We have worked with more than 10 DPS teachers and have now brought in more than 50 CU Boulder graduate and undergraduate students in arts, science, and education working as a network to impact more than 350 elementary school students to date in Colorado.

Beyond our direct impact, we also aim to combat the image of a scientist or engineer for these students. We aim to bring together a diverse community and show students on classroom visits that they, too, can become scientists.

Reference:

Multimodal Core-Shell Nanocomposites for Biomedical Applications

Multimodal Core-Shell Nanocomposites for Biomedical Applications

Multimodal nanomaterials are an important class of materials in the rapidly developing field of nanoscience. These nanomaterials have deserved a lot of attention due to their wide variety of applications including targeted cellular drug delivery, biomedical imaging and cell labelling. The main aim of this project was to develop new magnetic metal carbonate core-shell structures for potential biomedical applications. Calcium carbonate (CaCO₃) and magnetite (Fe₃O₄) were chosen as the functional materials for this research, thus combining the modalities of biocompatibility and magnetisation.

Magnetic nanoparticles (NPs) have been prepared by a precipitation approach using both Fe²⁺ and Fe³⁺ salts as iron precursors in the presence of poly(sodium styrene sulfonate) (PSS). These stabilised NPs exhibited high monodispersity and stability making them ideal for further functionalization. For the very first time, the PSS-Fe₃O₄ NPs were encapsulated into CaCO₃ shell by a novel dry ice carbonation method resulting in distinctive morphological structures. The new composites were loaded with a specific cationic dye as a model to investigate their potential drug uptake and release processes. The testing was monitored using UV-Vis spectroscopy. This research opens up a route to new multimodal nanomaterials with unique properties making them of great interest.

Bibliography

Enhanced Immobilization of EDTA on Graphene Oxide Sponge by Siloxane Bridge for Multi-Pollutants Removal in Wastewater

Sheng Meng, Richard J. Paddock, Robert G. Compton, and Michael T. Smith

Enhancing the performance of graphene oxide (GO) sponges by immobilizing EDTA via siloxane bridge for the removal of multi-pollutants in wastewater.

References:


Session Chairs: Liangzi Deng, Elif Ertekin, Toshinori Ozaki, Kristen Rahilly and Ajay Ram Srimath Kandada

Photoexcitation is a powerful means in distinguishing different interactions and manipulating the properties of matter, especially for charge transport and phase transitions in complex quantum systems.

Here we show that laser-controlled coherent phonon excitation enables orders of magnitude enhancement of carrier mobility via accelerating polaron transport in a prototypical material, lithium peroxide (Li$_2$O$_2$). The selective excitation of specific phonon modes, whose vibrational pattern directly overlaps with the polaronic lattice deformation, can remarkably reduce the energy barrier for polaron hopping. The strong nonadiabatic couplings between the electronic and ionic subsystem play a key role in triggering charge transport. These results extend our understanding of charge transport dynamics to the nonequilibrium regime and allow for optoelectronic devices with ultrahigh on-off ratio and ultrafast responsibility competitive with those of state-of-the-art devices. We also investigate photoexcitation induced ultrafast phase-transition dynamics in two-dimensional materials, where we identify a laser-induced collective pathway from 2H phase to 1T phase in MoTe$_2$ that is significantly different from thermal phase transitions. Our results provide insights from a new perspective on the coherent electron and lattice quantum dynamics in materials upon photoexcitation.

References:


Final Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Temperature-dependent photoluminescence and Raman spectroscopy can be utilized to identify these materials’ different optical transitions and phonon properties. In this study, kinetic information gleaned from the molecular-dynamics simulations, can help identify optimal experimental processing conditions during MBE growth and guide the selection of other film phase diagram.

Layered semiconductors formed by van-der-Waals stacked atomic planes offer a great quantum materials platform for the study of coupled dynamics with accessible and technologically relevant energy and timescales. The quantum space confinement of mobile carriers reduces the dielectric screening, stabilizing the excitons and favoring their coupling to lattice vibrations [2].

In our work, by means of ultrafast broadband optical spectroscopy combined with ab-initio calculations of the layered semiconductor bismuth triiodide (BiI₃), we set the spectral fingerprints for the optical detection of exciton-phonon coupling in van-der-Waals layered semiconductors [2]. Our joint experimental and theoretical effort allows us to unravel the impact of exciton-phonon coupling by microscopically relating a photoinduced coherent energy modulation of the excitonic resonance to coherent optical phonons. This further enables us to track the extent of the photoinduced atomic displacement in real space with unprecedented subpicometer resolution. These findings eventually solve the debate between experiment and theory on the spectral evidences of exciton-phonon coupling, and establish the role on the ultrafast exciton dynamics.

Further, we address the effect of dynamical screening on the exciton-phonon coupling in BiI₃ [3]. To this goal, we investigate the ultrafast broadband optical spectroscopy under excitation condition either resonant or off-resonance with the excitonic resonance in order to either exclude or enable the excitation of a population of quasi-free carriers. We find evidences that the dynamical screening breaks the coupling of excitons to coherent optical phonons, thereby hindering the photoinduced modulation of the excitonic resonance.

Finally, these complementary works move a step forward in the detection of many-body couplings in layered materials by ultrafast optical spectroscopy, paving the way to optical control of an excitonic resonance on the picosecond timescale.


11:15 AM BI02/MT01/QTO1/QTO4.03
Temperature-Dependent Phonons and Photoluminescence of WS₂ Monolayer to Bulk Rown by CVD. Selena Cova¹, Kedar Johnson², Indika Matura Kankanamge³ and Michael Williams³;
¹Clark Atlanta University, United States; ²Morehouse College, United States
WS₂ is a layered material with unique band gap properties, making it highly promising for developing advanced electronics and optical devices. While bulk WS₂ has an indirect band gap in the near-infrared, monolayer WS₂ has a direct band gap in the visible spectrum. The optical and bandgap characteristics of WS₂ can be temperature dependent. Understanding the temperature-dependent phonon properties of materials is crucial for managing heat in electronic devices, as they impact thermal properties and scattering effects. In addition, self-heating can alter the vibrational properties of WS₂ layers, and how the electrons and phonons interact. Further, understanding the temperature-dependent A and B excitonic peaks is significant in device applications. Temperature-dependent photoluminescence and Raman spectroscopy can be utilized to identify these materials' different optical transitions and phonon properties. In this study, we present a systematic analysis of temperature-dependent bandgap, optical transitions (including A and B exciton), electron-phonon coupling, and strain effect of WS₂ grown by chemical vapor deposition. The layers will be analyzed using photoluminescence and Raman spectroscopy techniques.

11:20 AM BI02/MT01/QTO1/QTO4.04
Quantum Machine Learning for the Synthesis of Photocathodes by Epitaxial Growth Selena Cova¹, Jason B. Gibson and Richard Hennig; University of Florida, United States
We present a high-throughput, material-agnostic strategy to study promising new photocathode materials for their epitaxial growth. C₅₃Sb films grown on 3C-SiC(100) substrates with molecular beam epitaxy (MBE) display lattice parameters intermediate to fully epitaxial layers and bulk structures, indicating partial relaxation at a thickness of only 38 Å. The surface phase diagrams and structures for monolayer thin films of epitaxial C₅₃Sb photocathodes on SiC substrates have been predicted using a genetic algorithm (GA) coupled with density functional theory (DFT) calculations. This information helped identify the experimental growth conditions for uniform and stoichiometric films and possible surface reconstructions. However, the computational cost of DFT calculations limits the study to a single monolayer, and the nucleation and growth of these films cannot be studied with this method.

Hence, we employ machine learning accelerated GA simulations to predict complex surface structures with larger in-plane unit cells and increasing film thickness to model the transition from monolayer to bulk. Following this, the growth of C₅₃Sb layers on (100) and (001) 3C-SiC substrates is studied with exascale molecular dynamics (MD) simulations. Our atomistic modeling aims to elucidate the structural transition from potentially epitaxial monolayers to bulk structures and identify structures, nucleation mechanisms, and film growth processes on (100) and (001) 3C-SiC substrates. The GA and MD simulations are powered by machine-learned ultra-fast force fields (UF³) trained on the data from the previous GA/DFT studies, greatly reducing the computational cost. The resulting structures obtained from the simulations are compared with experimental XRD and RHEED patterns, and the structural energies provide the basis for a thin-film phase diagram.

While the work here is presented for C₅₃Sb films on a SiC substrate, the framework can be applied to any material system to create similar phase diagrams. These phase diagrams, along with kinetic information gleaned from the molecular-dynamics simulations, can help identify optimal experimental processing conditions during MBE growth and guide the selection of other materials systems.

11:35 AM BI02/MT01/QTO1/QTO4.05
Data-Driven Discovery of Dynamics from Time-Resolved Coherent Scattering Nina Andrejevic, Tao Zhou, Qingteng Zhang, Suresh Narayanan, Mathew Cherukara and Maria K. Chan; Argonne National Laboratory, United States
Coherent X-ray scattering (CXS) techniques, including X-ray photon correlation spectroscopy (XPCS), play a critical role in the investigation of mesoscale phenomena evolving at time scales spanning several orders of magnitude. However, obtaining accurate theoretical descriptions of complex dynamics is often limited by one or more factors – the ability to visualize dynamics in real space, computational cost of high-fidelity simulations, and accuracy of approximate models. Here, we aim to bridge the gap between theory and experiments by extracting mechanistic models of dynamics directly from CXS data. To do so, we develop a data-driven framework which employs neural differential equations to parameterize unknown real-space dynamics and a computational scattering forward model to relate real-space predictions to reciprocal-space observations. This framework is shown to recover dynamics of several computational model systems, including domain synchronization, particle clustering, and source fluctuation, under various simulated conditions of measurement resolution and noise. We further demonstrate the practical application of this approach in the context of two proof-of-concept experiments. Our framework represents a general and versatile platform to discover dynamics from time-resolved CXS measurements without solving the phase reconstruction problem for a complete time series of diffraction patterns.

11:50 AM BI02/MT01/QTO1/QTO4.06
Pressure-Dependent Thermodynamics of Cubic Lu-H-N Solid Solutions by First-Principles Calculations and Graph Neural Networks
Pinwen Guan, Matthew Witman, Catalin Spataru, Vitalie Stavila and Peter A. Sharma; Sandia National Laboratories, United States

Metal hydrides are an important class of materials with high scientific significance, finding applications in various fields such as hydrogen storage, batteries, gas sensors, nuclear reactions and high-temperature superconductivity. Pressure, among others, is an important variable to control their properties. Previous computational studies of metal hydrides under high pressures usually treat them as stoichiometric compounds, without lattice disorder considered. However, when pressure becomes more moderate, lattice disorder gets more significant, as shown in the recent claimed room-temperature superconductor at near-ambient pressures, N-doped Lu hydrides, where three constituents (hydrogen, nitrogen and vacancy) have disordered occupancies in the tetrahedral and octahedral interstitial sites in the fcc Lu lattice. To consider lattice disorder dependent on pressure, in addition to other variables including temperature and composition, first-principles calculations are computationally demanding. In this work, a model of the cubic Lu-H-N solid solutions is developed by combining first-principles calculations and lattice graph neural networks to learn pressure-dependent thermodynamic quantities in the configurational space, and composition-pressure-temperature phase diagrams are derived to describe the relationship between the synthesis conditions and the resulted phase equilibria. This work can improve the thermodynamic understanding of the Lu-H-N system and help rational synthesis of N-doped Lu hydrides, as well as demonstrate an efficient approach to model pressure-dependent thermodynamics of multi-component solid solutions.

SYMPOSIUM SB01

Bioresponsive Nano-theranostics
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SESSION B02/SB01/SB03/SB05: Joint Virtual Session
Session Chairs: Dimitra Georgiadou and Kristen Rahilly
Thursday Morning, May 9, 2024
SB01-virtual

8:00 AM *B02/SB01/SB03/SB05.01
Biodegradable Luminous Porous Silicon Nanoparticles in Cancer Diagnosis and Therapy
Liubov A. Osminkina 1,2; 1Lomonosov Moscow State University, Russian Federation; 2Institute of Biological Instrumentation, Russian Academy of Sciences, Russian Federation

The development of new intelligent drug delivery systems to overcome unwanted side effects and maximize the therapeutic effectiveness of chemotherapy for cancer diseases is one of the main tasks of modern medicine. Active research is being conducted to explore various nanosized drug carriers (nanocarriers) for these purposes. The use of porous silicon nanoparticles as the basis for nanocarriers is due to the unique properties of these solid-state nanomaterials, such as high biocompatibility [1] and complete biodegradability into non-toxic silicic acid [2]. The porous structure of the nanoparticles, with porosity values reaching up to 80% of their volume, provides a high drug-loading capacity for efficient drug delivery [3]. The simplicity of surface modification methods for the nanoparticles enables specific targeted delivery of various hydrophobic and hydrophilic drugs, radiochemicals, proteins, peptides, RNA, etc. into cells. The presence of efficient luminescence in porous silicon nanoparticles allows their utilization as contrast agents for bioimaging of cells and tissues [5]. The properties of porous silicon nanoparticles, acting as photosensitizers [6], sensitizers of high-frequency electromagnetic fields [7] and therapeutic ultrasound [8], provide them with therapeutic functions and the potential for stimuli-triggered drug release from the nanopores of nanocarriers.

The research is supported by Russian Science Foundation Grant No. 24-45-20009.

References:
Ultrasound-Guided STING Activation by Nucleotide Nanocomplex-Decorated Microbubbles for Cancer Immunotherapy
Sina Khorsandi1, Xuelfeng Li2, Yifan Wang2, Kristin Huntoon3, Adam Woodward1, Nazia Hajeeva1, Katherine Nguyen1, Connor Endslow1, Julien Santelli1, Wen Jiang2 and Jacques Lux1; 1University of Texas Southwestern Medical Center, United States; 2MD Anderson Cancer Center, United States

The recent success of immunotherapy for treatment-refractory metastatic melanoma, lung cancer and renal cell carcinoma has provided a new hope that immunotherapy can be generalized to a broader range of cancers. However, many cancers do not respond to immune checkpoint inhibitors, which has limited their use to a subset of patients. There is now greater recognition that to generate optimal antitumor immunity requires activation of both innate and adaptive immune systems in patients. Innate immune cells, including macrophages and dendritic cells (DCs), possess phagocytic and antigen presenting capabilities that enable the initial immune recognition of tumor cells and serve as a link between the innate and adaptive immune systems through antigen cross-presentation and subsequent priming of T cells. In order for these professional antigen-presenting cells (APCs) to perform these immune functions, several cellular processes must be activated, including the innate immune sensor cyclic GMP-AMP synthase-stimulator of interferon genes (cGAS-STING). Agents that target the innate immune regulators, such as STING agonists are now being investigated as potential therapeutic targets for a wide range of human cancers. However, because STING is a cytosolic innate immune sensor, the intracellular delivery of agonists such as the negatively charged 23'-cyclic-GMP-AMP (cGAMP) is very challenging. Equally important, non-specific global STING activation can cause systemic inflammatory responses and toxicity. Systemic administration of STING agonists leads to dose-dependent T cell death that facilitates tumor immune evasion, further hindering the translation of STING agonists into the clinic.

To address this technical challenge and meet the clinical need, we developed a technology termed MUSIC (Microbubble-assisted Ultrasound-guided Immunotherapy of Cancer) that utilizes gas-filled microbubbles (MBs) conjugated with APC-targeting antibodies, and cationic polymers to efficiently load cGAMP via formation of nanocomplexes on the MB surface.

Our preliminary results show that, upon exposure to US, MUSIC produces robust STING activation and type I interferon responses in APCs and more efficiently primes antigen-specific CD4+ and CD8+ T cells in vivo. These immune stimulatory effects of MUSIC directly translated into antitumor responses in vivo, where we showed that the MUSIC was able to generate antitumor effects against syngeneic orthotopic primary (EO771) and metastatic (4T1) murine breast cancer models. Both models showed dramatic antitumor responses following local treatment of the primary tumor. Specifically, 6 out of 10 EO771 tumor-bearing animals were tumor-free after 50 days while 4T1 tumor-bearing mice exhibited a significant decrease of the systemic disease burden including lung metastases. We also established the following mechanism of systemic immune memory following MUSIC treatments as mice rejected tumor cells upon re-challenge. MUSIC was also evaluated in two syngeneic murine melanoma models (B16-F10 and D14) with 100% of D14-tumor bearing animals and 50% of B16-tumor-bearing animals achieving complete remission when treated with a combination of MUSIC and immune checkpoint inhibitors.

MUSIC showed efficient antitumor immune responses in localized and metastatic murine breast cancer models as well as in two melanoma models leading to the establishment of immune memory (i.e., in situ vaccination). This microbubble-conjugated microbubble platform enables more efficient loading and release of cGAMP and provides a new drug delivery vehicle for further functional modifications including for loading drug or gene delivery for cancer treatment and/or vaccines.

8:45 AM *B102/SB01/SB03/SB05.03
Neuromorphic Thin-Film-Devices for Process-In-Sensor Applications
Sung Kyo Park; Chung-Ang University, Korea (the Republic of)

These days, the development of sensory systems for observing the surrounding environment information is drawing a lot of attention in various fields such as self-driving, security, robotics, and internet of things (IoT). In order to efficiently convert and recognize an external stimulus into an electrical signal, the high-performance sensory system is required. However, conventional sensor devices have been difficult to maintain and pre-process the transformed information due to their rapid recovery properties. In this regard, the human-like neuromorphic sensory systems that can efficiently recognize external information by sensing and memorizing the incoming stimulus signals is emerging. Nevertheless, to interpret incoming information, many electronic systems often need more complementary components, such as various filters or logically connected circuit structure. Such architectural complexity can limit the development of high-density and high-resolution systems.

In this talk, neuromorphic sensory systems based on thin-film-devices such as amorphous indium-gallium-zinc-oxide (a-IGZO) and CNT thin-film-transistors (TFTs) circuits are demonstrated by constructing hybrid heterojunction structure with various nanostructured materials as a sensing material. Specifically, through utilizing a quantum dot, nano-scaled materials, and metal chalcogenide layers integrated with a-IGZO TFTs exhibits evidently enhanced environmental detection ability with neuromorphic memory function. Furthermore, we will discuss a promising strategy for the facile artificial sensory systems such as neuromorphic olfactory, self-defense, and auto-controllable visual system that have low power and small size which are significant factors in neuromorphic applications.

9:15 AM *B102/SB01/SB03/SB05.04
Biomolecular Neuristors from Voltage-Activated Lipid Membranes
Michelle Makhoul-Manour and Stephen A. Sarles; The University of Tennessee, United States

Spiking neural networks (SNNs) show promise as energy-efficient and fast computing devices for adaptive spatiotemporal data processing and classification, which is critical for applications requiring efficient acquisition, and processing of time-dependent data. Taking inspiration from their biological counterparts, the artificial neuristors in SNN hardware systems have been typically designed to generate dynamic voltage spikes - i.e., action potentials- when a cumulative stream of received electrical inputs crosses a critical threshold. However, unlike biological neurons, action potential generation in man-made systems is achieved using complex circuitry of many solid-state devices that are often non biocompatible. Examples of artificial neurons, and neuristor circuits, include those based on threshold-switching memristors[1] and organic electrochemical transistors[2].

We recently demonstrated the use of voltage-activated lipid membranes as artificial synapses for neuromorphic computing. Advantages of this approach include the available diversity of functional biomembranes, the low voltage and power requirements, and the potential for greater biocompatibility and scalability. To-date, we have developed voltage-activated biomembranes that exhibit tunable memory resistance[3], memory capacitance[4], and various forms of activity-dependent plasticity that provide specific computational advantage[5].

Herein, we study the behaviors of biomolecular neuristors consisting of voltage-activated lipid membranes exposed to alamethicin (ALM), protamine and histidine peptides. Remarkably, two distinct types of action potentials - fast (∼10 ns) and slow (∼1 s) - have been observed, with their characteristic speeds and spike shapes differing based on the composition of the device and the direction and amplitude of the applied current. We have conducted experiments at varying compositions and concentrations of biomembranes to identify the molecular mechanisms to drive these behaviors and develop mathematical models able to capture these behaviors.

While earlier approaches depended on complex multi-device circuitry, a biomolecular neuristor achieves this within a single stimul-responsive biomembrane. This simplifies the fabrication processes by reducing complexity, material volume, and cost, all while maintaining its adaptability to various input types. Leveraging the characteristics of synthetic biomembranes, this work can help unlock the potential for creating compact, energy-efficient, and biocompatible neuristors, thus driving progress in the realm of neural interface technology and spiking neural networks (SNNs).

characteristic time by introducing lump circuit elements such as a series resistor. The FETs under study are micrometer-sized Au-LaAlO3-SrTiO3 transistors [3], which have the advantages of a single-crystal diodelectric – boosting endurance and a low room-temperature mobility of ~1 cm2/Vs – lowering the conductance G to ~1 µS and thus readout power P = U²/G.

Our experimental results reveal various transient effects, which we identify to be related to characteristic RC times and the FET transit time. Some transients affect the final state of the synapse and must therefore be related to the charging behavior of the gate; other transients do not and must therefore be related to the coordination of the channel to this charging. These results establish experimental methods to study the dynamics of field-effect artificial synapses – and FETs themselves – in detail, which are key to developing design principles that will reveal the true potential of field-effect artificial synapses as building blocks for neuromorphic hardware.

**References**


**9:45 AM BI02/SB03/SB05.06**

**Economical and Convenient Fabrication of Antifouling Hydrogels for Implantable Medical Devices**

Hasan G. Jayasinghe and Arunachalam Muthaiyan; The University of New Mexico - Gallup, United States

Hydrogels garnered special attention as a biomaterial because these soft materials can mimic the natural environment of human tissues and are compatible with the human body. Poly(2-hydroxyethyl methacrylate)-based (poly(HEMA)-based) hydrogels have been used for biomedical applications such as soft contact lenses for decades. Despite the versatility of applications of poly(HEMA)-based hydrogels attributed to their excellent biological, chemical, and mechanical properties, they show poor cell attachment. The low cell attachment on this soft material is beneficial for fabricating antifouling materials. Thus, poly(HEMA)-based hydrogels have potential applications in the medical field to prevent the growth of biofilms on medical implants and devices that stay in the human body for prolonged times. When a device remains in the human body for a long time, bacteria attach to the substrate and grow in clusters of cells known as biofilms. Biofilms are thick cell masses and resistant to antibiotics, so treating biofilms-related infections is challenging. Consequently, the biofilms grown on an implant may cause detrimental issues to the patient or damage the medical device. Therefore, searching for materials that can prevent biofilms has a vital importance. This study investigates the fabrication of a HEMA-based hydrogel with antifouling properties. Surface charge and functional groups are the key factors controlling bacterial attachment to a substrate. Therefore, we synthesize copolymers by blending HEMA with monomers such as 2-(Dimethylamino)ethyl methacrylate (DMAEMA). We prepare the polymers by changing the composition of the monomers in the reaction mixture to optimize the chemical composition of the polymer. The polymer with the optimum chemical composition should restrict the attachment of bacteria while maintaining the desired chemical and mechanical properties. The crosslinked network structure of a hydrogel determines its mechanical properties and supports the mechanical integrity of the polymer. Crosslinks also allow the polymer to absorb water excessively, making high water retention a unique feature of a hydrogel. However, the number of crosslinks in the polymer regulates its water retention capacity. Therefore, we vary the number of crosslinks by changing the amount of crosslinking agent in the reaction mixture to optimize the polymer with desirable mechanical and water retention properties. Furthermore, we investigate the effect of surface charge on controlling the bacterial attachment by introducing ionic groups to vary the surface charge. Additionally, we look into the conditions that make the synthesis process more controllable. In this study, we use a thermal initiator to initiate the polymerization reaction. Since the thermal initiation does not require sophisticated instruments, our technique makes the synthesis process convenient, simple, and economical.

**10:00 AM BI02/SB01/SB03/SB05.07**

**Biomaterials Research Mentoring for High School Students**

Andrew Ulaszek, John Peponis and Yawen Li; Lawrence Technological University, United States

As a primarily undergraduate institution (PUI), Lawrence Technological University (LTU) provides ample opportunities for students to participate in research. Over 50% of the undergraduates in the Biomedical Engineering (BME) Department have conducted at least one research project before they graduate. The most active research in the BME Department is on biomaterials, with strong student interest and faculty support. Over the past five years, many high school students are also involved in semester-long biomaterials research with the BME faculty, staff and students.

One group of high school students are from the Bloomfield Hills High School (BHHS) Biomedical Pathway Program (BPP), the first and only Center for Advanced Professional Studies (CAPS) program in Michigan and a nationally recognized innovative high school program that partners with industry and post-secondary institutions to provide authentic immersive learning experience for students. BPP students spend two class periods each week in their junior and senior years to develop biomedical related knowledge and skills in an immersive project-based environment. In the first year, students take classes that provide formative skills in biomedical engineering with limited classroom exposure to research and career pathways. During the second year, they are placed in host organizations that fit their career interests. Built on partnership between the BPP program and the BME Department, BME students with ongoing research projects can choose to mentor BPP students in the second year. Students from other high schools participate in research in the BME department either through their school internship/externship programs or over the summer. Since Fall 2019, 19 high school students have conducted research with BME faculty, staff and students. Of these 19 students worked on biomaterials related projects, ranging from decellularized spinach leaves, metal 3D printing, to skin tissue engineering, and bioprinted wound dressing mesh.

We have developed a process effectively mentor high school students on biomedical research. This includes targeted orientation and training of BME mentors and high school mentees, clear definition of the research scope and objectives, regular progress check and oversight of the faculty and staff, and periodic evaluation of the student learning. We report in this talk our high school research mentoring process, example projects, experience gained and lessons learned in our continuing effort to involved high school students in biomaterials research to produce high quality project outcomes with enhanced learning for all students involved.

**SESSION SB01.01:** Bioreponsive Nanotheranostics

**Session Chairs:** Jessica Hsu and Bella Maneshan

**Tuesday Morning, April 23, 2024**

**Room 428, Level 4, Summit**

**10:30 AM BS01.01.01**

**Engineering Biofunctional Metal–Phenolic Materials via Supramolecular Assembly**

Frank Caruso; University of Melbourne, Australia

The development of rapid and versatile coating strategies for interface and materials engineering is of widespread interest. This presentation will focus on our studies on the formation of a versatile class of metal–organic materials, metal–phenolic networks (MPNs), which can be formed on various substrates by coordinating polyphenols and metal ions through self-assembly. This robust and modular assembly strategy is substrate independent (covering organic, inorganic, and biological substrates) and has been used for the preparation of various materials, including thin films, particles, superstructures and macroscopic assemblies. It will be shown that a range of polyphenols and a library of metal ions are suitable for forming MPNs and that by altering the type of metal ions, different functional effects can be incorporated in the MPN materials, ranging from fluorescence to MRI and catalytic capabilities. Furthermore, the use of polyphenol and proteins to form engineered coatings and particles for a range of biological applications will be highlighted. The ease and scalability of the assembly process, combined with the tuneable properties of MPNs, provide a new avenue for functional interface engineering and make MPN potential candidates for biomedical, environmental, and advanced materials applications.

**11:00 AM BS01.01.02**

**DNA Origami Directed Virus Capsid Polymorphism**

Iris Seitz and Mauri Kosttainen; Aalto University, Finland

**Final Abstract Book PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]**
Most known viruses protect their genome by encapsulating it inside a protein capsid. Viral capsids can adopt various geometries, most iconically characterized by icosahedral or helical symmetries. The assembly process of native capsids is highly cooperative and governed by the protein geometry, protein-protein as well as protein-nucleic acid interactions. Importantly, the high control over the size and shape of virus capsids would have advantages in the development of new vaccines and delivery systems. However, tools to direct the assembly process in a programmable manner are exceedingly elusive or strictly limited to specific structures. Here, we introduce a modular approach by demonstrating DNA origami directed polymorphism of single protein subunit capsids. We achieve control over the capsid shape, size, and topology by employing user-defined DNA origami nanostructures as binding and assembly platforms for the capsid proteins. Binding assays and single-particle cryo-electron microscopy reconstruction show that the DNA origami nanostructures are efficiently encapsulated within the capsid. Further, we observe that helical arrangement of hexameric capsomers is the preferred mode of packing, while a negative curvature of the origami structure is not well tolerated. The capsid proteins assemble on DNA origami in single- or double-layer configurations depending on the applied stoichiometry. In addition, the obtained viral capsid coatings are able to efficiently shield the encapsulated DNA origami from nucleic degradation. Our approach is, moreover, not limited to a single type of virus capsomers and can also be applied to RNA-DNA origami structures. We have for example demonstrated folded mRNA structures and identified key folding strategies to enable protein translation, without a separate origami unfolding step. Therefore, these findings may in addition find direct implementations in next-generation cargo protection and targeting strategies.


### 11:15 AM SB01.01.03

**Protein Cages as Responsive Tools for Nanomedicine**

Jeroen Cornelissen; University of Twente, Netherlands

Different types of protein cages are nowadays studied in the fields of nano- and materials science, because of their well-defined size and structure in the nanometer regime. Compared to more traditional polymer-based nanostructures, these – often – virus-based materials are extremely uniform, and the position of functional groups is precisely defined. Encapsulins are protein cages found in bacteria that have interesting properties with respect to (thermal) stability and cargo loading. In the past we and others have studied the application of encapsulins, but so far, their preparation, durability and functionalization are restricted to fundamental studies.1

Recently, we reported the design of encapsulins from two different origins (e.g., *T. maritima* and *B. linens*) with functional loops on its surface.2 This allows for future site specific genetic or chemical modification. We, furthermore, optimized the cages’ production and showed that, under the selected conditions, these are stable over time periods of a least a year. Both the genetic and chemical manipulation of the encapsulin based protein cages allows for the introduction of functional compounds, such as fluororescent proteins for recognition of enzymes for therapeutic applications. Exciting new developments are the introduction of moieties that respond to an external trigger, where promising results are obtained with - amongst others - light responsiveness. The research presented in the contribution, therefore, paves the way for further design, engineering and production of encapsulins, for instance for drug delivery, vaccine development or other theranostic applications.

### 11:30 AM *SB01.01.04

**Continuous Growth of Monodisperse Water-Dispersible Iron Oxide Nanoparticles for Potential Biomedical Applications**

Jing Qu1, Joanna Wang2, Jianghong Rao2 and Yonefeng Zhao3; 

1Jackson State University, United States; 2Stanford University, United States

A direct synthesis of highly water-dispersible magnetic nanoparticles has been of great interest for biomedicine, but systematic control over size has not been achieved. Here, we have developed a general method to synthesize monodisperse water-dispersible iron oxide nanoparticles with nanometer-scale size increments, ranging from 4 nm to 15 nm, in a single reaction. Precise size control was achieved by continuous growth in an amphiphilic solvent, diethylene glycol (DEG), where growth step was separated from nucleation step by sequential addition of reactant. There was only one reactant used in the synthesis, and no additional capping agents and reducing agents were required. This approach suggests the “living growth” character of the synthesis of iron oxide nanoparticles in an amphiphilic solvent. The synthetic method demonstrates high reproducibility. The as-prepared iron oxide nanoparticles are highly water dispersible without the need for any surface modification. Furthermore, the synthesized 9 nm iron oxide nanoparticles exhibit extremely high transversal and longitudinal relaxivities, as reported in the literature for sub-10 nm spherical nanoparticles. Additionally, the iron oxide nanoparticles were studied for magnetic particles imaging (MPI). The performance of MPI increases with the increase of nanoparticles size. This study will not only shed light on the continuous growth phenomenon of iron oxide nanoparticles in amphiphilic solvent but also stimulate the synthesis and application of iron oxide nanoparticles.

### SESSION SB01.02: Bioreponsive Nanotheranostics II

Session Chairs: Ruirui Qiao and Hao Song

Tuesday afternoon, April 23, 2024

Room 428, Level 4, Summit

### 1:30 PM *SB01.02.01

**Understanding Nanomaterial Behavior in a Physiological Environment Promotes their Translational Exploration**

Tianjiao Chu, Christy Maksoudian, Irati Perez Gilabert, Mukaddes Izi, Bella Manshan and Stefanim Szesen; KU Leuven, Belgium

The interest in the biomedical use of nanomaterials has been quite strong for several years, yet despite the excellent preclinical proof of concept data, the clinical translation of nanomedicines has remained somewhat low. One potential issue in this regard are the uncertainties related to the biodistribution and bio-effects that nanomaterials will have upon systemic administration. In the present contribution, we aim to provide an overview of some recent examples on how developments in imaging and analysis can help to overcome some of the hurdles currently associated with biomedical research involving nanomaterials. This presentation itself will focus primarily on the role that non-invasive (optical) imaging can play in better determining the true therapeutic efficacy or potential toxicity of nanomaterials. Recent data will be discussed on the detailed characterization of tumor heterogeneity and how nanomaterials delivery to solid tumors can be improved through manipulating tumor physiology. These gained insights also led to recent advances in nanomaterial effects at the tumor site, where we specifically look at the combined effects of nanomaterial chemistry and tumor parameters on the degree of metastases and how this can influence the choice of nanomaterials to be used. We also explore the use of engineered nanomaterials to promote anti-tumor immunity and, lastly, demonstrate the ability to investigate the use of pDNA-loaded nanomaterials for therapeutic use. Together with examples of novel imaging modalities and the need for fully quantitative data, we hope that this presentation will help any interested scientists in uncovering the full potential that nanomedicines have to offer.

### 2:00 PM SB01.02.02

**Core-Shell Semiconducting Polymer Nanoparticles for Detection and Photothermal Ablation of Breast Cancer**

Nicole Levi and Santu Sarkar; Wake Forest University School of Medicine, United States

Triple negative breast cancer (TNBC) is one of the deadliest among other subtypes of breast cancers due to its absence of standard biomarker expressions, and the aggressive nature of TNBC leads to low patient survival. Current treatment strategies include surgery, chemotherapy, and radiation therapy, although photothermal therapy is an evolving treatment strategy. It has recently been shown that breast cancer can harbor intracellular bacteria, which may impact therapeutic responses. Here we present the use of semiconducting theranostic polymer nanoparticles composed of a photothermal poly([4,4-bis(2-ethylhexyl)-cyclopenta[2,1-b;3,4-b]dithiophene-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl]) core with a fluorescent poly([9,9-dihexylfluorene]-co-2,1,3-benzothiadiazole-co-4,7-dithiophene-2,5-diyl)] core with functional loops on its surface. This allows for future site specific genetic or chemical modification. We, furthermore, optimized the cages’ production and showed that, under the selected conditions, these are stable over time periods of a least a year. Both the genetic and chemical manipulation of the encapsulin based protein cages allows for the introduction of functional compounds, such as fluororescent proteins for recognition of enzymes for therapeutic applications. Exciting new developments are the introduction of moieties that respond to an external trigger, where promising results are obtained with - amongst others - light responsiveness. The research presented in the contribution, therefore, paves the way for further design, engineering and production of encapsulins, for instance for drug delivery, vaccine development or other theranostic applications.

SESSION SB01.02: Bioreponsive Nanotheranostics II
Session Chairs: Ruirui Qiao and Hao Song

Tuesday afternoon, April 23, 2024

Room 428, Level 4, Summit

### 3:00 PM *SB01.02.01

**Understanding Nanomaterial Behavior in a Physiological Environment Promotes their Translational Exploration**

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2:15 PM SB01.02.03 Remote Stimuli-Responsive Nanomaterials for Regenerative and Cancer Therapy
Heemin Kang, YURI KIM, Hyunsook Hong, Nayeon Kang, Sungkyu Lee and Sunhong Min; Korea University, Korea (the Republic of

Cells constantly interact with native nanostructured extracellular matrix at the molecular level. Nanomaterials responsive to tissue-penetrative remote stimuli can be designed to present bioactive ligands or deliver functional molecules as a nanomedicine to regulate or elucidate dynamic nanoscale cell-material interactions. In this talk, I will demonstrate the design of dynamic nanomaterials that can be remotely and spatiotemporally controlled via various remote stimuli, such as magnetic field, light, self-assembling molecules, or their combinations.

In particular, I will show that magnetic field can control the motion of magnetic nanomaterials, such as reversibly controlling RGD ligand nano-coupling, nano-blocking, nano-stretching, and nano-connection with gravity theory-based analysis, which can regulate the focal adhesion-mediated mechanotransduction and resultant differentiation of stem cells. Near-infrared light can activate photonic nanomaterials to trigger photosensitization, thereby mediating the swelling of ligand-supramolecular self-assemble, which can be reversibly deswelled by visible light. Such photonic control enables in vivo stability imaging and spatiotemporally controlled molecular delivery to regulate the adhesion-dependent pro-inflammatory vs. pro-regenerative polarizations of macrophages. Furthermore, molecules and ions can reversibly induce in situ self-assembly of biofunctional nanomaterials.

I will also introduce a couple of representative examples of recent cancer therapies and diagnostic imaging controllable by remote stimuli, such as magnetic field, light, and ultrasound, which utilize mechanical force, 1-D nanomaterials, in situ self-assembly, ferropot, and others. These strategies can present benefits for safe personalized precision therapies while minimizing drug resistance and side effects.

2:30 PM SB01.02.04 Recent Progress on Phototherapy
Byoung Yoon; Ewha Womans University, Korea (the Republic of

Switchable phototheranostic nanomaterials are of particular interest for specific biosensing, high-quality imaging, and targeted therapy in the field of precision nanomedicine. Here, we develop a "one-for-all" nanomaterial (NanoPCTs) that self-assembles from flexible and versatile phospholipamine building blocks. Fluorescence and reactive oxygen species (ROS) generation could be triggered depending on a targeted, protein-induced, partial disassembly mechanism, which creates opportunities for low-background fluorescence imaging and activatable photodynamic therapy (PDT). On the other hand, the in vivo specific binding between albumin and PEs, arising from the disassembly of injected NanoPc, was recently confirmed using an inducible transgene mouse system. In a recent investigation, we devised a novel molecular design approach to create heavy-atom-free photosensitizers for thionaphthalimides and BODIPYs. The thionaphthalimides display dramatically enhanced quantum yields for photosensitized singlet oxygen formation.

Photodynamic antibacterial therapy is also regarded as an innovative and promising antibacterial approach due to its minor side effects and lack of drug resistance. Recently, we suggested that reactive differences may pave a general way to design selective photodynamic agents for ablating gram-positive bacteria-infected diseases.

3:00 PM BREAK

3:30 PM SB01.02.06 Advanced Tissue Engineering Scaffolds Incorporated with Gold Nanoparticle-Based Theranostics for Postoperative Cancer Patients
Lin Guo, Qilong Zhao, Liwu Zheng and Min Wang; The University of Hong Kong, Hong Kong

Cancer causes millions of human deaths each year and surgery has been the most commonly used method for treating many types of cancers. After surgical removal of the tumor, new tissues need to be formed at the resection site for restoring body functions. Scaffold-based tissue engineering has emerged as a viable approach for regenerating tissues in the body. Another major issue for many cancer patients, such as sufferers of gastrointestinal (GI) tract cancer, is the high cancer recurrence rate. Therefore, new strategies should be investigated to detect and treat recurrent cancer for patients after their initial cancer treatment. In nanomedicine, nanodevices that provide both diagnostic and therapeutic functions (the so-called "theranostics") appear to be highly promising for the early detection and effective treatment of cancers. In the current study, a new concurrent electrospinning and co-axial electrospray technology was developed for fabricating advanced tissue engineering scaffolds incorporated with gold nanoparticles (AuNP)-based theranostics for treating cancer patients. Model scaffolds designed for GI tract cancer patients were made using this technology. It was shown that a controlled release of AuNP-based theranostics could be achieved for the advanced scaffolds. The study using NIH/3T3 mouse fibroblasts indicated good biocompatibility of released theranostics. HeLa cells, which have a high level of folate receptor (FR) expression, and MCF-7 cells, which have a low level FR expression and thus could provide a negative control in the current study, were employed for investigating the designed functions of the theranostics. In vitro investigations showed that the theranostics released from scaffolds could provide both diagnostic and therapeutic functions, including strongly amplified Raman signals via the surface enhanced Raman scattering (SERS) effect, active targeting, cellular imaging and photothermal therapy for HeLa cells. Our other studies also showed the potential of these advanced scaffold for GI tract tissue regeneration. Altogether, these novel scaffolds are highly promising for offering the treatment for postoperative cancer patients.

3:45 PM SB01.02.07 Structural Immunotherapy: Spherical Nucleic Acid (SNA) Immunotherapy for HPV-Associated Head and Neck Cancer
Chad A. Mirkin,1,2 and Sergey Kudruk,1,2; Northwestern University, United States; 1International Institute for Nanotechnology, United States

Squamous cell carcinoma of the head and neck (SCCHN), ranked 6th in global cancer mortality, is witnessing a transformative shift in its causation due to the escalating prevalence of human papillomavirus (HPV). Current HPV-SCCHN treatment options include surgery, chemotherapy, and radiation. Immunotherapy for HPV-SCCHN has so far been limited to commercially available immune checkpoint inhibitors targeting PD-1 or PDL-1 as a synergistic treatment to chemotherapy. However, even with these options, on average 50% of patients with SCCHN will experience a recurrence/metastasis which has a poor prognosis and a median overall survival <1 year. Therefore, there is a critical need for the development of new and improved treatment options for HPV-SCCHN. To that end, HPV oncoproteins E6 and E7 have emerged as promising targets for vaccine-based therapies. Here we employ chemically tunable spherical nucleic acid (SNA) nanomaterials, consisting of a nanoparticle core densely functionalized with DNA, that incorporate selected HPV-SCCHN-specific antigens in a controlled orientation. Indeed, the three-dimensional presentation and overall structural design of SNAs enables effective entry into cells and perturbations to structural and compositional parameters can be altered to achieve a desired therapeutic outcome. Thus, SNAs for immunotherapy allows one to explore the implications of structural presentation of vaccine components in generating epitope-specific T cells. In this study, SNA-based therapeutic cancer vaccines are designed to efficiently deliver adjuvants and tumor-specific antigens, thus activating both innate and adaptive immune systems. We evaluated multiple HPV-16 antigens, with the goal of maximizing immune responses in tumor-burdened humanized murine models and patient-derived tumor spheroid samples. To identify the most potent antigen, a formulation, generation of antigen-specific CD8+ T-cells, cytokine production, and HPV cancer-specific cell killing were evaluated. Overall, this work highlights how the structure of SNAs is critical to designing effective therapeutics while providing insights into the molecular interactions between the immune system and cancer cells.

4:15 PM SB01.02.08 Spatiotemporally Delivery of Multiple Growth Factors from Electrospun Scaffolds through Photothermal Effect to Manipulate Skin Wound Regeneration
Xindan Zhang and Jiaying Xue; Beijing University of Chemical Technology, China

Due to the increasing incidence of full-thickness skin injuries caused by mechanical trauma, burns, as well as conditions like diabetes and malignant tumors, the repair of skin wounds has become a major medical challenge in the field of wound healing. During the process of skin wound repair, different types of growth factors play specific roles at various stages, collectively promoting wound healing. In this study, we fabricated a nanofiber scaffold with surface topographical features using electrosprinning. Furthermore, the scaffold was functionalized to provide the required microenvironment for skin wound repair by incorporating growth factors. To enable the spatiotemporal controlled release of these growth factors, we combined photothermal therapy with phase change materials and introduced a photomask strategy. Specifically, a three-layered sandwich-like photothermal scaffold was prepared by in conjunction with coaxial electrospraying, using polycaprolactone as the base material. The scaffold consisted of an inner layer of radially aligned nanofibers, an outer layer of random nanofibers, and an intermediate layer containing growth factors and photothermal agents in the form of phase change microspheres. By utilizing near-infrared light irradiation and the photomask strategy, the spatiotemporal controlled release of the growth factors was achieved. The multi-layered structure of the scaffold was confirmed by surface morphology analysis, and the modified surface was found to promote cell adhesion according to water contact angle measurements. Photothermal experiments and studies on growth factor release demonstrated that the scaffold could achieve spatiotemporal controlled release while maintaining photothermal stability, and the released growth factors retained their pro-angiogenic activities. In vivo experiments showed that the scaffold not only promoted cell proliferation but also facilitated cell migration through the combination of its topographical and the spatiotemporal controlled release of growth factors. Finally, an animal full-thickness skin wound model was employed to evaluate the wound healing effectiveness of the scaffold, revealing the regulatory patterns and effects of growth factors in vivo under programmable photothermal stimulation. In conclusion, the nanofiber scaffold with photothermal-triggered controlled release of growth factors effectively integrates the topographical structure of the nanofibers with the controllable release of growth factors. It provides a novel approach for the design of skin wound repair scaffolds and their combination with photothermal therapy to promote skin wound healing. This research holds significant potential in the fields of tissue regeneration and controlled release.
Incorporating injectable hydrogels have been investigated extensively to incorporate drugs for tumor treatment because those materials can simultaneously deliver multiple drugs to the target sites with rational ratios and minimal invasion, and elevate their tumor accumulation, blood stability, and half-lives. Importantly, the local treatment of hydrogel-encapsulated drugs showed superior tumor growth inhibition compared to the local or systemic delivery of non-encapsulated chemotherapeutics and immunomodulators. However, since current studies regarding injectable chemo-immunotherapeutic hydrogels are mainly based on the intratumoral gelation of soluble precursors, sol-gel transformation may be impeded by the complex physiological environment, resulting in the reduced cross-linking degree, drug leakage, and unpredictable pharmacokinetics. Besides, conventional polymers lack molecular, structural, and functional programmability, which results in significant challenges in tailoring the biofunctionalities of hydrogel scaffolds for intimately interacting with tumor tissue.

Here, we describe an unprecedented injectable DNA hydrogel in which the repeats of cytosine-phosphate-guanine oligodeoxynucleotide (CpG ODN) and adenosine triphosphate (ATP) aptamers are encoded on the ultralow DNA binding blocks by RCA-mediated polymerization. By sequentially incorporating DNA hydrogel with immune checkpoint inhibitor anti-programmed cell death protein ligand 1 (aPDL1) and chemotherapeutic agent doxorubicin (DOX), a chemo-immunotherapeutic DNA hydrogel adjuvant (aPDL1/DOX) DNA Gel is formed. Due to its super-property, this DNA hydrogel encoded with ATP aptamers can be readily injected into tumor tissues in which the overexpressed ATP binds to the corresponding aptamer. This results in the conformational change of aptamer and volume expansion of the gelmatrix to stimulate the distinct release kinetics of co-encapsulated therapeutics. DOX is first released to induce immunogenic cell death that intimately works together with the polymerized CpG ODN in gel scaffold for effectively recruiting and activating dendritic cells. While, the polymerized CpG ODN displayed very high tumor retention with a significant reduction of the systemic circulation, which is attributed to the restricted in vivo motility and metabolism of the polymerized CpG ODN, thereby reducing the adverse effects of CpG ODN while enhancing its tumor immunomodulatory efficacy. Furthermore, aPDL1 antibody was subsequently released from DNA hydrogel to block the immune inhibitory checkpoint molecules PD-L1 on the tumor cell surface, thus reversing the tumor microenvironment immunosuppression through potentiating T-cell mediated immune responses. The programmed aPDL1/DOX DNA Gel demonstrated potent suppression of tumor growth and lung metastasis via the induced strong systemic immune response and immune memory effect. This work thus contributes to the first proof-of-concept demonstration of a programmable super-suit DNA hydrogel system that perfectly matching the sequence programmability to the synergetic therapeutic modalities based on chemotherapeutic toxicity, in situ vaccination, and immune checkpoint blockade. With the high programmability of design principle, we believe that our approach can be combined with DNA-protein conjugation chemistry, DNA nanotechnology, and microfluidic technique to develop a library of biomaterial systems in new biomedical applications beyond chemo-immunotherapy of tumors.
synthesis of continuous metal-organic framework (MOF) thin films offer a solution that increases material density, reduces light dispersion, and ensures long-lasting durability. The tightly interconnected and precisely oriented growth structure of continuous MOF thin films results in a significant reduction in light scattering. Consequently, the inherent characteristic of diminished light dispersion holds great promise for enhancing spatial imaging resolution in X-ray scintillators. Herein, we present a versatile approach rooted in situ electrochemical-directed assembly, dedicated to crafting MOF thin films tailored for exceptional X-ray imaging capabilities. Through this electrochemical process, a series of coherent MOF thin films have been successfully synthesized, employing interconnected lanthanide metals and terephthalic acid linkers. This specific MOF thin film emerges as a standout contender, enabling high-resolution X-ray imaging while retaining X-ray sensitivity. This achievement is attributed to its superior material density, reduced light scattering, and simplified manufacturing procedure. Notably, this particular MOF thin film surpasses the majority of documented organic and traditional inorganic scintillators, achieving an X-ray imaging resolution exceeding 32 line pairs per millimeter (lp/mm). This research has the potential to elevate MOFs as highly efficient scintillators for X-ray imaging, opening up exciting opportunities in the fields of radiology and security screening applications.

References

5:00 PM SB01.03.15
Advancing Breast Cancer Therapy: Thermosensitive Hybrid Hydrogel (PLGA-PEG-PLGA) with Metallic Nanoparticles Enhancing Withaferin-A Release
Mythili Srinivasan; School of Health Sciences and Technology, Dr. Vishwanath Karad MIT-World Peace University, India

Background: Drug-delivering copolymers respond to temperature through sol-gel transitions. Lower transitions involve micellar growth, while upper transitions bring about micellar structure breakage. The fine-tuned PLGA-PEG-PLGA hydrogel, embedding silver or zinc nanoparticles, achieved a prolonged release of Withaferin-A. Aim: This study sought to develop a hybrid hydrogel with in situ gel-forming for sustained release, utilizing the PLGA-PEG-PLGA copolymer and incorporating silver and zinc nanoparticles entrapped with Withaferin-A to address breast cancer.

Materials and Methods: PLGA (75:25) to PEG copolymer (3:1 ratio) formulated as in situ gel-forming hybrid hydrogel. Characterization involved DSC NMR, dynamic light scattering, and rheology. Silver and zinc nanoparticles were green synthesized using Camillia sinensis extract, and the characteristics of the prepared nanoparticles were analyzed through FTIR, Zeta potential, XRD, TEM, and FE-SEM. Subsequent to the drug entrapment into a hybrid hydrogel, in vitro drug release studies were conducted using a trans-diffusion cell apparatus. In vitro cell studies using MCF-7 and MDA-MB-231 were conducted.

Results: Silver and zinc nanoparticles exhibited a particle size of 255 nm and 128.5 nm, respectively, with zeta potentials of -17.5 mV and -12.9 mV. XRD analysis confirmed 2-theta (deg) values of 56.20 and 56.64 for silver and zinc nanoparticles, respectively. FE-SEM and TEM reports displayed spherical-shaped silver nanoparticles and cylindrical-shaped zinc nanoparticles. Hydrogels demonstrated controlled release of Withaferin-A over 39 to 43 days based on polymer concentration. Effective internalization and antiproliferative impact in MCF-7 and MDA-MB-231 breast malignancy cell lines with negligible hemolytic effects. Zn NPs induce selective cytotoxicity and apoptosis. Silver NPs exhibited dose-dependent cytotoxicity, inducing cell death and cell cycle hindrance in breast cancer cells.

Conclusion: The temperature-responsive PLGA-PEG-PLGA copolymer-based hybrid hydrogel, developed by incorporating silver and zinc nanoparticles, facilitated the sustained and controlled release of Withaferin-A. The formulation exhibits potential for efficient drug delivery in breast cancer therapy, promising physicochemical properties and drug release kinetics.

5:00 PM SB01.03.16
Advancing Glioblastoma Treatment: Aptamer-Mediated, Long-Circulating, Catonic, PEGylated Hybrid Liposomes with Bavachalcone
Ashwini Y. Chandane; Abbivain Education Society's, College of Pharmacy, India

Background: Glioblastoma, a formidable brain tumor, poses a significant therapeutic challenge. Current treatments face limitations due to the infiltrative nature and resistance of glioblastoma cells.

Aim: To explore the brain-targeting efficacy of cationic, long-circulating, targeting PEGylated liposomes incorporating transferrin, folate vitamins, and cationic albumin as aptamers (hybrid-liposomes). These liposomes are entrapped with poly (lactic-co-glycolic acid) (PLGA) nanoparticles containing the anticancer ligand Bavachalcone (BCN), with the goal of advancing therapeutic strategies for glioblastoma.

Materials and Methods: PLGA nanoparticles were formulated to encapsulate Bavachalcone. Characterization involved TEM, FE-SEM, FT-IR, XRD, particle size, and zeta potential analysis. Formulation and characterization involved the synthesis of lipidic nanoparticles. Liposomes were prepared via the ethanol-injection method and characterized using a particle size analyzer, zeta potential, TEM, and DLS. In silico studies encompassed network pharmacology, docking, and simulation for efficacy assessment. In vitro cell line studies utilized U87MG, LN-229, and T98G to evaluate cytotoxic effects.

Results: In silico studies unveiled the potential inhibitory effects of BCN on glioblastoma growth. Prepared NPs exhibited a particle size of 187 ± 0.5 nm, zeta potential of -33 mV, and drug entrapment efficiency of 89.33 ± 0.5%. Liposomes displayed a favorable particle size of 175.5 ± 0.29 nm with a positive surface charge of 8.72 ± 0.53 mV. Encapsulation efficiency was measured at 77.8 ± 0.61% for BCN. In vitro drug release studies demonstrated significantly higher cumulative release rates of BCN over 82 h. Hybrid liposomes exhibited superior cytotoxicity and accelerated apoptosis in glioblastoma cell lines (U87MG, LN-229, and T98G) through MTT assays. Cellular uptake studies confirmed enhanced internalization in glioblastoma cells. Cell viability assays demonstrated improved cytotoxic effects on glioblastoma cells.

Conclusion: Bavachalcone exhibited promise against glioblastoma, supported by in silico and in vitro studies. Hybrid liposomes offer an innovative approach for enhanced drug delivery, addressing BBB challenges. This approach sheds light on the potential of natural compounds and nanotechnology for enhanced glioblastoma treatment.

5:00 PM SB01.03.17
Thermosensitive Nitric-Oxide-Releasing Nitroel for Strengthening Antitumor Immune Responses with Tumor Collagen Diminution and Deep Tissue Delivery during NIR Laser-Assisted Photoimmunotherapy
In-Kyu Park1 and Yong-Kyu Lee2; 1Chonnam National University, Korea (the Republic of); 2Korea National University of Transportation, Korea (the Republic of)

Combined cancer immunotherapy has demonstrated promising potential with an amplified anti-tumor response and immunosuppressive tumor microenvironment (TME) modulation. However, one of the main issues that cause treatment failure is the poor diffusion and insufficient penetration of therapeutic and immunomodulatory agents in solid tumors. Herein, a cancer treatment approach that combines photothermal therapy (PTT) and nitric oxide (NO) gas therapy for tumor extracellular matrix (ECM) degradation, along with NLG919, an indoleamine 2,3-dioxygenase (IDO) inhibitor that reduces tryptophan catabolism to kynurenine, and DMXAA, a stimulator of interferon gene (STING) agonist that stimulates antigen cross-presentation, is proposed to overcome this issue. NIR (808 nm) laser irradiation, NO-GEL achieved the desired thermal ablation by releasing sufficient tumor antigens through immunogenic cell death (ICD), NO delivery triggered local diffusion of excess NO gas for effectively degrading tumor collagen in the ECM, homogeneously dissolved and released NLG919 throughout the tumor, inhibited IDO expression that was upregulated by PTT, and reduced the immune suppressive activities. The sustained release of DMXAA prolonged dendritic cell maturation and CD8 T cell activation against the tumor. In summary, NO-GEL therapies offer a significant tumor regression during PTT supplements the immunotherapy by reducing the T cell apoptosis and immune suppressive cell infiltration to TME. NO-GEL with the STING agonist and IDO inhibitor is an effective therapeutic combination to counter possible limitations during solid tumor immunotherapy.

Additional unification of IDO inhibition during PTT supplements the immunotherapy by reducing the T cell apoptosis and immune suppressive cell infiltration to TME. NO-GEL with the STING agonist and IDO inhibitor is an effective therapeutic combination to counter possible limitations during solid tumor immunotherapy.

5:00 PM SB01.03.18
Sodium Chloride Nanoparticles as RadioSENSITizers
Xinning Lai; University of Georgia, United States

Previous studies have demonstrated that SCNP can enter cells through endocytosis and disrupt osmotic balance by releasing sodium and chloride ions. This process leads to cancer cell death. It's speculated that the SCNP might affect the levels of other ions in the cells and have a significant impact on the redox balance. The research suggests that combining SCNP with radiotherapy could enhance the effectiveness of the treatment. Radiation therapy works by ionizing molecules, especially water, to produce radicals that damage biomolecules like DNA. SCNPs might enhance this effect by promoting the production of reactive oxygen species (ROS).

In particular, we are interested in exploring SCNP as a radiosensitizer for head and neck squamous cell carcinoma (HNSCC). HNSCC, a significant and increasingly common malignancy, often requires treatment through surgery or radiotherapy. However, these treatments have limitations, including toxicity and a high risk of recurrence. Combining chemotherapy with radiotherapy increases efficacy but also the risk of systemic toxicities. SCNP is considered as a potential new treatment modality that could improve efficacy without adding toxicity.

In this study, we synthesized and characterized folate-conjugated sodium chloride nanoparticles (SCNP@folate) and explored their potential as radiation sensitizers in HNSCC. Our results showed that the nanoparticles exhibited proficient cellular uptake and increased intracellular levels of sodium and chloride. Interestingly, the increase in sodium levels also causes calcium influx through the NCX, triggering an increase in ROS. We found that the ROS-promoting effect works in tandem with IR, leading to GSH depletion, resulting in DNA and lipid damage, and...
ultiately cell death. Our in vitro results showed that there is a synergistic effect between SCNPs@folate and IR. In vivo studies showed that intratumorally injection of SCNPs@folate combined with irradiation resulted in a significant improvement in tumor growth inhibition compared to IR alone and a higher percentage of tumor-free mice. Taken together, our studies suggest a great potential of SCNPs@folate as a radiosensitizer in HNSCC.

SESSION SB01.04: Bioreponsive Nanotheranostics III
Session Chairs: Ruirui Qiao and Hao Song

8:15 AM SB01.04.01
Multi-Pronged Approach for Targeting Oral Biofilms

Multi-Pronged Approach for Targeting Oral Biofilms

The oral microbiome is a complex system consisting of numerous bacterial species that plays host to both beneficial and harmful organisms. Among the pathogenic species in the oral cavity is Streptococcus mutans (S. mutans), the primary agent responsible for dental caries. Different antimicrobial-based strategies have been developed to tackle this problem, but the rise of antibiotic resistance among microorganisms necessitated the development of new and effective therapeutics. One such solution is the de novo antimicrobial peptide (AMP), GH12, which has shown potency against cariogenic bacteria. GH12 has a high content of α-helical structures that facilitate pore formation on bacterial membranes. Quorum sensing molecules such as competence stimulating peptides (CSP) have been used as biomarker for detecting bacterial species that are used to monitor not only their own but other species in their surroundings. Recently, polyserotonin (PSe) has emerged as a photothermally active nanomaterial that shows promise towards biomedical applications. In this work, we made a cocktail combining all three of the aforementioned components—AMP for bacterial killing, CSP for targeting, and PSe for localized heating—to develop a multi-pronged approach aimed to increase antibiotic efficacy. My findings indicate that the presence of both peptides, membrane damaging and competence stimulating, in conjunction with the photothermally active Pse, effectively inhibited the growth of S. mutans in both planktonic and biofilm states. Overall, these results reinforced that the strategic use of multi-pronged therapeutic approaches could reduce cariogenic bacteria within the oral microbiome.

8:30 AM SB01.04.02
Developing MRI-Based Therapeutic and Diagnostic Tools: From Cancer to Chemical Weapons

Developing MRI-Based Therapeutic and Diagnostic Tools: From Cancer to Chemical Weapons

Magnetic resonance imaging (MRI) is a powerful non-invasive technique which becomes considerably more potent when contrast agents (CAs) are introduced. Molecular contrast agents based on Gd-chelates (e.g. Dotarem®) are regularly used in the clinic, however these usually lack specificity for selective disease or biomarker diagnostics, and can also suffer from poor signal-to-noise and blood circulation half-life, which can limit their clinical utility. Carefully designed contrast agents, and contrast agents based on nanomaterials have the potential to overcome these issues. In this talk, I will introduce our approaches to the careful design and development of MRI contrast agents tuned for different applications. I will describe nanostructured composites capable of reporting on drug release in a unique non-invasive way, of use for the pharmacokinetic mapping of drug release towards personalised medicine. I will also discuss recent advances in the diagnosis of chemical weapon poisoning using molecular contrast agents.

9:00 AM SB01.04.03
Precision in Colorimetric Sweat Sensing through Machine Learning

Precision in Colorimetric Sweat Sensing through Machine Learning

Sweat contains diverse biochemicals that can serve as a source for detecting biomarkers, particularly in individuals with chronic conditions like diabetes. Non-invasive sweat sensors have gained popularity in various applications, promoting personalized healthcare and daily convenience. Different methods, including electrochemical, fluorescence, and colorimetric approaches, have been employed for real-time sweat analysis. Among these methods, colorimetric sensors stand out for their accuracy, stability, and portability in addition to their scalability in production processes. However, the main challenge in colorimetric sweat sensing currently lies in two areas: the need for improved sensor accuracy and the precise detection of color changes resulting from sweat exposure.

In this presentation, we will showcase the development of our sensors, offering real-time, stable, and rapid monitoring of glucose concentration and pH value without causing discomfort. The detection process takes approximately five minutes. Most notably, we address the challenge of detecting subtle color changes, which are virtually imperceptible to the naked eye, by leveraging artificial intelligence. We will discuss how the utilization of a breathable, bio-compatible, acid-base-balanced cotton substrate is the key to achieving higher color differences. In a series of experiments, we cover the fabrication and testing of two generations of pH sensors and two types of glucose sensors. We will then demonstrate the application of machine learning to our sensors and how it significantly enhances prediction accuracy. Three machine learning algorithms, namely Linear Discriminant Analysis (LDA), Support Vector Machine (SVM), and Convolutional Neural Network (CNN) are applied, demonstrating stable and excellent prediction accuracy of 90% for the test results. Finally, we will showcase the practical application of our combined pH and glucose sensors within a single substrate. This work contributes to the advancement of sensor preparation techniques and underscores the critical role of accurate machine-learning algorithms in the successful utilization of sweat sensors across various domains.

9:15 AM SB01.04.04
Collectively Interacting Colloidal Magnetic Nanoparticles with Strong AC Field Response for Remote Imaging and Thermometry

Collectively Interacting Colloidal Magnetic Nanoparticles with Strong AC Field Response for Remote Imaging and Thermometry

Colloidal magnetic nanoparticles (MNPs) are an important class of nanomaterials being investigated for use in a host of therapeutic and diagnostic modalities such as medical imaging, remote sensing, drug delivery, and hyperthermia. These nanoparticles exploit the very soft ferrimagnetic magnetic behavior found in certain materials, often ferrites, when they are confined to tens of nanometers in diameter or less. Such nanomagnets can produce a strong collective response to applied alternating current (AC) magnetic fields, while simultaneously remaining dispersed in liquid media.

Recently, remote magnetic imaging of temperature has been identified as an exciting potential diagnostic application of colloidal MNPs. This thermometry measurement employs dispersed particles to construct a 3D visual representation of temperature throughout a volume. The technique, which is a variation on the magnetic particle imaging (MPI) modality, is based on the temperature-dependent response of MNPs to an applied AC field. By using high-frequency magnetic fields, these MNPs can also generate localized heating, thus allowing them to function as nanotheranostics. However, significant challenges remain in the development of this technology, including a need to finely engineer MNPs to increase both their magnetic thermosensitivity and magnitude of AC field response.

Here, we report on our development of MNPs, both as liquid dispersions and solid assemblies, specifically designed with a robust response to applied AC magnetic fields for imaging, thermometry, and temperature control. A series of colloidal nanocrystals based on ferrites were synthesized via highly tailorable and commercializable solution chemistry routes. Careful selection of the synthetic reagents and precursor thermal decomposition kinetics allow for control of the resultant MNP composition (Fe, Co, Zn, V ratios) and size (~5-80 nm). These MNPs were then investigated using solid- and liquid-phase AC and DC field magnetometry measurements. A home-built arbitrary-wave magnetic particle spectrometer was employed to perform relaxometry and measure magnetic AC susceptibility, allowing for a rigorous analysis of the temperature- and frequency-dependent AC response from 1 Hz to 30 MHz. The results were cross-correlated with detailed structural characterization including X-ray diffraction, light scattering, optical spectroscopy, and high-resolution electron microscopy to develop a set of structure-property relationships.

Finally, we tune these parameters to optimize spatial imaging of MNP magnetic response and a robust thermosensitive AC magnetic signal using magnetic particle imaging and thermometry instrumentation specifically developed for these applications. We find particle size and compositional doping act as levers to optimize the AC response through the manipulation of interparticle and intraparticle magnetic spin interactions. Using these guidelines, we find the set of structural parameters that produce the most robust thermosensitive magnetic response and conduct imaging experiments whereby spatial reconstructions of colloidal MNP magnetic response are generated. The key to this improved performance, in both liquid and solid media, is the field-induced linear alignment of strongly interacting MNPs, resulting in a substantially augmented magnetic anisotropy. Collectively, these studies illuminate the complex behavior of MNPs under AC driving fields, reveal extensive correlations between nanoscale structure and magnetic response, and provide guidelines for the design of MNPs used in magnetic imaging, sensing, and therapeutic applications.

Inspired by the living systems that constantly undergo dynamic processes to maintain metabolic homeostasis, the Dynamic Nano-Assemblies have been developed to tackle complicated diseased environment for various biomedical applications. The materials composing the nanoparticles produce fascinating and diverse functionalities. The controllable assembly mediated by a multitude of different ligands would lead to the flexible modulation of nanomaterials’ fate in vivo, endowing the nanoplatform with targeted delivery and accumulation to disease lesions. The clever combination of different functional components via the ligands directed co-assemblies would lead to the development of multifunctional nano-biomedical platforms for nanoligand-targeted therapy, fast diagnosis, biological regulation and efficient therapy. Furthermore, the ingenious control over the assembly/disassembly process based on small-sized functional nanoparticles could achieve both in vivo targeted delivery and stimuli-responsive disassembly for efficient disease therapy and bioelimination. Overall, dynamic nano-assemblies based biomaterials and drug delivery systems can achieve the improved diagnostic accuracy and therapeutic efficacy in many diseases including cancer, infection and neurodegenerative diseases.

10:00 AM BREAK

10:30 AM *SB01.04.06

Curcumin Derived Nanoscale Coordination Polymers for Modulating Stress Response in Plants Xin Zhang, Kangkang Feng, Yiyang Cong, Binqing Tao and Hao Hong; Jiangsu Academy of Agriculture Sciences, China; Nanjing University, China

**Introduction:** Different stressing factors (e.g. drought, viral infection, insects, etc.) can impose significant survival threats to plants, especially in agricultural scenarios. Strategies to alleviate these stress burdens are able to improve plant physiology and adapt them to more “unfriendly” environment. Nanotechnology is a rising star to ameliorate plant stress situation. The goal of this study is to develop a curcumin-metal coordination nanoplatform with intrinsic protecting capacity against various stressing factors in chosen plants (Arabidopsis thaliana and wheat selected as the patients), and it can simultaneously deliver therapeutic cargos to further improve plants survival against various stressing factors.

**Materials and Methods:** Curcumin (Cur) was reacted with manganese acetate or zinc acetate by a solvothermal method to form porous nanostructures. X-ray diffraction analysis revealed the crystal structures from both Cur-Mn and Cur-Zn. The morphology, stability, and other physical properties from Cur-Mn and Cur-Zn were also evaluated. The biocompatibility of Cur-Mn/Cur-Zn was tested in Arabidopsis thaliana and wheat cells and plants. Subsequently, the biological impacts of Cur-Mn/Cur-Zn along with their distribution profiles in these plants were measured post the spay of a suspension of 50 μg/mL. The cargo accommodating and releasing capacity was tested for fludioxonil, a broad-spectrum bacteria and fungi killing molecule. Finally, the molecular mechanisms of Cur-Mn/Cur-Zn for stress resistance in these two plants were also explored.

**Results:** Cur-Mn and Cur-Zn had a size range of 60-90 nm (measured by TEM) with good dispersity and production yields. In their structures, curcumin was coordinated with manganese/zinc to form framework structures. Cur-Mn and Cur-Zn could be internalized into Arabidopsis thaliana and wheat cells with no noticeable toxicity. Once applied in the plant leaves, these materials could be absorbed quickly and transported via vessels inside plant stem, and reached the roots and other plant parts in a timely manner. Pure Cur-Mn and Cur-Zn could add the drought resistance capacity to these plants, and the molecular mechanisms were clarified by RNA-seq techniques. Moreover, Cur-Zn could accommodate more than 40%w/w of fludioxonil, and protect it from UV degradation. Once applied in the field of wheat, fludioxonil@Cur-Zn could protect wheat plants from fusarium blight in a more persistent manner.

**Conclusion:** As a natural compound from the plant, curcumin can coordinate with different metals to form nanosized materials, and our findings revealed that this “from plant, to plant” strategy could be an efficient tool to protect plants from multiple critical stress factors, broadly applicable in plant rescue.

11:00 AM SB01.04.07

Understanding Structure and Stability for The Development of Novel Artificial Oxygen Carriers Martin A. Schroer, Jan-Eric Sydow, Fabian Nocke, Ozan Karaman and Katja B. Ferenz; University of Duisburg-Essen, Germany; University Hospital Essen / University of Duisburg-Essen, Germany

Red blood cell structures (RBCs) are an indispensable tool in various clinical scenarios; however, the available quantity is already highly limited, which will become an even more severe problem in the future. To overcome these peculiarities and limitations of RBCs, we developed albumin-derived perfluorocarbon-based artificial oxygen carriers (A-AOCs), that are comprised of a perfluorodecalin (PFD) nano-emulsion core and an albumin shell, and have already successfully supplied oxygen in extra-corporally perfused hearts and various animal models [1].

The structure and stability of A-AOCs is sensitive to changes of the carrier solution, so we need to learn more about the structure and structural changes on the nanoscale. Conventional characterization techniques lack the spatial resolution (e.g. light scattering) or need dried and consequently non-physiological samples (e.g. SEM, TEM), and thus yield limited information on A-AOC structure in solution. We therefore use X-ray scattering techniques to study A-AOCs, which do not have such limitations and allow also to study dense, opaque suspensions.

In this contribution, we present recent results of X-ray scattering measurements on A-AOCs covering a wide, clinical-relevant concentration and temperature range. We investigate A-AOCs from different synthesis approaches, using ultra-sound [2] and microfluidizing techniques, which reveal different sizes and stabilities. Based on these findings, it is now possible to optimize the synthesis parameters, in order to yield stable A-AOCs of desired size and dispersity.

This study demonstrates the huge potential of X-ray scattering for the study of pharmaceutical and medical-relevant samples [3], with direct implications for the development of new formulations.

**References:**

11:15 AM SB01.04.08

Versatile Application of Nanoscale Metal-Organic Frameworks for Intratumoral Delivery Eunseo Choi and Conroy Sun; Oregon State University, United States

Recent preclinical and clinical studies have highlighted the improved outcomes of combination radiotherapy and immunotherapy. Concurrently, the development of high atomic number (high-Z) metallic nanoparticles as radiation dose enhancers has been explored to widen the therapeutic window of radiotherapy and potentially enhance immune activation. Due to their high X-ray attenuation and high density, these nanoparticles also have the potential to serve as imaging agents. Exploiting high-Z metal nanoparticles would provide clinical advantages for image-guided radiotherapy for targeted cancer treatment. Despite the numerous advances in the field of drug delivery, there are still unmet needs that could lead to the development of a therapeutic molecule delivery carrier. In this study, we seek intratumoral delivery of metal-organic frameworks to induce a robust stimulation of antitumor immunity for a systemic and long-lasting therapeutic benefit. By utilizing hafnium and iron-based metal-organic frameworks, we target immune cells with other targeted cancer therapies for synergistic advantages. We employ this nanomaterial as a pharmaceutical carrier system for the delivery of a wide range of materials, from small molecules to macromolecules. Radiotherapy-induced local tissue damage and inflammation have the potential to generate tumor antigen and release danger-associated molecular patterns. Nanoscale metal-organic frameworks are a versatile platform for combination radiotherapy. In addition to serving as drug carriers, our high-Z metal-organic frameworks are attractive nanomaterials that serve as contrast agents in biomedical imaging. We conducted phantom studies in vitro and in vivo, using microCT for real-time monitoring, which will facilitate advanced analysis of tumor cells and their responses to therapy. Intratumoral immunotherapy provides the capacity to manipulate the tumor microenvironment by targeting cells within the tumor microenvironment, making it an attractive therapeutic approach.

11:30 AM *SB01.04.09

Understanding Biological Processes Using Responsive Polymers and Bio-Orthogonal Chemistries Kristofer J. Thurecht, Nicholas Fletcher, Gayathri Ediriweera and Craig Bell; The
The evolution of therapeutic systems for cancer therapy has offered the opportunity to treat more complex and refractory disease. However, there still remains key challenges around quantitatively determining the tissue specific drug release profile of therapies. It is crucial, then, for materials to be precisely engineered to allow direct assessment of their behaviour in biological systems, as well as provide feedback on biological responses. Central to this thinking is the development of theranostics, which are materials that are able to provide both spatial and temporal information about therapeutic delivery and efficacy. Our research explores a number of avenues related to materials engineering that can provide unique insights into therapeutic efficacy of nanomedicines, where biological cues can be utilised to give realtime feedback of drug effects. Alternatively, exogenous stimuli can also be applied resulting in material changes to the delivery system. Such stimuli can be administered as applied radiation (often in the form of visible/near infrared radiation), or through chemical stimuli that take advantage of the bio-orthogonality of defined covalent reactions. Bio-orthogonal reactions that take advantage of pre-targeting, allow diagnostic and therapeutic probes to be administered with greater site-specificity to diseased tissue. In this presentation, I will present our experimental approaches to utilise the pre-targeting strategy and bio-orthogonal reactions to improve therapeutic delivery to tumours while provided realtime readout of therapeutic activity. By exploiting the multivalency and multimodality of polymeric nanomaterials, the true advantages of theranostics can be realised in nanomaterial systems.

**SESSION SB01.05: Bioresponsive Nanotheranostics IV**

**Wednesday Afternoon, April 24, 2024**

**Room 428, Level 4, Summit**

**1:45 PM **SB01.05.01 Biomaterials to Boost Cancer Immunotherapy Zhuang Liu and Bella Manshian; Soochow University, China

Cancer immunotherapy has attracted tremendous attention in recent years. In our recent studies, by employing rationally designed biomaterials as well as nanoscale delivery systems, we are able to enhance cancer immunotherapy via developing novel nano-vaccines, modulating tumor microenvironment, and achieving combinational immunotherapy, as evidenced by various animal model experiments. In this presentation, I would introduce our latest efforts in this exciting research direction. In particular, we have tried to combine various types of local tumor treatment approaches with immunotherapy using biomaterials as the bridge. Stimulated by the tumor antigens released after local tumor ablation, the triggered immunological responses if in combination with immune checkpoint blockade (ICB) therapy could result in effective inhibition of tumor cells remaining in the body, promising for treatment of cancer metastasis. A strong immune-memory effect could also be observed after such treatment. Beyond that, we are also working on biomaterials that are capable of modulating tumor microenvironment for enhanced immunotherapy. A start-up company has been founded based on the technologies from our laboratory. Several pipelines are now being tested in clinical trials.

**2:15 PM **SB01.05.02 Lactate Oxidase Nanocapsules Boost T Cell Immunity and Efficacy of Cancer Immunotherapy Zheng Cao\(^1\), Duo Xu\(^1\), Wenting Chen\(^1\), Yunfeng Lu\(^2\) and Jing Wen\(^1\); \(^1\)University of California, Los Angeles, United States; \(^2\)Beijing University of Chemical Technology, China

Cancer immunotherapy has reshaped the landscape of cancer treatment, but its effectiveness in solid tumors is limited by the overproduction of lactate by cancer cells. Extensive trials are being conducted to reduce lactate concentrations through inhibiting lactate dehydrogenase. However, such inhibitors often disrupt the metabolism of healthy cells and cause non-specific toxicity. In contrast to these strategies, we target lactate itself with an enzyme, lactate oxidase, which effectively reduces lactate concentrations and releases hydrogen peroxide, an immunostimulatory molecule, in the tumor microenvironment. However, recombinant lactate oxidase from microorganisms possesses short circulating half-life, low enzyme activity, and potential immunogenicity. To circumvent this limitation, we report herein a nano-encapsulating strategy to encapsulate lactate oxidase molecules within a thin polymer shell through in-situ polymerization, allowing the synthesis of nanocapsules. The nanocapsules stabilize lactate oxidase and prevent it from proteolysis and denature, minimize the immunogenicity, prolong the circulating half-life, enabling their use as a potent therapeutic for cancer immunotherapy. Lactate oxidase nanocapsules can promote the proliferation and activation of effector T cells and suppress tumor-resident regulatory T cells in vitro. As further demonstrated in a murine melanoma model and a humanized mouse model of triple-negative breast cancer, nanocapsules abet tumor immunosuppression and enhance anti-tumor T cell immunity by upregulating gene expression for T cell recruitment and activation, as confirmed by single-cell RNA sequencing. Such multifunctional lactate oxidase nanocapsules lead to improved efficacy of immunotherapies for solid tumors.

**2:30 PM BREAK**

**3:30 PM **SB01.05.03 Electrospun Nanofibers for Tissue Repair and Regeneration Jiajia Xue; Beijing University of Chemical Technology, China

Electrospun nanofibers have been widely applied for tissue repair and regeneration because of their advantages of mimicking the structure and composition of extracellular matrix to a certain extent. We have developed a series of scaffolds based on electrospun nanofibers to promote the repair and regeneration of peripheral nerve, bone, and skin. To improve the repair efficacy of peripheral nerve injury, we have constructed a nerve guidance conduit based on electrospun nanofibers in a bionic design to simulate the microenvironment required for nerve repair. Nerve growth factor and indocyanine green were loaded in phase change material particles and then deposited between two layers of electrospun nanofiber membranes to obtain a photothermal-responsive scaffold. Upon the irradiation of a near-infrared laser, nerve growth factor was triggered to be released from the scaffold, promoting the axon extension. In addition, we deposited a density gradient of bioactive nanoparticles on the surface of uniaxially aligned fibers to guide the axon extension and accelerate cell migration along the direction of increasing the density of the nanoparticles. We further constructed degradable hydrogels in the lumen and regulated the degradation rate of the hydrogel to be increased from the proximal to distal position, allowing for the long-term delivery of growth factor loaded in the hydrogel and promoting the regeneration of sciatic nerve in rat. Additionally, we conducted large animal experiments in sheep to explore the effects of multi-channel nanofiberous conduit on sheep nerve injury repair. For the repair of skin wounds, according to the demand of various growth factors in each stage of repair period, we constructed a multi-layered nanofibrous scaffold with a radially aligned nanofibrous inner surface. The scaffold effectively integrated multiple induced signals such as topography, bioactive factors and photothermal response to achieve spatiotemporally controlled delivery and accelerated wound healing. Combined with photothermal effects, we constructed a multifunctional bone repair scaffold to recruit stem cells and induce their osteogenic differentiation to improve the repair of bone defects. We also developed gradient self-assembled activated fiber scaffolds to induce osteogenic differentiation of stem cells. In summary, electrospun nanofibers can be applied to construct multifunctional tissue repair materials to promote tissue injury repair and regeneration.

**4:00 PM **SB01.05.04 Effects of Sequential Ultrasound Irradiation in The KHz and MHz Bands on Transdermal Administration of Biopolymeric Drugs Kenko Matsuura and Yuta Kurashina; Tokyo University of Agriculture and Technology, Japan

### Introduction

Biopolymeric drugs are expected to have high efficacy and minimal side effects due to their specificity. Meanwhile, a minimally invasive method of administering these drugs is difficult to establish. As one of the attracting methods, sonophoresis is a method of drug-administering by disrupting the stratum corneum layer through the collapse of cavitation bubbles and drug infusion by the microjets generated from cavitation bubbles. However, the amount of drugs administered by conventional techniques is limited, since the randomness of the microjets generated from cavitation bubbles makes stable drug infusion difficult. This is because the position of the bubble nucleus for the generation of cavitation bubbles is unstable and not directional. Here, we propose an ultrasound irradiation method with microbubbles to achieve efficient transdermal administration of biopolymeric drugs. Especially, the synergistic effect of cavitation induced by low-frequency and acoustic streaming induced by high-frequency on drug administration is demonstrated by sequentially irradiating in the kHz and MHz bands with fluorescence-modified ovalbumin (OVA, for nano-sized drug model).

### Materials and methods

Thermal administration experiments with fluorescence-modified OVA to porcine skin irradiated by ultrasound (US) were carried out on effective acoustic streaming by sequential irradiation in the kHz and MHz bands. Here, the irradiation distance of the acoustic streaming on the drug dosage was evaluated. Ultrasound irradiation was performed under the following four conditions. As a conventional method (i), US in the kHz band was applied for 10 min (control). (ii)-(iv) As the method proposed, US in the kHz band and MHz band was sequentially applied for 5 min, respectively. The MHz band was irradiated at a distance of (ii) 1 mm, (iii) 2 mm, and (iv) 3 mm. After irradiation of multiband US, the skin from each condition
was lysed, and the fluorescence intensity of cyanine 5 modified OVA was measured by a spectrofluorometer to evaluate the dose of the nano-drug model quantitatively.

**Results and discussion**

In order to investigate the effect of acoustic streaming on the proposed method, the ultrasonic irradiation device was constructed using two types of transducers. A Langvin transducer with a resonance frequency of 45.9 kHz was used for kHz band irradiation (X. Xie, et. al., *J Drug Deliv Sci Technol* 2022), and a piezoelectric device with a resonance frequency of 1.97 MHz was utilized for MHz band irradiation. The velocity of acoustic streaming is expressed as a function that depends on the distance from the irradiation source (J. Friend et. al., *Lab Chip* 2019). The results obtained from the function suggest that under the conditions of this study, the flow velocity rises with increasing irradiation distance in the MHz band. This calculated outcome shows that the drug dosage increases in the range of 1 mm to 3 mm. The results of fluorescence intensity measurements for each condition suggested that the highest drug dose was obtained when the US in the MHz band was irradiated at an irradiation distance of 3 mm after irradiation of the US in the kHz band. Furthermore, as with the theoretical value, the drug dose significantly rose with increasing irradiation distance ((i) vs (iv): *p* < 0.05, (ii) vs (iv): *p* > 0.01, Student's t-test). These results suggest that sequential irradiation of the kHz and MHz bands is more effective than conventional irradiation of only the kHz band. Therefore, the acoustic streaming induced by the MHz band contributes to the improvement of drug dosage for sonophoresis.

The development of the multiband US administration method enables us to propose minimally invasive biomacromolecule drug administration as an alternative to injection. Therefore, this method is expected to contribute to the development of research on biopolymeric drug materials.

**4:15 PM SB01.05.05**

**Magnetic Liquid Marbles as Thermo-Responsive Materials under Alternating Magnetic Fields**

Rafal Bielas1, Tomasz Kubiak1, Matus Molcan2, Ivo Safarík3 and Arkadiusz Jozefczak1; 1Faculty of Physics, Adam Mickiewicz University in Poznan, Poland; 2Institute of Experimental Physics, Slovak Academy of Sciences, Slovakia; 3Biology Centre, ISB, Czech Academy of Sciences, Czechia

Responsible materials are essential in various scientific and industrial fields. Within this context, the potential to control these materials using external stimuli, such as magnetic fields, is of great interest. Magnetic liquid marbles—airborne droplets surrounded by particles—are emerging as suitable candidates for such purposes. For example, their ability to open and close on-demand using static magnetic fields makes them ideal for specialized tasks, such as testing fragile entrapped species [1].

When exposed to alternating magnetic fields, the internal temperature of liquid marbles rises, a phenomenon attributed to magnetic energy dissipation due to magnetic relaxation and hysteresis processes. Elevated temperature can be employed for functions like amplifying DNA contained within the particle shell of these marbles [2]. Building on this, we propose utilizing magnetic heating to modulate thermo-responsive liquid marbles.

In our experiments, we prepared liquid marbles with a ferrofluid, which included agar powder and either maghemite nanoparticles or magnetosomes (nanoparticles from magnetotactic bacteria). The droplets were coated with either polymer or bio-particles and then exposed to an alternating magnetic field with a kHz frequency. The resulting temperature increase inside the liquid marbles initiated varied reactions depending on their particle coating. With polymer particles, a combination of partial particle fusion and enhanced evaporation led to the creation of rigid magnetic shell residuals, which could be seen as precursors to a new generation of liquid marbles [3]. On the other hand, for non-thermo-responsive particle coatings, such as lycopodium shell, the liquid core underwent partial disintegration driven by reversal process of gelation. The diverse structures observed after the magnetic heating procedure may provide new way for developing materials suitable for applications like smart lotions or creating new types of capsules for theranostic procedures.

The work was supported by Polish National Science Center through the project no. 2019/35/N/ST5/00402.

**References:**


**4:30 PM SB01.05.06**

**Radiation-Activated Ferroptosis with Liposome Nanoparticles Encapsulating 7-Dehydrocholesterol Enhancing Antitumor Immune Responses**

Jianwen Li, Zhizi Feng, Xinning Lai, Wei Yang, Shuyue Zhan and Jin Xie; University of Georgia, United States

In this project, we explore an approach that triggers ferroptosis and enhances antitumor immune responses by external radiation. The key component of this technology is 7-dehydrocholesterol (7DHC), a natural biosynthetic precursor of cholesterol. This zoosterol can react with radiation-induced reactive oxygen species (ROS), initiating a radical chain reaction between 7DHC and polyunsaturated fatty acids (PUFAs) in cell membranes. We show that this interaction leads to direct lipid peroxidation, culminating in cell death via ferroptosis. In terms of delivery, we show that 7DHC, similar to cholesterol, can be incorporated into the lipid layer of liposomes. To improve targeting, we incorporated NTSα, a ligand for NTS1 that is overexpressed in multiple malignancies, into liposomal nanoparticles. Our results show that these NTSα-incorporated and 7DHC-loaded liposomal nanoparticles are minimally toxic, but significantly enhance the efficacy of radiation by activating ferroptosis in cancer cells. As a highly immunogenic cell death (ICD) pathway, ferroptosis induced by our treatment further triggers the increased secretion of danger-associated molecular patterns (DAMPs) and elevated surface exposure of “eat-me” signals such as ATP, IFN-γ and calreticulin. These patterns are then sensed by antigen-presenting cells such as dendritic cells (DCs), in turn boosting T cell-driven adaptive immunity. Such a strategy of controlled activation of ferroptosis offers a favorable therapeutic index and opens avenues for clinical application.

**4:45 PM SB01.05.07**

**Advancing Targeted Drug Delivery via Optimization of Drug-Loaded Polymeric Nanoparticles and Red Blood Cell-Mediated Approaches**

Hermyn P. Girmatsion1,2, Vincent Lenders1,2,3, Bella Manshian1,2,3 and Gu Van den Mooter1,2; 1, IKU Leuven University, Belgium; 2, IKU Leuven, Belgium

Bronchopulmonary Dysplasia (BPD) represents a complex pathophysiological challenge in neonatal care, predominantly affecting preterm infants. Current interventions, such as mechanical ventilation and supplemental oxygen, often yield suboptimal outcomes, necessitating the exploration of novel therapeutic modalities. The administration of Dexamethasone (DEX), while effective in reducing mechanical ventilation dependency, is hindered by its severe long-term neurodevelopmental impacts and crystalline structure leading to poor solubility.

In response, our study pioneers an advanced drug delivery system involving the encapsulation of DEX within poly(lactic-co-glycolic acid) (PLGA) nanoparticles (NPs), subsequently coupled to red blood cells (RBCs). This approach aims to produce a polymer-matrix-stabilized amorphous form of DEX, ensuring sustained and localized pulmonary release. By leveraging these DEX-loaded NPs (DEX-NPs) in combination with RBCs, we aim to optimize drug circulation time, biodistribution, and targeted lung delivery, thereby attenuating systemic adverse effects of DEX.

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We employed the nanoprecipitation method to synerize drug-free DEX-loaded NPs, thoroughly characterizing their size, polydispersity index, zeta potential, encapsulation efficiency, and DEX stabilization capability. Our results demonstrate that these polymeric NPs effectively encapsulate and stabilize DEX up to 3 mg, with higher amounts leading to crystallinity. Solvent, polymer, and drug compatibility studies indicated that PLGA stabilizes about 15% of its weight in DEX (3 mg) with aceton or acetone: DMSO as solvents. Notably, aceton and DMSO blend markedly improved encapsulation efficiency and drug stability in PLGA nanoparticles.

In addition to these findings, we successfully coupled various types of NPs to mouse RBCs, examining the efficiency of this coupling and the biocompatibility of the resultant constructs. This element of our research was critical in assessing the feasibility and safety of the NP-RBC conjugates for *in vivo* applications. *In vitro* toxicity assessments across various cell lines revealed that while plain NPs exhibited limited toxicity, DEX-NPs showed higher cytotoxicity at concentrations above 0.05 mg/mL. *In vivo* studies on term-born neonate CD-1 mouse pups highlighted the superior lung targeting of NP-hitchhiked RBCs compared to free NPs.

This study emphasizes the potential of DEX-PLGA NP-RBC conjugates in revolutionizing BPD treatment. Our findings not only advocate for the targeted pulmonary delivery of therapeutics but also set a foundation for subsequent investigations into the efficacy and safety of this novel approach in the context of neonatal lung diseases.
Mimicking the spiky morphology of pollen and virus, which allowed enhanced interactions at bio-interfaces, here, we showcase our recent progress in the development of spiky nanoparticle-based mRNA delivery. Recent advances in nanotechnology have greatly boosted the development of novel delivery systems for therapeutic and vaccine applications, in particular highlighting the great success of lipid nanoparticles (LNPs) and liposomes. Nonetheless, there still exist fundamental issues, my group has been focusing on the development of platform technologies for producing nanoparticle libraries with reproducible and systematically varied properties; (2) incomplete understanding of the interactions between nanoparticles and biological systems; (3) targeted delivery. To address these fundamental issues, my group has been focusing on the development of platform technologies for producing nanoparticle libraries with reproducible and systematically varied properties (liposomes, polymer nanoparticle and nanocapsules) with high drug loading. We also developed different strategies for improving targeted delivery. Particularly, we developed a biosynthesized nanotechnology integrating naturally derived cell membranes for enhanced biointerface capabilities and nanoparticles for incorporation of various payloads for targeted delivery, which provides a revolutionising strategy for fabricating nanoscale artificial cells. We have also developed biomimicking chips (Tumor-on-a-Chip, Tumor- Vasculature-on-a-Chip) to fundamentally understand nanoparticle extravasation and their tumor accumulation.

The ideal synthesis of lipids involves adhering to key principles, such as operating under solvent-free conditions, employing a straightforward reaction process, and eliminating the need for purification steps. These criteria aim to enhance product purity and streamline production, thereby increasing the likelihood for clinical translation. Current lipid synthesis methods involve Multiple additional, epoxide ring-opening, reductive amination, and thiol-ene reactions. Furthermore, an effective lipid should encapsulate a high mRNA payload for improved expression in vivo and exhibit favorable biosafety without significant adverse effects. Notably, a common soybean oil derivative, rich in epoxy groups, can readily undergo ring-opening reactions with amino-containing compounds. Since soybean oil is FDA-approved and has excellent biocompatibility, it may give rise to a new class of synthetic lipid materials with the potential for mRNA delivery applications.

In our system, epoxidized soybean oil and amino-containing compounds with varying carbon chain lengths, structures, and numbers of N were the sole reactants. Lipids were synthesized via epoxide ring-opening reactions and subsequently purified through heating and rotary evaporation, all without the use of solvents. We found that the majority of lipids derived from soybean oil showed high mRNA loading capacity, thereby enhancing mRNA expression both in vitro and in vivo, while the overall mRNA synthesis remained quite efficient. In our in vivo studies of Lue mRNA delivery, we observed that certain lipids could enhance mRNA expression in the spleen, while others could achieve high expression in the lungs or liver. This highlights the potential utility of these lipids for precise and tunable organ targeting in the treatment of relevant diseases. In addition, soybean oil-derived lipids displayed exceptional performance in delivering Cre mRNA for gene editing. Encouraged by these results, we anticipate that soybean oil-derived lipid materials can assume a more prominent role in the realm of mRNA delivery for a diverse range of bioprocesses. The synthesis of novel lipids utilizing FDA-approved substances remains a promising domain yet to be fully explored.

Nature-Inspired Nanoparticles for Therapeutics and Vaccine Delivery

Recent advances in nanotechnology have greatly boosted the development of novel delivery systems for therapeutic and vaccine applications, in particular highlighting the great success of lipid nanoparticles-based mRNA vaccines fast responding to the COVID-19 outbreak. To lead a successful nanomedicine technology, the key lies in the rational design and fabrication of safe and efficient nano-cargo delivery. The delivery performance could be maximized by custom-designed nanoparticles considering the unique bio-interface configurations towards both cargo biomolecules and cell/tissue surfaces. Mimicking the spiky morphology of pollen and virus, which allowed enhanced interactions at bio-interfaces, here, we showcase our recent progress in the development of spiky nanoparticle-based smart thermodynamics. Through a simple sol-gel synthesis approach, colloidal nanoparticle with an intrinsic spiky surface are fabricated and characterized by the advanced microscopy techniques of electron tomography. We demonstrated the precise control over the delicate nanotopography of spiky nanoparticles, engineering the surface chemistry, and amyotrophy of the particles. We explored the interactions of these nature-inspired unique spiky nano-features towards both biomolecules and cells, gaining new understandings of the bio-nano-interfaces. Our findings underpinned the development of (1) a bacterial-adhesive antimicrobial nano-agent; (2) a nano-buzz targeting the rope-like DNA/mRNA molecules for efficient intracellular delivery, which allowed sufficient enzymatic protection of gene molecules and enabled an unprecedented translation; (3) a pathogen mimetic adjuvant that boosts the vaccine delivery performance, including our most recent study in developing DNA and subunit (RBD) spiking nano-vaccines for SARS-CoV-2.

From bench to market, this spiky nanoparticle-based delivery platform is on the translation collaborated with industrial partners toward novel nanomedicine. Our journey from fundamental research to the launching of ‘NUVEC’ will be also shared in this talk.

Keywords: Hydrogen medicine, targeted delivery, nanomedicine, molecular imaging, nanocatalytic medicine

Reference

Gel Containing Brinzolamide loaded Nano Structured Lipid Carrier and Its Evaluation

Development of In-Situ gel was prepared by the cold method. The drug content was determined by HPLC. In vitro release of BRZ-loaded NLC gel was found by real time imaging of hydrogen molecules, Nat. Commun. 2023, 9, 4241.

Nanozymes and Polymers for Nitric Oxide Delivery from Prodrugs

Ultrasound-Induced Cascade Amplification in Mechanoluminescent Nanotrigger for Sono-Optogenetic Deep Brain Stimulation

A Hitchhiker's and Backpacker's Guide to Drug Delivery

Nitric oxide (NO) is a potent biological molecule that contributes to a wide spectrum of physiological systems, including the cardiovascular, immune, and central nervous systems. However, NO therapeutic delivery technology has been severely limited by the physiological properties of NO: 1) NO has a short half-life in human tissues (seconds); 2) NO can only diffuse over short distances (~100 μm), thus limiting its action to only areas near the source of delivery; and 3) NO can exert protective or deleterious effects depending on its concentration. Current strategies for NO delivery focus on encapsulation of NO donors into pre-fabricated scaffolds or an enzyme-prodrug therapy approach. The latter is limited by the finite pool of NO donors available, while the latter is challenged by the inherent low stability of natural enzymes. Enzyme mimics are attractive substitutes for their natural counterparts in diverse biomedical applications because they have excellent stability against biological degradation compared with natural enzymes. In this work, we present nanoparticles and polymers for synthesizing red polymeric carbon nitride capable of near-infrared-photo catalytic NO production, Adv. Mater. 2021, 33, 2104155.

Remote and minimally invasive neouromodulation is a promising approach in the advent of clinical applications. Ultrasound-triggered mechanoluminescent technology offers a promising approach for achieving remote brain modulation. However, its application has thus far been limited to shallow brain depths due to challenges related to low sonochemical reaction efficiency and restricted photon yields. Here we report a self-amplifying mechanoluminescent nanotrigger based on cascade reactions in liposomes to achieve efficient light emission upon ultrasound stimulation. As a result, blue light was generated under ultrasound stimulation with sub-second response latency. Leveraging the high energy transfer efficiency of focused ultrasound in brain tissue and the high sensitivity to ultrasound of these mechanoluminescent nanotrigger, we are able to show efficient photon delivery and activation of ChR2 expressing neurons in both the superficial motor cortex and deep ventral tegmental area (VTA). Our novel lipidosome nanotrigger can enable minimally invasive deep brain stimulation for behavioral control in animals via a flexible, mechanoluminescent sono-optogenetic system.

Ocular drug delivery system is most challenging and complicated to deliver drugs to the target site with its therapeutic dose. Intracellular bioavailability is only 5 to 10% of total eye drop administered. In past few decades, researchers have attracted to nanotechnology-based drug delivery system in which lipid based Nanostructured lipid carriers (NLC) appear as effective ophthalmic drug delivery system, which have, higher drug loading, stability and biocompatibility as compare to other lipid carried due to use of physiologically biodegradable lipid. The Nanostructure carrier provides more retention time, better permeation, targeted delivery, improve bioavailability, Non-toxic. Now a days, the conventional eye drops replace by Polymeric eye drop i.e. in-situ gel, they are liquid in nature after instillation it undergoes gelation to form viscoelastic gels triggered by stimulation such as temperature, pH and ion activation. Consequently, gel formed increases residence time, extended drug release, enhances bioavailability, reduce dosing frequency and patient compliance.

The aim of this work to develop and evaluate in-situ gel containing Brinzolamide loaded Nano structured lipid carrier to increase its retention time, Bioavailability, Corneal permeation, reduce dose and dosing frequency. The saturation solubility study was used to select lipid solubility. The solubility of Brinzolamide was determined in several solid lipids such as Bees wax, Stearic acid, Gelucire50/13, Palmitic acid, Glycerol mono stearate (GMS), Precirol ATO 588, cetyl palmitate. Compatibility between selected lipids was examined by preparing mixture of solid lipid and liquid lipid in a ratios of 9:1, 8:2, 7:3, 6:4, 5:6, 4:7, 3:7, 2:8 and 1:9. Only one single phase Mixtures were selected for further study. High speed homogenization method was used to prepare Brinzolamide loaded NLCs. A three-factor, three-level Box- Behken design experimental design (BBD) was applied for evaluation of critical experimental conditions to maximize experimental efficiency and minimize experimental errors to optimize the size and particle size parameter (DPI) of the NLCs was determined using the dynamic light scattering (DLS) at a fixed angle of 90° at physical state of BRZ-loaded nanostructured lipid carriers demonstrated by DSC characterization technique. BRZ-loaded NLC in situ gel was prepared by the cold method. The drug content was determined by HPLC. In vitro release of BRZ-loaded NLC in situ gel was measured on Franz diffusion cell. Transcorneal permeation studies were carried out on freshly excised goat cornea. HET CAM (Hen's egg chorioallantoic membrane) study is an alternative to the Draize rabbit for the recognition of ocular irritations. Therapeutic activity study was conducted with albino rabbits (1.5–2 kg) under the permission of Institutional Animal Ethics Committee (IAEC).

From solubility data Gelucire 50/13 and Oleic acid were selected as the solid and liquid lipid for NLC preparation. Amongst various ratios of solid and liquid lipid 9:1, 8:2, 7:3, 6:4, and 5:5 no phase separation and homogenous mixture was observed for 8:2 ratio, which was selected as lipids mixture. The SEM analysis reveals that spherical and smooth surface of NLC with uniform distribution of particles. BRZ content in formulated in situ gel was determined and found to be in range of 99.34-98.58%. BRZ-NLC shows rapid release of drug (68.33%) within 4 h and within 7 h it completely release (94.33%) drug. This initial rapid release of drug due to the unentrapped drug which release from NLC) Whereas, BRZ-NLC in situ have extended and slow release of drug (96.44%) up to 15 h.

A Hitchhiker's and Backpacker's Guide to Drug Delivery

Nanoparticle-based drug delivery systems are widely explored to improve the biological outcome of chemo and immunotherapy. However, poor vascular circulation, limited targeting and the inability to negotiate many biological barriers are key hurdles in their clinical translation. Biology has provided many examples of successful “carriers” in the form of cells, which routinely overcome the hurdles faced by synthetic nanoparticle systems. We are exploring hitchhiking and backpacking approaches which involve combining synthetic particles with cells to drastically alter the in vivo fate of the particles as well as the cells. We will provide an overview of the principles and examples of hitchhiking and backpacking approaches for drug and cell therapy.
Characterizing Dynamic Processes of Materials Synthesis and Processing via In Situ Techniques
April 23 - May 7, 2024

Symposium Organizers
Liang Jin, Bioland Laboratory
Dongsheng Li, Pacific Northwest National Laboratory
Jan Ringnalda, FEI Company
Wenhui Wang, National University of Singapore

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10:30 AM *SB01.02.05
Ultrathin Nanosheets for Catalytic Cancer Therapy Sophia Gu; University of New South Wales, Australia

Nanotechnology has emerged as a promising approach for precision treatment of cancers. Two-dimensional nanoparticle-based therapeutic agents have been developed for safe and efficient treatment of cancers. In this talk, I will present our recent work on development of nanosheets for catalytic cancer therapy. We have developed a sustainable method to synthesize ultrathin layered double hydroxide nanosheets via a polymer-assisted bottom-up approach, and demonstrated high catalytic activity to disproportionate hydrogen peroxide in tumors and in-situ generated hydroxyl radicals efficiently to kill tumor cells. Without any drug loading, the nanosheet exhibited highly selective and specific anti-tumor effect. The hydroxyl radical generation-induced anti-tumor effect was further enhanced by cascade catalytic reactions triggered by photocatalysis. We also showed that the nanosheet generated oxygen bubbles and promoted the long-distance and directional movement toward the tumor microenvironment, thus achieving targeted delivery of therapeutic nanomedicine without traditional surface ligand modification.

References


SYMPOSIUM CH01

Characterizing Dynamic Processes of Materials Synthesis and Processing via In Situ Techniques
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10:30 AM *SB01.02.05
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References

Here we show the effect of nano-textured functionalized surfaces on calcium carbonate crystallization. We fabricated and quantified a rationally designed nano-textured surfaces using blockcopolymer lithography, ensuring a significant amount of surface curvature features in an order of magnitude to the critical nucleus size for calcite. The fabricated nano-textured surfaces are functionalized with carboxyl groups and compared to smooth functionalized surfaces to isolate the effect of the nano-texture onto the crystallization. The investigation of the crystallization at different supersaturations provides a holistic understanding of the effect on the thermodynamic as well as the kinetic barrier. *In situ* optical transmission microscopy coupled with digital holography and spectroscopy characterize the nucleation and single-crystal growth rates in a microfluidic cell with controlled calcium carbonate supersaturation through mixing. The analysis of the acquired microscopy images is using trained instance segmentation algorithms for accurate crystal detection.

This work shows that nano-textured surfaces promote the calcium carbonate nucleation by more than one order of magnitude compared to a smooth surface at the same supersaturation. This difference can be described by the classical nucleation theory, explaining an increasing kinetic barrier of nucleation and a decreasing thermodynamic barrier. For the tested supersaturations and nano-textures, the decreasing thermodynamic barrier outperforms the increasing kinetic barrier. While the increasing kinetic barrier is affected by a decreased monomer collision probability in the confined volumes of the nano-texture pits, the thermodynamic barrier is lowered by surface curvatures in the pits within an order of magnitude to the critical nucleus size. Besides higher nucleation rates, calcium carbonate crystallization on nano-textured surfaces shows lower induction times, higher site densities, and lower single-crystal volume growth rates. We expect that this work will provide guidance for the design of interfaces, which are needed to advance technologies relying on the understanding of the crystallization of calcium carbonate and other inorganic minerals.

This project has received funding from the European Research Council (ERC). Starting Grant, under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 853257).

11:15 AM CH1.01.03 Autonomous Flow-Synthesis of On-Demand Hybrid Perovskite Quantum Dots based on a Closed-Loop Feedback Control System

Huang Khang Bui and Tae Seok Seo; Kyung Hee University, Korea (the Republic of)

Nanostructured hybrid organic–inorganic lead halide perovskites quantum dots (QDs) have gained enormous attention and hold the potential to surpass traditional semiconductor nanocrystals as versatile photonic sources for displays, lighting, light-emitting diodes (LED) as well as light harvesters for photovoltaic devices, and solar cell. Moreover, due to the unique quantum-size effects, their optical bandgap and emission wavelength can be finely tailored by the ease of compositional control between halide ratio and adjusting the stoichiometry leading to the production of visible electromagnetic spectrum QDs. Currently, conventional flask-based synthetic platforms encounter a range of challenges from unwanted batch-to-batch variations such as precursor stability, temperature fluctuations, macro-environmental kinetics. A promising alternative is the use of continuous flow technology for the auto-production of perovskite QDs. The flow reaction chemistry in microfluidics has demonstrated rapid heat and mass transfer to speed up the chemical reaction time, precise control of the reagent volume, and reaction kinetics to produce uniform nanomaterials. Microfluidic synthesis can be integrated with an *in-situ* detection module so that the synthetic nanomaterials could be analyzed in real-time, which is inaccessible to the traditional flask-based methods. Moreover, all steps of microfluidic synthesis and product characterization can be software-controlled, thus ensuring time- and labor-effective synthesis with high reproducibility. One of the strategies for accelerating the identification of the most effective reaction conditions relies on automation. Automating synthesis enables quicker and more accurate procedures, including reagent loading, mixing, heating, and in-process product characterizations. Here, we implemented an automated feedback control module allows for the automatic optimization of reaction conditions, helping to generate the target nanomaterials with low cost and high speed. Developing a convenient and novel intelligent algorithm capable of data acquisition and analysis for resetting the reaction conditions could accelerate the transition from a manual synthetic batch process in an ordinary laboratory to a fully automatic continuous synthetic platform.

In the current work, we report an autonomous platform for self-control synthesis of desired perovskite QDs, which utilizes familiar yet efficient Proportional-Integral-Derivative (PID) algorithm. The PID controller has been used in industrial control applications for a long time since it minimizes overshoot in steady state response and less settling time. The PID controller has three tuning parameters: the controller gain (P term), the integral time constant (I term), and the derivative time constant (D term). The Internal Model Control methodology is a model based PID tuning techniques that has gained significant attention since it only requires one tuning parameter, namely the closed loop constant time. With microfluidic synthesis, the PID drives an optimization in precursors regulations to rapidly return accurate specifying reaction conditions which leads to precise on-demand optical properties. To demonstrate the feasibility and efficiency of our proposed method, we have synthesized MAPbBrxI3-x perovskite QDs with controlled fluorescence emission spectra in various P, I, D parameters to apparently indicate the effect of controlling to the outputs. The self-driving PID-based QDs synthesis strategy is a trade-off between target reaching time and stability, which are showcased clearly in this studies. Finally, we successfully produced two representative candidates for red-shift QDs at 650 nm and blue-shift QDs at 550 nm. This study further guides the production in large scale with simple, adaptable PID algorithm for not only lab bench synthesis but also industrial manufacturing.

11:30 AM CH1.01.04 Epitaxial Si on Epitaxial-Gd2O3/Si(111) Virtual Substrate Using Low-Cost RF Sputtering for Silicon on Insulator (SOI) Application

Shubham Patil1, Adityanarayan Pandey1, Swagata Bhunia1, Sandip Lashkar2, Apurba Lah2, Veeresh Deshpande2 and Udayan Ganguly1; 1Ilindan Institute of Technology Bohnbay, India; 2Institute of Technology Gandhinagar, India

There is an ever-growing need for 5G communication technology and the Internet of Things to achieve better-performing systems in speed and power consumption. Research has shown SOI technology to be very promising among different technologies (it offers low voltage and high-frequency operation capability) [1]. However, the costly smart-cut method for manufacturing SOI wafers is a challenge. Alternatively, the notion of using epitaxial rare earth (RE) oxides onto Si followed by epi-Si growth is a potential alternative to enable cheaper and high-volume manufacturing (HVM) of SOI wafers. Gd2O3 oxide is the most promising among all rare oxides due to its large bandgap, sufficient band offsets, stable oxidation state, and low lattice mismatch with Si(111). In this context, our group patented a methodology to produce semiconductors on an insulator substrate using an HVM-friendly RF magnetron sputter system [2,3]. In the work, we report an epitaxial Si on epitaxial-Gd2O3/Si(111) virtual substrate using RF magnetron sputtering for SOI application. The fabricated heterostructure is characterized through XPS, HRXRD, cross-sectional HREM, and TED analyses, providing compelling evidence for the formation of the epSi(111) layer on the epGd2O3 surface. The cap-Gd2O3/Top-Si/BOX-Gd2O3 (capping layer (cap)/channel (Top-Si)/Buried-oxide (BOX)) stack is deposited on Si(111) substrate using RF sputtering. The box layer is deposited at 750 °C with 20 W RF power (~0.12mm/min) for 100 min, followed by intrinsic-Si deposition (~0.3 mm/min) at 100 °C temperature. The Gd2O3 capping layer is deposited at a higher temperature (750 °C) to crystallize the channel layer. The heterostructure is subsequently annealed at 850 °C to study the impact of rapid thermal annealing. The heterostructure thickness is 12 mm/15 mm/16 mm confirmed using the internal etch rate and the derivative time constant (D term). The Internal Model Control methodology is a model based PID tuning techniques that has gained significant attention since it only requires one tuning parameter, namely the closed loop constant time. In the current work, we report an autonomous platform for self-control synthesis of desired perovskite QDs, which utilizes familiar yet efficient Proportional-Integral-Derivative (PID) algorithm. The PID controller has been used in industrial control applications for a long time since it minimizes overshoot in steady state response and less settling time. The PID controller has three tuning parameters: the controller gain (P term), the integral time constant (I term), and the derivative time constant (D term). The Internal Model Control methodology is a model based PID tuning techniques that has gained significant attention since it only requires one tuning parameter, namely the closed loop constant time. In the current work, we report an autonomous platform for self-control synthesis of desired perovskite QDs, which utilizes familiar yet efficient Proportional-Integral-Derivative (PID) algorithm. The PID controller has been used in industrial control applications for a long time since it minimizes overshoot in steady state response and less settling time. The PID controller has three tuning parameters: the controller gain (P term), the integral time constant (I term), and the derivative time constant (D term). The Internal Model Control methodology is a model based PID tuning techniques that has gained significant attention since it only requires one tuning parameter, namely the closed loop constant time.
to be predominantly irregular, with only small areas exhibiting regular patterns. To advance the fundamental understanding, we study the debrunnification coupling of TBATT directly on pristine Au(111). When the sample is annealed at temperatures between 200 °C and 220 °C, debrunnification is activated, resulting in predominantly irregular networks. Interestingly, the measured intermolecular distances agree with the DFT calculated values of organometallic carbon-Au carbon bonds instead of direct carbon-carbon bonds. Subsequently, TBATT was deposited on iodine passivated Au(111) (I-Au(111)), where we observed intact molecules either forming organized supramolecular structures or existing as dispersed single entities. Subjecting these samples to annealing temperatures of 200 °C to 220 °C induced a significant structural transformation, shifting from densely packed to a porous grid-like network. The remarkable stability of the TBATT-derived organogold networks as evidenced by high temperature annealing, is attributed to the π-conjugation. This motivated further investigation of the network’s electronic properties. The calculated electronic band structure revealed a surprisingly narrow band gap of 0.71 eV, together with dispersive bands. To confirm these DFT calculations experimentally, Scanning-Tunneling-Spectroscopy (STS) experiments were performed. The differential conductance dI/dV versus voltage V spectra indicate an electronic band gap of the order of 1.0 eV.

In conclusion, our study has demonstrated the feasibility of using I-Au(111) surfaces as effective substrates for the on-surface synthesis of covalent 2D networks through debrunnification. In particular, when using the TBATT precursor on I-Au(111), we achieved highly regular organogold networks, in contrast to the poor structural order observed when synthesized on pristine Au(111).

Although the domains are still relatively small, they contain a sufficient number of repeat units to allow the antha-tetrathiophene network to develop an electronic band structure. This convergence is partly due to the 2D topology, which allows a faster evolution of electronic properties compared to 3D structures, mainly because more intermolecular bonds are formed per monomer. The influence of the iodine monolayer on the formation of highly regular organogold networks is twofold: On the one hand, iodine induces reversibility of the robust carbon-Au carbon bonds, facilitating dynamic error correction, as confirmed by experiments where the organogold networks disintegrated when annealed in an iodine atmosphere. On the other hand, the presence of the iodine monolayer does not impose spatial constraints but instead supports the formation of exceptionally regular networks.

SESSION CH01.02: Crystal Growth II
Session Chairs: Jungwon Park and Jan Ringnalda
Tuesday Afternoon, April 23, 2024
Room 442, Level 4, Summit

1:30 PM *CH01.02.01
Multi-Phasic Growth Mechanism of Colloidal Nanoparticles by Statistical Liquid Phase TEM Jungwon Park; Seoul National University, Korea (the Republic of)

Nanoparticle nucleation and growth have long been of great interest in science and industry. Despite impressive advances in nanotechnology, the thermodynamic origin of nanocluster nucleation is still a mystery, and there is no quantitative understanding of nanoparticle growth dynamics. It is because of the complexity that intrinsically exists in nanoparticle growth pathways. A comprehensive understanding of the growth mechanism requires experimental investigation of nanoparticle growth from two different aspects: individual growth trajectories and kinetics in ensemble average. To address this issue, we monitor hundreds of individual trajectories of growing nanoparticles using liquid-phase transmission-electron-microscopy. Statistical analysis of ensemble growth trajectories reveals that the growth of nanoparticles can be classified into multiple distinct types and stages. We present a microscopic model and statistical mechanical theory that provide unified, quantitative understanding of the time-dependent mean, variance, and distribution of nanoparticle size at all stages of the nanoparticle growth processes observed. We find that strongly-nonexponential free energy originating from a nanoparticle’s edge interaction, motion, and conformational degeneracy, which has received little attention so far, plays an essential role in the nanocluster nucleation and non-classical growth dynamics.

2:00 PM CH01.02.02
Emergence of a Novel BCT Phase in Eutectic High Entropy Alloys during Laser Powder Bed Fusion Bingbing Zhou1, Qingsong Shu1, Ming Chen2 and Lanting Zhang1; 1Shanghai Jiao Tong University, China; 2Northwestern University, United States

High entropy alloys, composed of a minimum of four principal elements, exhibit exceptional combinations of strength and ductility, along with impressive corrosion resistance and microstructural adaptability. Recent strides in eutectic high entropy alloys (EHEAs), a subset within this category, reveal multi-phase structures and uniform microstructures in their as-cast state. Traditional metallurgical processing of EHEAs leads to limited improvements in strength and ductility due to the formation of a coarse lamellar structure. Additive manufacturing, particularly laser powder bed fusion (L-PBF), enables the construction of intricate three-dimensional structures by incrementally adding thin layers, overcoming geometric constraints. However, the phase transition process of EHEAs from liquid to as-deposited state is constrained, particularly during the rapid heating and cooling inherent in the L-PBF process. This can induce metastable phases under these non-equilibrium conditions, significantly affecting the properties of the printed EHEA. The implementation of an operando X-ray diffraction device at a synchrotron beamline, harnessing the high brilliance and swift detectors available, serves as the vital bridge to numerical methods. Our pre-alloyed powder, with a nominal composition of Ni30Co30Fe11Cr11Al18, exhibits a lamellar structure consisting of B2 and FCC phases as predicted by thermodynamic phase equilibrium calculations. During the L-PBF process, a novel BCT phase emerges during solidification. Operando X-ray diffraction, employed during L-PBF, provides a real-time measurement of phase transitions and structural evolution in EHEA. This study not only establishes the relationship between processing and phase constitution but also illustrates how kinetics influence morphology and property control.

2:15 PM CH01.02.03
Understanding Graphene Inception and Growing by Investigating Early-Stage Particle Formation Örnulf Padilla1, Kyle J. Daun2, Hartmut Wiggers1 and Christof Schulz1; 1IVG, Institute for Energy and Materials Processes – Reactive Fluids, and CENIDE, Center for Nanointegration Duisburg Essen, University of Duisburg-Essen, Germany; 2University of Waterloo, Canada

Microwave-assisted plasma synthesis is a promising pathway for large-scale production of few-layer graphene flakes. One of the challenges associated to the advancement of this process, is to develop a better understanding of the stages of inception and growth of graphene, as well as of the connection between the gas phase synthesis, the reaction conditions in the gas phase, and the quality of the material obtained. In a microwave-assisted plasma reactor, the carbon-bearing precursor enters the plasma region and gets decomposed into smaller reactive fragments, such as C, H, H2, C2, C2H2, and CO. These reactive fragments then leave the plasma region, where they form nuclei that rapidly grow into graphene1. The literature suggests connections between the type of structure formed and the temperature gradient, residence time, and carbon concentration in the nucleation and growing zones23. Further, the use of low precursor content is common to prevent or reduce soot formation. In this work, ethanol and ethylene are used as precursor to study graphene formation. The first one is a common precursor used in the literature, and the second one is a known key intermediate species during graphene formation. Key species formed during precursor decomposition which later become building blocks for graphene formation downstream have been analyzed in situ and through exhaust gas sampling. Optical emission spectrometry (OES) has been performed at different heights above the nozzle of the reactor, and light collection with a plano-convex lens was used to provide good spatial resolution. Following the approach described in Ref. 1, several wavelength regions of key species light emission were selected, and for each wavelength region the measurement conditions were fixed for proper comparison of signals at different heights above the nozzle (HAN). Spectra corresponding to C and C2 appeared at higher HAN. When increasing HAN, light emission corresponding to CH first increases and then decreases in intensity for both precursors. Emission from the H2 Balmer, important for determination the electron density, could be well distinguished from background radiation. With ethylene as precursor, C, CH, C2, and H emissions were stronger than with ethanol. Analysis of collected material by TEM show characteristic folded layers of graphene. With ethylene as precursor graphene and soot were formed in parallel, while ethanol led to the formation of graphene only. FTIR, light scattering, and thermophoretic sampling from the post-plasma region will provide further information about particle nucleation and growth. References


2:30 PM CH01.02.04
In Silico Observation of (Trans-) Formation of Oxide Nanoparticles during Chemical Vapor Synthesis Shraddha R. Joshi, Martin A. Schroer, Maximilian Stepponat and Markus Winterer; Universität Duisburg-Essen, Germany

Characteristics of nanoparticles (NPs) such as microstructure and morphology determine their physicochemical properties and thereby their application potential. Particle characteristics and correlated properties may be optimized by tuning relevant process parameters [1].

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Chemical vapor synthesis (CVS) is a dynamic gas phase reaction to generate NPs where the formation and transformation of NPs is mainly governed by the time-temperature T(t) profile in the reactor [2]. Usually, the synthesized NPs are collected and characterized ex situ to determine various characteristics. This often leads to the loss of information due to artifacts during particle collection, oxidation, hydration, surface reactions or ageing of NPs. Ex situ methods also limit insight into intermediate species. Reliable information about the dynamic processes in CVS and related particle characteristics is only accessible via in situ observation.

Here, we present results on CVS of tin oxide (SnO$_2$) and iron oxide (FeO$_x$) NPs investigated in situ using high energy X-rays at synchrotron beamlines [3]. The key challenge in these experiments is the low number density of the particles generated in the gas phase process which is about three orders of magnitude smaller than in corresponding bulk systems [4]. However, due to high intensity X-ray sources at contemporary synchrotron radiation facilities and modern X-ray detectors it is nevertheless possible to obtain scattering and spectroscopy data. A novel mobile CVS reactor is designed for these experiments which enables control of process parameters, especially the time-temperature T(t) profile and oxygen partial pressure p(O$_2$) to produce oxide NPs. In situ small and wide-angle X-ray scattering (SAXS and WAXS) are used to study microstructure, morphology, phase composition and crystal structure. X-ray absorption spectroscopy (XAS) is performed to study electronic and local structure.


Acknowledgements: This research is conducted at PETRA III at DESY, Hamburg under the proposal numbers: I-20211391 at beamline P64 for EXAFS, I-20211320 and I-20220812 at beamline P62 for SAXS/WAXS and I-20220890 at beamline P21 for XRD. We gratefully acknowledge the German Research Foundation (DFG) for funding through research unit FOR 2284 ‘Model-based scalable gas-phase synthesis of complex nanoparticles’ (WI-981/14, INST 20876/395-1 FUGG).

2:45 PM BREAK

3:15 PM CH01.02.06
Synthesizing Well-Defined Pre-Catalysts for Multi-Modal Studies of Electrocatalysts under Reaction Conditions See Wee Chee; Fritz Haber Institute of the Max Planck Society, Germany

Chemical conversion through renewable energy-powered electrocatalysis is a crucial technology in our green energy strategy. However, we still lack the fundamental understanding of working catalytic structures under reaction conditions needed to enable the rational design of optimal catalysts for such applications. Even though operando studies can be used to investigate catalysts during reaction, no single operando technique provides complete information about an electrocatalyst under reaction conditions because the relevant catalytic processes span several orders of magnitude in length and time scales. Hence, multiple techniques are usually needed for such studies. Ensuring that we are looking at catalysts under self-consistent reaction conditions in the different tools is not easy. The starting point towards addressing this challenge is the ability to make the samples in a controllable and reproducible manner. In this talk, I will discuss my group’s work using different methods to synthesize model pre-catalysts with well-controlled characteristics for operando microscopy studies. Using such transferable synthesis protocols, we further bridge the gap between various techniques with targeted measurements that correlate the structure and the properties of catalysts during reaction.

3:35 PM CH01.02.07
In-Situ Synchrotron Light Studies of Cobalt Ferrite and Cobalt(II) Oxide Synthesis via The Polyol Method: Uncovering Intermediate Phases through In-Situ XRD and SAXS Monitoring Miran Baricic1,2, Roxana Mirshahi2, Youssef Snoussi1, Jasper Plaisier3, Lara Gigli1, Alessandro Mariani1, Barbara Sartor1, Sophie Nowak1, Paolo Centomo5, Davide Peddis5, Souad Ammar2 and Carlo Meneghini1; 1Université Paris Cité, France; 2Université des Studi di Roma TRE, Italy; 3Elettra Sincrotrone Trieste ScpA, Area Science Park, Italy; 4Università degli Studi di Padova, Italy; 5Università degli Studi di Genova, Italy

The synthesis of cobalt ferrite (CFO) and cobalt (II) oxide (CO) nanoparticles (NP-CFO, NP-CO) through the polyol method has garnered considerable interest due to their promising applicative potential in fields such as catalysis, electronics, biomedical engineering, and magnetic materials science. Detailed knowledge of the processes taking place during synthesis is crucial for the precise adjustment of synthesis parameters. We have used synchrotron radiation X-ray diffraction (SR-XRD) and small-angle X-ray scattering (SR-SAXS) at the Elettra synchrotron radiation facility, to monitor in situ the formation of NP-CFO and NP-CO during polyol synthesis. The analysis of time-resolved XRD and SAXS patterns provides insight into the evolving crystallographic structure and morphological changes during synthesis. Our findings reveal curious and original insights into the evolution of the reactant during the synthesis, such as the presence of intermediates (e.g., layered hydroxide salts, LHS) and the appearance of sub-nanometre-sized precursor phases likely active as pre-nucleation clusters of NP-CFO phases. The in-situ monitoring allowed us to capture the dynamic evolution of these intermediates, providing valuable information on their formation pathways and growth kinetics, which significantly affect the nucleation and growth processes of the cobalt-based nanoparticles. The unambiguous identification of these intermediates sheds light on the intricate mechanisms governing the process and represents a crucial step towards optimising the polyol synthesis and improving the purity and crystallinity of the final products.

The understanding of the synthesis dynamics and mechanistic insights gained from this in-situ study advance tailored synthesis strategies for producing high-quality NP-CFO and NP-CO materials. This also provides relevant details for better interpretation of the magnetic properties of antiferromagnetic materials such as CO, which is critical to avoid ambiguities given its relatively low magnetic signal.

4:00 PM CH01.02.08
Multiscale Insights into Amalgamation Synthesis of Intermetallic Nanocrystals via In Situ X-Ray Scattering Florian Schenk1, Christian Prehal2 and Maksym Yarema1; 1ETH Zurich, Switzerland; 2University of Salzburg, Austria

Bimetall nanocrystals are a family of materials with over > 20,000 potential members with a multitude of applications in catalysis, energy conversion and storage, plasmonics and magnetics.[1,2] Recently, a general synthetic approach for intermetallics via amalgamation was presented,[3] unlocking up to 1,000 potential new intermetallic nanocrystals. Combining pre-synthesized metal seeds with a liquid metal, the intermetallic compound is formed via fast diffusion dynamics. This overcomes challenges of combining two dissimilar metals at the nanoscale, such as contrasting oxidation potentials or epitaxial constraints. With accurate and predictive control over the size and composition, this synthesis provides access to a wide range of tailor-made intermetallic nanocrystals. Further optimization and expansion of the amalgamation synthesis, however, requires understanding of the process on the atomic as well as on the particle scale.

Here, we turn to in situ small- and wide-angle X-ray scattering as an ideal tool for observing size and size dispersion, as well as crystallinity and phase-dynamics in colloidal systems.[3-6] We track multiscale reaction dynamics of colloidal intermetallics (Au-, Ag- and Pd-based alloys) in real time using a tailor-made reactor and reveal unprecedented reaction mechanisms in the formation of intermetallics. Furthermore, we also provide a toolbox for in situ studies of nearly every nanocrystal synthesis since the combination of reactor and in situ scattering can be applied to highly air- and moisture-sensitive protocols at temperatures up to 300 °C and down to millisecond timescales.


4:15 PM CH01.02.09
Controlled Synthesis of Self-Reduced CoO Decorated Co3O4 via In-Situ X-Ray Scattering Florian Schenk1, Christian Prehal2 and Maksym Yarema1; 1ETH Zurich, Switzerland; 2University of Salzburg, Austria

Nitrogen dioxide (NO$_2$) is a common toxic gas in automobile exhaust emissions, industrial combustion, and power generation. Long-term exposure to nitrogen dioxide will not only cause photochemical smog and acid rain to pollute water, soil, and air but cause harm to human health, such as respiratory distress, heart failure, and pulmonary edema. Precise detection and emission control of nitrogen dioxide are thus critical.

In this study, Co$_3$O$_4$ nano-assemblies with different morphologies, including sphere, pillowy-shape, and star-shape, were successfully produced via the polyol method at different reaction temperatures. The appropriate operating temperature of these three nano-assemblies for having the highest gas responses were then evaluated under 1000 ppm NO$_2$ and were then found to be
130 °C. The observed highest response approaching 207% was found for the pillow-shaped nano-assembly. The spherical Co3O4 nano-assembly was selected for the subsequent self-reduction study due to its relatively regular morphology among these three nano- assemblies. The spherical Co3O4 nano-assembly was then reduced in a mixture of 95% nitrogen and 5% hydrogen with various controlled temperatures and time for having a nanocomposite comprising coexisted multiple cobalt oxides. The Rietveld, x-ray photoelectron spectroscopy (XPS), and energy-dispersive x-ray spectroscopy (EDX) were mainly performed to identify the phase fraction and chemical composition.

It was found that after reduction at 250 °C for 120 minutes, a heterogeneous nanocomposite comprising CoO (Co2+) (43 wt%) and Co3O4 (Co2+ /Co3+)(57 wt%) can be successfully obtained. The XPS analysis confirmed that the amount of the surface adsorbed oxygen (Oc) and the oxygen vacancy (Ov) associated with O2- ions in oxygen-deficient regions within the matrix of Co3O4 increase with the increase of Co2+ ions newly formed via the reduction procedure from Co3O4 to CoO, which is considered to be beneficial for improving gas sensing performance. The sensing response at 400 ppm NO2 at 130 °C increases from 61% of the unreduced Co3O4 nano-assembly to 91% of the self-reduced CoO / Co3O4 one. Compared with CH3, C2H6, C3H8, CH3OH, and CO, the self-reduced CoO / Co3O4 nano-assembly exhibits excellent selectivity to NO2. The response of NO2 is four times higher than that of other gases. Based on the dynamic recovery test, the self-reduced CoO / Co3O4 nano-assembly shows a reproducible response.

Keywords: gas sensor, nitrogen dioxide sensing, Co3O4, reduction, selectivity, nano-assembly.
To investigate the patch growth under well-mixed conditions, we use a continuous inline spectroscopy setup which consists of a polycrystalline T-mixer connected to a rectangular borosilicate glass tube. The latter is mounted on a linear stage on an optical pegboard. Via an automated protocol, the glass tube is moved through a fixed measurement position of a fiber spectrometer. Thus, each position along the glass tube corresponds to a specific reaction time. An adjustable spacer tube can be used to obtain data at later residence times.

Using measurements at different reaction conditions, we collect kinetic data for model development. To validate our measurements, we utilize a quenching approach which freezes the metal patches at various growth stages and thus enables them to be investigated via ex situ characterization techniques. Correlating in situ and ex situ data, we show that a kinetic model for the formation of patchy particles valid for a wide range of reaction conditions can be established, paving the way for further process optimization and automation.

9:30 AM BREAK

10:00 AM *CH01.03.05
In Situ Liquid Phase TEM of Chemical Reactions and Materials Transformations

Haimei Zheng, Lawrence Berkeley National Laboratory, United States

The recent development of liquid phase transmission electron microscopy (TEM) has enabled break-throughs in characterizing various chemical reactions and materials transformations. It has unveiled many developments in liquid-phase transformation dynamics, and the structure and bonding evolution in situ/in operando with high spatial resolution. Since the electron beam for imaging can also induce perturbation to the chemical processes, it has been a concern that the observed phenomena in a liquid cell may deviate from the real-world processes. Strategies have been developed to overcome the electron-beam induced issues, and to connect the observation with the real-world chemical reactions. Here, I will discuss various strategies in using liquid cell TEM to study nucleation, growth, and self-assembly in solution, where electron beam is often used to initiate the reactions. Due to the complexity of the liquid cell TEM experiments, strategies are often employed simultaneously, for example, low dose imaging, advanced electron microscopy techniques, carefully designed control experiments, multimodal characterization, and so on. The multidisciplinary research has opened many new opportunities by merging different expertise and approaches together stimulating innovations and fostering novel discoveries.

10:30 AM CH01.03.06
Early-Stage Nucleation Behavior of GaAs Nanowires on Si Substrate based on In-Situ TEM

Chen Wei1,2, Jean-Christophe Harmand2 and Federico Panciera2; 1Université Paris-Saclay, France; 2Centre National de la Recherche Scientifique, France

To take advantage of the unique physical properties of nanowires (NWs), it is crucial to accurately control their geometry, crystal structure, and doping level. This goal will ultimately be achieved by a deeper understanding of the growth mechanisms.

Meanwhile, the initial stages of the growth process are the least understood and have been investigated almost exclusively by ex-situ techniques. Here, we present real-time observations of the nucleation and growth of self-catalyzed GaAs nanowires using a transmission electron microscope (TEM) equipped with molecular-beam-epitaxy (MBE) sources. Custom-made floating substrates, in the form of electron-transparent <111>-oriented Si membranes, were fabricated using MEMS (Micro-electromechanical Systems) technology. A combination of finite-element simulations and Raman spectroscopy was used to accurately calibrate the sample temperature and optimize its design. The results were in good agreement and further verified by the dimension and distribution of pre-deposited Ga droplets.

Nanowires were grown directly on the membrane inside the microscope via a vapor-liquid-solid mechanism as a practical MBE configuration and the process was monitored by simulations and Raman spectroscopy was used to accurately calibrate the sample temperature and optimize its design. The results were in good agreement and further verified by the dimension and distribution of pre-deposited Ga droplets.

10:45 AM CH01.03.07
Multiscale Mechanisms of Twisted Carbon Nanotube Yarns Probed In Situ by Soft X-Rays during Tensile Loading

Philip M. Jean-Remy1, Daniel Malone1, Alec Schwartz1, Cheng Wang2, Adam Golder1, Eric Meshot3 and Xavier Lepro Chavez1; 1Lawrence Livermore National Laboratory, United States; 2Lawrence Berkeley National Laboratory, United States; 3Atomic Machines, United States

Resonant soft x-ray scattering (R-SoXS) can help realize the promise of data driven research in hierarchical materials whose structure spans multiple length-scales, such as carbon nanotube (CNT) assemblies. Our prior work demonstrated the wealth of high-resolution and statistical data R-SoXS provides about chemical and structural morphologies across different length scales in CNT materials [1]. CNTs are known as the strongest 1D material due to their covalent sp2 carbon bonds, hexagonal lattice, and cylindrical shape. However, piecing together CNTs into assemblies has proven to be so far a failed strategy to achieve the same elite performance metrics as individual CNTs. This highlights a critical deficiency in understanding the effects that the processing of individual nanostructures has on the performance of their derived macroscale assemblies, thereby hindering the development of a process-structure-performance map for these materials.

In this work, we propose a new method to decouple the distribution orientation of nanoscale tortuosity and the macroscale twist of CNT dry-spun yarns under applied loads via in-situ R-SoXS probing at high energy (1200 eV) and low energy (280 eV), respectively. With this decoupling enabled by in-situ R-SoXS, we gain new insights on the deformation mechanisms of these yarns which have been structurally reinforced with a novel vapor-phase polymer that is subsequently self-crosslinking [2]. Further, we examine how both the distribution orientation of the nanoscale tortuosity of CNT bundles and the macroscale twist of the yarns evolve as a function of applied load for different processing conditions, including yarns with plasma-enhanced surface reactivity prior to the polymer reinforcement. Better understanding of the multiscale structural behavior of CNT yarns as a function of processing will allow advances for the manufacture at large scale of products based on ultra-stiff, flexible, conductive fibers for aerospace, defense, communications, wearables, and biomedical industries.


11:00 AM CH01.03.08
Synthesizing New Ternary Nitrides with Guidance from In Situ X-Ray Diffraction

Christopher Romy1, Shaun O'Donnell1,2, Kayla Huang1,3, Rebecca Smaha1 and Andriy Zakutayev1; 1National Renewable Energy Laboratory, United States; 2Colorado State University, United States; 3University of Illinois at Urbana-Champaign, United States

Ternary nitrides are an important class of functional solids, most famous for underpinning high-efficiency light emitting diodes. These materials are composed of nitrogen along with two other elements (e.g., InGa1-xN for those light emitting diodes). However, making these materials is challenging, in part owing to the low reactivity of elemental nitrogen gas (N2), and the propensity for nitrogen-containing solids to decompose at elevated temperatures (releasing N2). Metathesis reactions (also known as ion exchange reactions) can help us overcome these challenges and keep nitrogen in the solid state to synthesize new ternary nitrides. For example, we have recently discovered that starting from lithium-containing precursors (e.g., Li6W2N8), we can conduct metathesis reactions with ZnX2 salts (X = F, Cl, Br) to synthesize new Zn ternary nitrides (e.g., Zn6W2N8). This presentation will focus on our recent work studying these kinds of metathesis reactions using in situ x-ray diffraction, with an eye towards generalizing this synthesis approach to accelerate materials discovery.

11:15 AM DISCUSSION TIME

11:30 AM CH01.03.10
Distinguishing Classical from Non-Classical Nanoparticle Growth Mechanisms by In-Situ X-Ray Diffraction

Stephan Foerster, Manuel Wilke, Sascha Ehler and Martin Dulle; Forschungszentrum Jülich, Germany

Hot-injection and heat-up synthesis routes are very commonly used for the controlled synthesis of nanoparticles with narrow size distribution and high crystallinity. These synthesis routes can proceed via classical or different non-classical nucleation and growth pathways, the latter often involving pre-nucleation clusters or oriented attachment. For synthetic control it is important to have a better understanding of the reaction pathways. To obtain fundamental insights into the nanoparticle nucleation and growth kinetics for these reactions is particularly demanding, because these synthesis routes typically involve heating to temperatures above 200°C which is challenging for many in-situ experimental techniques.

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We designed glass flask reactors to perform in situ X-ray diffraction (SAXS/WAXS) experiments to investigate the nucleation and growth kinetics of noble metal, semiconductor and oxide nanoparticles during heat-up synthesis up to 340°C. The analysis of the growth curves for varying heating rates, precursor/ligand ratios and plateau temperatures shows that the kinetics proceeds via non-classical reaction paths involving the formation of amorphous prenucleation clusters, nucleation, oriented attachment and final growth by monomer consumption. [1,2] Although these pathways are more complicated compared to classical nucleation and growth, one can identify kinetic phases of induction, nucleation and growth that are typically transacted during the synthesis.

For a quantitative analysis of the growth curves we extended classical nucleation and growth theory to account for amorphous transient or precursor states and particle aggregation e.g. by oriented attachment during the nucleation and growth phases. We find that this non-classical model is able to quantitatively describe all experimental growth curves. The model provides fundamental insights into the underlying kinetic processes especially in the nucleation and growth phases with the occurrence of a transient amorphous state, the nucleation of crystalline primary particles, particle growth and particle aggregation, all proceeding on overlapping time scales.

The described in situ X-ray scattering experiments together with the extension of the classical nucleation and growth model quantitatively describe the two most important mechanisms of non-classical nucleation and growth routes, i.e. the formation of intermediate or transient species, and the particle aggregation processes.

in oxidation state with respect to changes in pH, air exposure, and applied potential as the cell operates and is measured simultaneously. Measured in the laboratory, synchrotron quality data of nanoparticle stability and assessment of cell performance is made possible, and through a sweeping series of experiments controlling pHs and applied potentials, a pseudo-Pourbaix diagram of nanoparticle Ni₂P can be constructed.

Droplet deposition and drying is a key process in many manufacturing processes including: the spray deposition of paints and coatings, inkjet printing, and the manufacture of large area electronics. During the drying of droplets that contain small particles in suspension, it is well known that, under certain experimental conditions, the dried residue does not form a uniform deposit related to the shape of the initial liquid drop but instead a migration of particles to the pinned contact line of the drop leads to a characteristic ring deposit or coffee stain. In dilute particle suspensions this phenomenon is believed to be initiated by contact line pinning during evaporation, which leads to a radial outward fluid flow along the base of the drop increasing the local particle concentration at the contact line because evaporation reduces the solvent. The precise conditions that trigger the formation of a coffee ring are still a topic of investigation but are believed to be associated with the mechanisms that lead to contact line pinning before the receding contact angle is reached during drying.

There has been considerable experimental study of the drop drying process and in situ imaging of dilute particulate suspensions using optical microscopy and individual particle tracking experiments has prove valuable for studying the dynamics of the coffee ring and fluid flow during droplet drying. However, many of the real-world applications of droplet-based manufacture use dense particulate suspensions as the fluid or ink and, although it is known that such dense suspensions can form a coffee ring, study of droplet drying in these cases has been limited to observing the change in drop shape.

Here, we present an in situ study of the drying of dense suspensions of sub-micron ZrO₂ particles in aqueous suspension using a synchrotron X-Ray source to track changes in drop volume and shape during drying at 20, 45 and 60 °C on glass, silicon and Kapton substrates that show different contact angles of 24°, 36° and 73° respectively. We show that if the drop retains radial symmetry during the drying process, the signal intensity across the drop image can be transformed to determine the local density of the suspension and from this a semi-quantitative measure of the particle concentration in the liquid as a function of drying in the drop. Hence, we can track the relative densification and radial particle suspension as a function of position during the drying of the drop.

Coffee rings are found to form more easily on the lower contact angle surfaces and at higher drying temperatures where evaporation is more rapid. Our results show that the density profile across drying drop is significantly different between drops that show uniform drying and those where a coffee ring forms. In the absence of a coffee ring, densification commences across the surface of the drop in a uniform manner and there is evidence for a possible surface crust during drying. However, under the conditions that lead to a coffee ring, initial densification is also more intense at the upper surface but is now much stronger towards the contact line. It is unclear whether the surface crust formation suppresses coffee ring formation or is a consequence of its absence.

**4:00 PM CH01.04.09**

**Continuous EELS Spectrum Imaging of Nano-Droplet Crystallization Heterogeneity**

**Benjamin Miller**, Lian Spillane and Cory Czarnik; Gatan, Inc., United States

Electron energy loss spectroscopy (EELS) is a powerful technique for characterizing nanomaterials. A number of materials properties can be extracted from the information-rich spectra. One application is nano-thermometry, where the local temperature of individual metal nanoparticles can be measured by a precise determination of the plasmon peak position. As thermal expansion increases a particle’s volume, the density of electrons decreases, and the energy loss of the plasmon peak shifts to lower energies. This same approach can be used to detect melting and crystallization, which result in much larger changes in the electron density. Continuous acquisition of EELS data enables precise determination of the melting and crystallization temperatures.

Using the new in-situ EELS spectrum imaging features of the Continuum GIF, a continuous series of drift-corrected spectrum images can be acquired over an ensemble of particles, and the melting and crystallization behavior monitored.

In this work, we show how a series of EELS spectrum images can be acquired and processed along with the temperature data from a MEMS-based heating holder. With modern fast detectors and spectrometers, spectrum images with thousands of spectra can be acquired in less than a second, making continuous in-situ spectrum imaging feasible. The holder temperature data is automatically synchronized and correlated with EELS spectrum image data. We also show how the entire series of in-situ EELS spectrum images can be rapidly fit using the built-in NILS tools in DigitalMicrograph, yielding series of synchronized fit maps. After summing over a single nanoparticle, plots of the peak position over time can be generated, and even plotted against the nominal temperature from the holder in scatterplots.

This new in-situ EELS spectrum imaging capability has been applied to a Sn nanoparticle sample which was oscillated above and below its melting temperature. Watching the maps of plasmon position over time reveals that while all the Sn particles crystallize during most cycles, and most particles crystallized during every observed cycle, some particles occasionally did not crystallize even though surrounding particles did. This heterogeneous and stochastic behavior at the nanoscale can only be observed with high spatial and temporal resolution. In-situ electron microscopy, and specifically in-situ EELS spectrum imaging is an excellent technique for exploring these dynamics.

**4:15 PM CH01.04.10**

**Solid Nanoparticles and Liquid Droplets on The Path to Crystallization in Solution: Some Fundamental Questions on Nucleation Addressed with Synchrotron X-Ray Scattering Methods**

**David Carriere**, CEA, France

Crystallization from solution often involves transient, non-crystalline states like reactant-rich liquid droplets and amorphous particles [1]. This state of affairs not only challenges the chemical engineering models used to rationalize laboratory- and industrial-scale processes, but also motivates deep experimental tests of the multistep nucleation theory proposed as an alternative to the well-known classical nucleation theory of Becker and Doering [2]. However, testing both engineering and physical models requires challenging quantification of the structures and phases (sizes, volume fractions, crystallinity, compositions), down to the millisecond reaction times and sub-nanometer characteristic lengths.

Here, I will illustrate how coupling synchrotron X-ray methods and electron microscopy can tackle challenging scientific questions in the crystallization of oxide nanoparticles, vanadates and rare-earth oxalates through: 1) providing evidence of transient structures, and sometimes multiple transient structures, together with growing crystals [3–6] 2) assessing the impact of these transient phases on the final product, in particular when it consists of nanometer-sized aggregates of nanocrystals [5] 3) providing evidence of an evolution in the chemical composition of the transient phases [6] and 4) assessing the impact of the transient phases on chemical engineering models [7].

**References**


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**SESSION CH01.05: Poster session I**

**Session Chairs: Liang Jin and Dongsheng Li**

Wednesday Afternoon, April 24, 2024

Flex Hall C, Level 2, Summit

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**5:00 PM CH01.05.01**

**Atomic Scale Imaging of Defects in Solution Grown Tin Disulfide**

**Naveen Goyal**, Rajeev Kumar Rai and N. Ravishankar; Indian Institute of Science, India

Tin disulfide (SnS₂), a layered material, has gained substantial attention in recent years due to its applications in various fields, including broadband photodetection spanning from UV to NIR regions, selective room-temperature gas-sensing of NO₂, serving as an anode material in sodium-ion batteries, and application in supercapacitors. These applications arise as a result of a
synergistic interplay between SnS₂'s inherent properties and the precise engineering of defects, such as vacancies, dislocations, and grain boundaries. Along with these, other defects such as riplocations are also present exclusively in layered materials. The control of such new defects and their influence on the properties and applications of layered materials is currently a wide subject of study.

In this study, we utilized the solution chemistry method to synthesize nanocrystals of SnS₂. The phase purity of these nanocrystals was confirmed through powder X-ray diffraction, and their uniform nanosheet morphology was evident from TEM images. We have conducted a comprehensive analysis of defects using advanced microscopic techniques, specifically using aberration-corrected scanning transmission electron microscope. By directly imaging the layers of SnS₂ along [100] zone axis, we identified the presence of various defects at the core of nanocrystal, including line and screw dislocations, voids and warping of layers. While dislocations and voids are well-documented in various materials, the riplocations appears to be a unique characteristic of van der materials like SnS₂. These defects are believed to result from local variations in supersaturation during the nucleation and growth of the crystallite. This type of investigation is expected to yield valuable insights for tailoring the properties of layered materials.

References:

5:00 PM CH01.05.03

**Synthesizing Nanomaterials with Optimal Properties using Closed Loop Optimization**

Brenden Pelkie, Abdul Moezez and Lilo D. Pozzo; University of Washington, United States

Many nanomaterial synthesis procedures require the selection of several experimental parameters to control the properties of the material that is produced. While this can provide detailed control over material properties, navigating this high dimensional parameter space to select values that enable desired outcomes can be an intractable process. While the applications of laboratory automation makes the systematic testing of parameter combinations more accessible, complete combinatorial explorations can still be inefficient or impossible for large systems. Closed loop optimization methods like Bayesian optimization provide a method to autonomously select experimental parameter values to test, on-the-fly during an ongoing experiment. These approaches use machine learning methods to select parameters that are likely to improve a material’s performance, as defined by a researcher-defined metric. Implementation of fully closed loop experiments requires capabilities for automated sample synthesis, characterization, and data processing. We are developing infrastructure to enable closed loop optimization for nanoparticle systems. To enable automated synthesis, we have developed an open hardware robotic motion platform to enable flexible lab automation for advanced synthetic capabilities and automated flow synthesis tools for nanoparticle synthesis. Online characterization is enabled by an autosampler and automated data processing workflow for lab-scale x-ray scattering. These capabilities are applied to gain morphological control of various nanoparticle synthesis processes.

5:00 PM CH01.05.04

**The Operando SAXS Characterization of The Binary Mixing of F127/L121 Pluronic Biomedical Hydrogels in The Self-Assembly**

Tz-Feng Lin and Wei-Chieh Wang; Feng Chia University, Taiwan

Pluronic biomedical devices (PBHs) was proposed to study the changes in the self-assembly of binary mixing copolymers. PBHs are served as a microenvironment and as a target drug delivery system offering many attractive benefits such as intrinsic biocompatibility and controllable prolonged drug delivery. Small angle X-ray scattering (SAXS) was used to discover the self-assembled structures of the PBHs in real time with respect to the temperature variations. According to the SAXS results, structural changes of the micelle and the lamellar affected the mixing behavior of hydrophilic segments and hydrophobic segments. Thus, the transformation between the flat lamellar amphiphilic boundary and the hydrophobic core was studied. Results show that the diffusion of the amphiphilic segments in the PBHs will affect a lot across the interface between the hydrophilic corona and the hydrophobic core. Evidence are observed for the self-assembly of PBHs at the temperatures from 25 to 45°C simultaneously.

10:30 AM CH01.06.01

In and Out-Of-Equilibrium Assembly Dynamics of Nanoparticles Oqian Chen; University of Illinois at Urbana-Champaign, United States

In this talk, I will discuss our recent efforts on utilizing liquid-phase TEM imaging and associated machine-learning or computational simulation methods to understand the fundamental colloidal forces in both equilibrium and out-of-equilibrium assemblies of nanoparticles. Anisotropic gold nanoparticles are our model systems, with intriguing plasmonic properties and directional interactions. We study their nucleation pathway and growth habits in real-time in solution at the nanometer resolution, where colloidal interactions balance with mass transport to ultimately determine the size, shape and surface morphology of assembled superlattice. We study the phononic relaxation of the superlattices, where complex colloidal interactions act effectively as nanoscale springs to determine the collective structural reconfiguration. Going beyond equilibrium dynamics, we also study the external field driven assembly of nanoparticle, where hydrodynamic effects drive the nanoparticles into active “swarms” with rapidly-changing patterns. We will show new structural control and new functional relevance in these particulate systems, when we consider both the colloidal interactions and all the other factors such as diffusivity, many-body effects, and ionic flows.

11:00 AM CH01.06.02

**Multiphase Silk Assembly for Two-Dimensional Bio-Crystal Film**

Chenyang Shi and James J. De Yoreo; Pacific Northwest National Laboratory, United States

Early insights into native silk fibroin (SF) architecture suggested that its unique structures and properties are determined by its multiscale assembly and the evolution of its secondary structure. Yet the pathways of assembly and the relationship to that evolution are poorly understood. Here we investigate SF self-assembly using in situ AFM and liquid phase infrared nanospectroscopy (nano-FTIR) and molecular dynamics. To do so, we assemble the silk at the interface between water and highly ordered pyrolytic graphite (HOPG). We find that SF grows heteroepitaxially on HOPG to highly ordered, monolayer-thick 2D nanocrystals consisting of 1D lamellae that exhibit β-sheet secondary structure and lie along the armchair direction of HOPG. Molecular dynamics simulations show that the armchair orientation is indeed energetically favored, as in polar packing to form a bilayer. As the SF concentration increases, SF assemblies into multi-layers via two pathways that can occur concurrently. One is a non-classical pathway by which a disordered metastable film forms on top of the lamellae of the first monolayer and gradually converts into the lamellar structure. The second is a classical layer-by-layer pathway by which new lamellae grow homoepitaxially on the underlying 2D lamellae nanocrystals without any evidence of an intermediate state. Applying synchrotron based tip-enhanced nano-IR to SF assembly for the first time, we demonstrate that the β-sheet conformation is adopted from largely unstructured SF in solution as the lamellae advance along the classical pathway or during the process of film transformation along the non-classical pathway. These new findings fill in the missing pieces of the puzzle showing how SF structure evolves at the liquid-solid interface and provides inspiration for the design of heterogeneous 2D SF bio-crystal film.

11:15 AM CH01.06.03

**Microfluidics for Programmable Self-Assembly of Gold Nanorods**

Pandillapally Ramu; Indian Institute of Technology Hyderabad, India

Self-assembly of nanomaterials is an effective tool for developing functional assemblies and nano devices that can be used for a multitude of electrical, biomedical, and mechanical applications to name a few. We focus on the self-assembly of anisotropic gold nanomaterials, gold nanorods (GNR) in our work, since gold nanorods possess unique optical properties that can be tailored based on their aspect ratios. The side-to-side, end-to-end and self-assembly of GNRs have been a subject of intense research due to both the challenges involved in achieving such assemblies and their application in surface enhanced Raman spectra (SERS) signal enhancements. Several studies show the assembly of GNR using solvents (Ethylene diamine tetra acetic acid (EDTA), tetra hydrofuran (THF), dimethyl formamide (DMF)), pH, temperature, surfactants, co-polymers and other conditions. However, a systematic analysis and thereby understanding of the mechanism of assembly/dis-assembly and the resultant influence of several contributing parameters is a limitation in these studies. The lack of reproducibility and kinetic control over the reaction make such analysis challenging in the methods used in the studies.

In the current work, we use droplet microfluidics to analyze the solvent based (EDTA) self-assembly of GNR. The GNR are encapsulated in a “micro-vessel” droplet within which reaction with EDTA happens is automated and proceeds reproducibly and controllably. We vary the concentrations of EDTA, change the drop size and also the ratio of aqueous to continuous flows and look at the shift in the resonance spectral wavelength of the clusters hence formed. The spectral shifts in these studies show the individual interaction of GNR with EDTA with respect to the aspect ratio of the GNR, size and shape of the individual particles. The study also shows the effect of mixing, leading to different results in each scenario. We performed a systematic analysis of the
Unraveling Self-Assembly with Liquid Resonant Soft X-Ray Scattering for In Situ Measurement of Mesoscale Structure with Chemical Specificity

Peter Beaucage, Lucas Flagg and Dean M. DeLongchamp; National Institute of Standards and Technology, United States

Resonant soft x-ray scattering (RSOXS) is a new characterization technique that offers insights into mesoscale structure with chemical specificity and the ability to probe molecular orientation. It does this by performing conventional small-angle x-ray scattering at a series of low photon energies (285 eV at the carbon K-alpha edge) as in x-ray spectroscopy. RSOXS was originally developed around and has been applied to great effect in morphological characterization thin films of organic semiconductors. Recently, our team has developed the first quantitative fitting engine for RSOXS data using GPU-accelerated forward simulation of real-space morphologies and applied this software to measure the orientation distribution in polymer-grafted nanoparticles, reverse osmosis water membranes, and several other families of industrial materials.

The promise of RSOXS as a label-free alternative to SANS has not been fully realized, however, largely due to great difficulties in the study of liquid samples, or indeed practically any sample without significant structure factor contributions. This limitation arises because of the very feature that makes RSOXS unique: at the low photon energies used for organic molecules, a typical absorption length is about 500 nm. RSOXS measurements are, therefore, overwhelmingly conducted on thin films and typically on highly concentrated samples due to the extremely small probe volume. The design of the NIST RSOXS beamline at the National Synchrotron Light Source-II addresses this issue by incorporating a TEM port holder in the chamber; the sample thicknesses required for electron beam transparency are similar to those required for soft x-rays. We have procured a commercial TEM liquid cell capable of encapsulating a 500 nm film of flowing liquid between two thin silicon nitride membranes.

This talk will discuss our recent work in the use of the cell, our first RSOXS measurements of dilute biomolecules in solution, and our recent efforts to combine solution RSOXS with solution SANS measurements to obtain a greater-than-sum-of-the-parts characterization of self-assembly processes and mechanisms in bioformulations. We will discuss the future extension of the liquid RSOXS technique to the in situ study of electrochemically active thin films in the hydrated state, and how measurements of pure form factor scattering enabled by the liquid sample environment and combined SANS-RSOXS experiments will enable quantitative understanding of the localization of additives during complex self-assembly processes.

SESSION CH01.07: Crystal Assembly and Transformation II
Session Chair: Wenhui Wang
Thursday Afternoon, April 25, 2024
Room 442, Level 4, Summit

1:30 PM *CH01.07.01
Filming Photoinduced Ultrafast Structural Transitions of Vanadium Dioxide At The Single Nanoparticle Level

Oh-Hoon Kwon; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Visualizing structural rearrangements at the atomic/molecular level is essential in understanding the functions of matter. Once isolated, a molecule's intermediate and transitional structures during a chemical reaction may be routinely determined via ultrafast spectroscopy with femtosecond temporal precision. When the structural degrees of freedom increase, e.g., condensed matter comprising countless atoms or organized molecular units, local nanoscale structural defects become prevalent, and thus, the physical processes of each singularity do not proceed as those in bulk and even diverge. If controlled, these structural defects may yield functional benefits and be exploited to overcome the current technological challenges ranging from quantum computing. Because the ensemble natures of spectroscopic measurements do not reveal the characteristic transition of each nanoscopic structure, simultaneous spatiotemporal imaging is required to resolve complex processes, hierarchically spanning small-amplitude, ultrafast atomic displacements to collective structural rearrangements at expanded spatiotemporal scales. As an energy filter in transmission electron microscopy has improved the precision of structural determination by filtering out inelastic imaging electrons, introducing the energy filter to ultrafast electron microscopy (UEM) can advance the time resolution to the domain of atomic motion. Imaging transient structures with femtosecond temporal precision was made possible by gating imaging electrons of narrow energy distribution from dense chirped photoelectron packets, thus typically posing picosecond duration. Presented are the concept and proof-of-principle demonstration of the energy-filtered UEM achieving the temporal resolution limited by the briefness of an optical excitation pulse, i.e., 500 fs in this study, filming ultrafast insulator-to-metal phase transition of vanadium dioxide (VO₂), a representative strongly correlated system. In this study, the heterogeneous phase transitions of VO₂ nanoparticles were revealed and attributed to the emergence of a transient, low-symmetry metal phase caused by different local strains. Our approach leads the access of electron microscopy to the timescale of elementary nuclear motions, visualizing the onset of structural dynamics of matter at nanoscales.

2:00 PM CH01.07.02
Characterization of Structural Transformations in Flash Annealed HZO Thin Films via Dynamic and Static Synchrotron Grazing Incidence X-Ray Scattering

Cristian Ruano Arenas¹, Valene Tjong², Balreen Saini¹, Jonathan Hartanto¹, Fei Huang², Chanyoung Yoo³ and Paul C. McIntyre²,³; Stanford University, United States; ²SLAC National Accelerator Laboratory, United States

In order to extend computational power beyond the era of conventional area scaling of semiconductor circuits, back-end-of-line (BEOL) integration is a promising pathway towards 3D integration of non-volatile memory with logic, to increase integration density and reduce latency and energy consumption associated with data transfer. With improved properties over perovskite-structured ferroelectrics, HfO₂-ZrO₂ (HZO) alloys are promising candidates for future nonvolatile memories because of their CMOS compatibility, sub-nanosecond switching speed, and scalability of ferroelectric properties to the nanoscale. However, synthesis of ferroelectric HZO typically requires rapid high temperature heating to form the ferroelectric phase. Flash lamp annealing (FLA) is a viable method for thermal processing of BEOL components in which sub-ns pulses of light potentially allow localization of steep temperature rises to the top layers of the device stack, and protect underlying interconnect and front-end-of-line (FEOL) structures while crystallizing higher level materials. However, the short time scales and non-equilibrium nature of the annealing technique complicates determining thermal gradients and has led groups to rely on model predictions, measurement of the underside temperature of the substrate, or comparison between the performance of devices processed using rapid thermal anneal (RTA) or FLA to estimate the temperature rise of the surface layers. Because of the strict thermal budget imposed on BEOL processing, it is vital to determine the temperature-time profile associated with non-equilibrium FLA processing.

Our work uses static and time-resolved synchrotron glancing incidence X-ray diffraction (GIXRD) for in-situ, quantitative temperature metrology to understand the temperature rise during FLA processing of TiN/HZO/Ti metal-ferroelectric-metal (FMF) capacitors. Time-resolved GIXRD was performed during FLA processing to observe, in real-time, the emergence of the ferroelectric orthorhombic phase, thermal expansion of the crystal lattice, and changes in diffraction intensity due to the Debye-Waller effect under various annealing conditions. Static GIXRD was subsequently performed to carefully monitor the changes in lattice parameter and diffraction intensity at discrete elevated temperatures. After careful calibration, we were able to compare the changes in both of these parameters and quantitatively determine the temperature rise associated with various FLA conditions.

Using a sequential learning Gaussian Process, we have explored the process manifold to fabricate FMF capacitors with good remnant polarization (P_r ~ 20 μC/cm²) and low coercive fields (E_c ~ 1.2 MV/cm) while being cognizant of the thermal budget necessary to achieve devices of this performance. Thus, careful calibration has enabled exploration of the FLA processing space in effort to yield optimal ferroelectric device performance within the strict thermal budget set by BEOL processing requirements. This study has advanced in-situ temperature metrology to explore temperature transients and FLA processing effects in BEOL device stacks.

2:15 PM CH01.07.03
Investigating The Dynamics of Photo-Reversible Polymer Hydrogels using In Situ Shear Rheology

Michael C. Burroughs, Eleanor L. Quirk, Brendan M. Wirtz, Tracy Schloemer, Dan Congreve and Danielle J. Mai; Stanford University, United States

Polymeric materials are often designed to be permanent, such that single-use convenience supersedes considerations of recyclability. For hydrogels, this approach has resulted in materials comprising many components such as polymer precursors, crosslinking agents, and photoinitiators; such complex formulations preclude the chemical recovery of the original constituents. To simplify the formulation of and encode recyclability into hydrogel materials, we report photo-reversible, network-forming polymers that are crosslinked and un-crosslinked using different wavelengths of light. Light-driven un-crosslinking has potential as a low-cost, low-energy, on-demand recycling technology. Photo-reversible polymer hydrogels comprise multi-arm star polyethylene glycol with terminal anthracene groups (PEG-anthracene). PEG-anthracene undergoes photo-crosslinking upon irradiation with ultraviolet light (UV, 365 nm) and un-crosslinking upon irradiation with deeper UV light (265 nm). The photo-reversibility of PEG-anthracene with 3, 4, 6, or 8 arms (5 kg/mol per arm) was compared using UV-vis absorbance spectroscopy and in situ dynamic rheology. Upon 365 nm UV exposure, PEG-anthracene solutions exhibited rapid gel formation indicated by crossovers from liquid-like to solid-like behavior during in situ small-amplitude oscillatory shear rheology. During photo-crosslinking, more arms generally led to the quicker formation of stiffer materials. In contrast, polymers with fewer arms underwent un-crosslinking more readily, indicated by changes from solid-like to liquid-like rheological responses. PEG-anthracene with fewer arms demonstrated liquid-like “recycling windows” that allow for facile polymer solution handling prior to re-crosslinking. These findings demonstrate opportunities for on-demand recycling of photo-reversible polymers, as well as polymer
Controlled Stepwise Wet Etching of Polycrystalline Mo Nanowires

Chia-Yin Cheng, Yi-Chen Chen, Chun-Hua Chen, Wen-Chieh Hsieh, Shang-Jung Wu, Yi-Wen Lin, Hong-Shuo Chang, Karian Girri and Yan-Lin Wang; National Yang Ming Chiao Tung University, Taiwan

Under the development of high industrialization, the excess of greenhouse gases has caused a global climate crisis, and thermal power generation is one of the primary sources of greenhouse gas emissions. With the rising awareness of energy conservation and carbon reduction in major industrial countries in recent years, the energy transition has become an important issue. Presently, hydrogen emerging as a potential sustainable energy source. The most significant advantage of using hydrogen (H2) fuel to generate electricity is that it significantly reduces carbon dioxide emissions. However, the combustion of H2 will still form nitrogen dioxide (NO2), and exposure to NO2 will cause damage to the human respiratory tract, lungs, and kidney functions. To reduce the risk of hydrogen leakage, explosion, and nitrogen dioxide harm to the human body, developing highly-sensitive gas sensing materials for detecting hydrogen and nitrogen dioxide has become an essential goal with great forward-looking and industrial application potential.

In this study, vanadium pentoxide (V2O5) and cobalt tetroxide (Co3O4) nanoassemblies with different morphologies were successfully synthesized by the polyol method at different reaction temperatures. The synthesized V2O5 nanoassemblies can exhibit high-performance H2 sensing properties at room temperature without catalyst modification. The Co3O4 nanoassemblies showed the highest response to NO2 at an operating temperature of 130 °C. In addition, in the later stage of Co3O4 synthesis, vanadium acetylacetonate (V(acac)) was introduced to form Co3O4-V2O5 nanomixed particles. Finally, a novel heterogeneous core-shell nanoassembly structure comprised a Co3O4 core and Co3O4-V2O5 mixed nanoparticle shell. When V2O5, an n-type oxide, is assembled with Co3O4, a p-type junction will result in a depletion region. The electrical charge increases when the target gases are adsorbed and desorbed, improving the sensing sensitivity. The specific surface area of the V2O5-modified Co3O4 nano-assembled spheres is 3.2 times that of the Co3O4 nano-assembled spheres. At 130 °C, the sensitivity to 400 ppm NO2 increased from 247 % to 421 %. The gas-sensing responses of the synthesized nano-assemblies are all reproducible through cyclic measurements. Compared with CH4, C2H6, C3H8, CO, NO gases, V2O5 and V2O5 modified Co3O4 nanoassemblies showed excellent selectivity for H2 and NO2, respectively.

2:45 PM BREAK

14:30 PM CH01.07.05

Thermodynamics and Kinetics of The Crystallization of Phase Change Materials from In Situ Microscopy and Nanocalorimetry

Isak McGregor1, Tamara D. Koledin1, Im Ciston2, Feng Yi3, David A. LaVan4 and Melissa K. Santala5; 1Oregon State University, United States; 2Lawrence Berkeley National Laboratory, United States; 3National Institute of Standards and Technology, United States

The thermodynamics and kinetics of crystallization are key to understanding the stability of glass-forming materials, including poor glass formers such as phase change materials (PCMs). PCMs are semi-conducting alloys with distinct optical and electrical properties in the amorphous and crystalline phases that make them useful for memory applications. In memory devices, amorphous bits are crystallized in nanoseconds by either laser or Joule heating, but the amorphous phase must also be stable against crystallization for long-term data retention. Crystal growth rates relevant to memory devices span orders of magnitude and fundamental questions regarding PCM crystallization mechanisms remain open, partly due to the difficulty in measuring crystallization kinetics in certain temperature regimes.

The crystal growth rate, u, has been directly measured from the glass transition, Tg, to the melting temperature for good glass formers owing to their low u. In contrast, u in PCMs can exceed 10 m/s. Thus, it is challenging to measure u directly with microscopic methods, because the small grain sizes demand high spatial resolution and the grains impinge rapidly. This has led to the use of indirect methods to study PCM crystallization such as differential scanning calorimetry (DSC). In this work nanocalorimetry with high-frame-rate transmission electron microscopy (TEM) imaging was used to investigate the thermodynamics and kinetics of the crystallization of AgInSbTe12 and GeTe above Tg. The PCMs were deposited on individually-calibrated nanocalorimeters designed to be operated in a TEM. Direct electron detectors capture the crystal growth in the milliseconds before impingement enabling direct measurement of u. The enthalpies of crystallization are calculated from nanocalorimetry measurements. Classical models for nucleation and growth are fit against these data and models that predict the growth rate solely from DSC data are compared to the direct growth rate measurements.

14:30 PM CH01.07.06

Controlled Stepwise Wet Etching of Polycrystalline Mo Nanowires

Khakimjon Saidov1, Ivan Erofeev2, Zainul Aadbain3, Antoino Paccio4, Harold Philippen5, Antony W. Hartanto1, Yifan Chen1, Hongwei Yan1, Weng W. Tjiu1, Frank Holsteyns3 and Utkur Mirsaidov6; 1National University of Singapore, Singapore; 2Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), Singapore; 3IMEC, Belgium

With the persistent downsizing of integrated circuits, molybdenum (Mo) is currently considered a potential replacement for copper (Cu) as a material for metal interconnects. However, fabricating metal nanostuctures with critical dimensions of the order of 10 nm and below is challenging. This is because the very high density of grain boundaries (GBs) results in highly non-uniform surface profiles during direct wet etching. Here, utilizing in-situ liquid phase transmission electron microscopy (LP-TEM), we track the etching of polycrystalline Mo nanowires (NWs) with a hydrogen peroxide solution in real-time [1]. Moreover, wet etching of Mo with conventional aqueous solutions is problematic, as products of Mo oxidation have different solubility in water, which leads to an increase in surface roughness. Next, we show a process for achieving a stable and uniform soluble surface layer of Mo oxide by wet oxidation with H2O2 dissolved in IPA at -20 °C. The oxide layer is then selectively dissolved, and by repeating the oxidation and dissolution multiple times. Ultimately, we demonstrate a uniform etch profile with a fine control over the metal recess. This etching process is used to fabricate complex nanostructures that are critical in developing next-generation electronic devices.


14:45 PM CH01.07.07

Forse Spectroscopy and Quantitative Imaging of Hard and Soft Materials

Vassileios Kontou; Univ of Edinburgh, United Kingdom

New modes of atomic force microscopy (AFM) such as Quantitative Imaging (QI) use force spectroscopy at a high rate with direct force control and allow the high-resolution topography imaging of material surfaces while collecting simultaneously high-resolution images of adhesion, stiffness, and moduli. We applied the force spectroscopy and in particular, QI mode in different systems showing its potential to reveal unprecedented information on local material properties. We mapped the local (surface) elastic modulus of engineering polymer blends and we compared it to the bulk modulus derived from macroscopic tensile testing. The results show a remarkable agreement. We also studied the interactions of natural rubber latex films with carbon black particles (attached to the AFM tip) in aqueous solutions of ultrapure water and ultrapure water with 0.7% Ammonia. We show that in the basic 0.7% ammonia ultra-pure water solution, hydrogen ions are drawn from the surfaces leading to significantly larger negative surface charges, and therefore resulting in repulsion between the carbon black and natural rubber latex films upon the tip approach. Furthermore, we have used the superior control of the applied forces (which can be very low at the range <10 nN) of the QI mode to image and interrogate mechanically biomedical phospholipid-based microbubbles. The results demonstrate the controlled collapse of the microbubbles revealing their mechanical properties and internal structure.

4:00 PM CH01.07.09

Revealing The Kinetic Phase Behavior of Block Copolymer Complexes Using In Situ Solvent Vapor Isotomers

Booyee Chang; Iowa State University, United States

Controlling the self-assembled morphologies in block copolymers heavily depends on their molecular architecture and processing conditions. Solvent vapor annealing is a versatile processive pathway to obtain highly periodic self-assemblies from high chi (χ) block copolymers (BCP) and supramolecular BCP complexes. Despite the importance of navigating the energy landscape, controlled BCPs has not been investigated in BCP complexes, partly due to its intricate multicomponent nature. We introduce in situ measurements of characteristic adsorption-desorption solvent vapor isotomers as an effective way to understand swelling and morphological evolution of BCP complexes. Using the sorption isotomers, we identify the glass transition points, polymer-solvent interaction parameters, and bulk modulus. These parameters indicate that complexion completely screens the polymer interchain interactions. Furthermore, we establish that the sorption isotomer of the homopolymer blocks serves to deconstruct the intricacy of BCP complexes. We applied our findings by developing annealing pathways for grain coarsening while preventing macroscopic film dewetting under SVA. Here, grain coarsening obeyed a power law, and the growth exponent revealed a kinetic transition point for rapid self-assembly. Overall, BCP-based sorption isotomers emerge as a critical method for understanding and developing annealing pathways for BCP complexes.
In order to investigate the influence of 50% hot-rolling on the microstructure, textural evolution, and tensile properties in Ti6Al4V-5Cu alloy, an electron backscattered diffraction (EBSD) was used. To obtain a reduced textural influence behavior on the alloy, dual heat treatment schedule was specially designed. The results show that hot-rolling at high temperature significantly promote the transformation of phases to a fully α-phase structure and lamellar microstructure with different grains structure starting from elongated to coarsened appearance was produced. Hot-rolling deformation contributed for increasing the alloy texture intensity, whereas the heat treatment is important for weakening textural intensity, however, the coarsening of grains are prominent. Deformation and heat treatment temperature, therefore, an important factor affecting the texture and grain size. Using tensile testing experiment by considering 0.02 strain offset method, the yield strength of the alloy were estimated. During tensile testing process, studying strength of a material is the primary concern. Material strength could be measured in terms of either the stress essential to cause noticeable plastic deformation or the maximum stress that material can withstand. The tensile testing also provides information on the material’s ductility behavior to measure how much the alloy can be deformed before fractured. Using specimen sectioned in rolling direction (90°), the true stress-strain curve revealed that the strength at which the alloy has significant plastic deformation under 0.02 offset yield strength method. The alloy revealed 35 MPa yield strength at 800 °C and its area reduction reached 168.5%, and elongation reached up to 83%.

The aim of this study is to investigate the structural evolution and mechanical properties of TiAlSiN coating when processed by the arc ion plating method. The nominal compositions of the ternary alloys were designed to be Ti$_40$Al$_45$Si$_{15}$ (wt.%) and mechanically alloyed by planetary ball milling to form a hard coating. The powders were densely compacted during a rapid sintering process into a ternary system coating. The evolution of the structural phase from a powder to a compact material is dominated considerably by phase states such as a solid solution or intermetallic compounds. The relationship between the physical and chemical properties during the coating process is considered to be the dominant factor controlling the orientation and morphology of that zone. The TiAlSiN coating layer was found to have hardness above 45 GPa and an adhesion above 100 N. In other words, understanding the evolution and structure of TiAlSiN helped us to produce a material with excellent properties that can be used as a hard coating. Specifically, these properties were induced by a grain refinement of the nano-crystallite structure that corresponds to an increase in the silicon nitride contents.

An in-situ observation of metallic solidification using a conventional optical microscopy has been limited due to high solidification temperatures and opacity of solid metal. Hence, this study was initiated from developing an in-situ imaging technique using a white X-ray source generated from the synchrotron beam line operated by the Pohang Accelerator Laboratory, Pohang, Korea. Since high X-ray energies affect the scintillator, the generated synchrotron X-rays were suppressed from 15 keV to 40 keV through a Si attenuator with a sensor size of 3 mm. Then, the penetrated X-ray signals were converted to visible light by a scintillator to observe dendrite formation behaviors using an optical microscope and to record the in-situ optical images. The recorded images were post processed to remove noise and to make video which provides entire formation and growth behaviors of dendritic structure. Ni-base alloys were prepared by the vacuum induction melting method and machined into coupons with a dimension of 10 x 10 x 0.25 (thickness) mm. To load and hold each coupon in the furnace, two boron nitride (BN) covers wrap around a coupon like a sandwich. The sapphire glasses in the middle of the two BN covers are exposed to allow X-rays to pass through each coupon. Temperature and vacuum inside furnace were set at 1600 °C and 10$^{-5}$ torr, respectively. Solidification commenced right after sample coupon was fully melted. Cooling rates were controlled by setting current on carbon heaters, -0.2, -0.5, and -0.8 A/min, respectively. Dendritic structure such as tip radius, arm spacing, and mushy zone under different solidification variables such as thickness of specimen and cooling rates were measured directly from in-situ optical images. The microstructural properties were further analyzed by optical and electron microscopes, and atom probe tomography to correlate the dendrite growth behavior, microstructure, and material properties.

The quest for highly efficient probes in the precise detection of single biomarkers has emerged as a compelling research field crucial for biological and biochemical studies. Over recent decades, this pursuit has been seen in not only small chemical probe molecules but also biomacromolecules such as enzymes, antibodies, and nucleic acids in the construction of biosensor platforms, enabling highly specific and efficient biomarker detection. Despite significant progress, there remains a pressing need to enhance biosensor performance, particularly for high-throughput clinical applications.

Among the tools contributing to single nucleotide detection, DNA-based biosensors stand out for their versatility. Their notable attributes, including good stability, high specificity, and excellent biocompatibility, make them valuable in both in vitro and in vivo applications. Here, we present a new DNA-modified CNT LoC sensor for single nucleotide detection. Together with the probing platform, our novel biosensor platform excels in measuring the electrical signals of DNA with single-molecule precision while also enabling prolonged high-throughput measurements and the efficient screening of valuable data.

We anticipate that this platform will prove beneficial to individuals interested not only in biosensor technology but also in the broader realm of single-molecular detection.

**In-Situ Liquid Cell Electron Microscopy for Characterization of Dynamic Processes**

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**In Situ Liquid Cell Electron Microscopy for Characterization of Dynamic Processes**

Shu Fen Tan; Nanyang Technological University, Singapore

Many important reactions take place in liquids, but these processes are particularly difficult to study. Liquid cell electron microscopy provides opportunities for visualizing processes in liquids with good spatial and temporal resolution. The combination of imaging and electrochemical quantification have proved especially useful in studies of crystal growth, corrosion processes and battery materials. However, it has been a significant challenge to improve the quality and quantification of liquid cell data due to the limitation in liquid cell equipment, control of local conditions and understanding of beam effects. In this seminar, I will discuss how I use in situ liquid phase electron microscopy to uncover the mechanisms of chemical transformation of catalytic nanoparticles under realistic reaction conditions. I will also talk about my recent work where I (1) developed a temperature-controlled electrochemical liquid cell for understanding the detailed mechanisms by which typical catalysts change their structures under electrochemical control in liquid electrolytes; and (2) incorporated 2D materials into the electrochemical liquid cell design to improve its achievable spatial resolution and electrochemical stability. My work lays the foundation for visualizing the nanoelectrochemical structure-function relationship in the electrochemical processes, which will open new opportunities for investigating a range of problems in energy storage and electrocatalysis.
The structural changes that take place due to the electrode-electrolyte interaction, we have developed different custom-made electrochemical cells to couple to spectroscopic techniques like X-
capacitance, potential windows and impedance, is studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). To have a deeper understanding of the fundamental
electrodes. The high electrochemical performance of the nanoporous rGO films can be explained by different phenomena such as ionic diffusion, ionic adsorption/desorption processes,
In this work, we combine different rGO electrodes during their electrochemical operation.

Second, it is well understood that the narrow gap between chips necessary to maintain thin enough liquid layers for good resolution in LPTEM experiments, introduces a myriad of potential artifacts due to confinement, including incomplete mixing, slow exchange of liquids and ion depletion [5]. Recently, we developed a new E-Chip configuration designed to balance both thin liquid layer required for optimal resolution and a deeper flow channel to improve liquid flow characteristics. This design utilizes a 10 micron channel etched into the silicon substrate of the E-chip. The viewing region, containing the amorphous silicon nitride membrane, is isolated within the center of the E-chip on an island type structure, such that the deep flow channel surrounds it like a moat and does not interfere with the gap between the top and bottom membranes. This significantly reduces the distance over which the liquid must diffuse to reach the narrow gap between the viewing windows from >1 mm to a few tens of microns, significantly improving liquid exchange within the critical region [6].

Finally, comprehensive analysis of the electron dose during in-situ studies is necessary to disentangle beam-induced changes and behavior from a samples’ inherent chemical or electrochemical behavior. We utilize a state-of-the-art machine vision software, AXON Dose, to calibrate and accurately track electron dose exposure throughout an experiment to create a record of both the electron flux, and the samples’ cumulative dose exposure, on a pixel-by-pixel basis [7]. Taken in these new features bring us closer to achieving the goal of accurately replicating, measuring, and observing bulk electrochemical processes at the nanoscale.

References:
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9:15 AM CH01.09.03
In-Situ/Operando Electrochemical Investigation of Reduced Graphene Oxide in Aqueous Solution

Maria del Pilar Bernicola García1, Jose A. Garrido1,2 and Elena del Corro1; 1Catalan Institute of Nanoscience and Nanotechnology, (ICN2), CSIC and BIST, Spain; 2CREA, Spain

The development of new carbon nano-porous materials with increased capacitance, high conductivity and electrochemical stability is of high interest for a variety of applications. It is reported an anomalous increase of the specific capacitance in nano-porous materials with a pore size below of 1 nm. However, the fundamental understanding of the mechanisms that involve these phenomena is still under study. Reduced graphene oxide (rGO) has gained significant attention due to its remarkable physicochemical properties such a high structural stability, large specific surface area, low cost, and availability. In the case of healthcare applications, highly porous rGO films have been widely studied because of their biocompatibility and biochemical sensing capabilities. A proper understanding of electrokinetic phenomena such as potential-controlled ionic diffusion within the nano-porous and reduction of functional groups during electrochemical operation is necessary to improve the ultimate performance of rGO-based electrodes. Also, for these applications, it is key to investigate the chemical and structural changes happening in the rGO electrodes during their electrochemical operation.

In this work, we combine different in-situ/operando spectroscopic techniques to understand the dynamics and irreversible/reversible chemical and structural changes within rGO-nanoporous electrodes. The high electrochemical performance of the nanoporous rGO films can be explained by different phenomena such as ionic diffusion, ionic adsorption/desorption processes, protonation/deprotonation and chemical and structural changes like those induced by defects or vacancies. The electrochemical performance of the rGO-nanoporous material, in terms of specific capacitance, potential windows and impedance, is studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). To have a deeper understanding of the fundamental phenomena that boost the electrochemical performance, we focus on the structural and chemical changes induced by the electrode-electrolyte interaction in the nano-porous electrode. To study the structural changes that take place due to the electrode-electrolyte interaction, we have developed different custom-made electrochemical cells to couple to spectroscopic techniques like X-ray diffraction (XRD) and Raman spectroscopy. In-situ XRD measurements experiments give information about the impact on the rGO structure of the electrochemical operation, such irreversible/reversible changes on the interlayer distance induced by the applied potential. Operando Raman spectroscopy is used to study the structural properties of such defects, disorder and reduction degree induced by the applied potential. In this study we are able to evaluate the nature of the defects generated during electrochemical operation that impacts on the electrochemical performance. Combined with analysis of CV coupled with electrochemical quartz crystal microbalance (EQCM), our results provide detailed information about ion adsorption and charge transfer processes at the electrode-electrolyte. This work aims at expanding the current understanding of the properties of rGO-based nanoporous electrodes for their use as electrode material in healthcare applications.

This work has received funding from the Project PID2020-113663RB-I00 (Neuro2Dtech) funded by MCIN/ AEI /10.13039/501100011033 (Neuro2Dtech)


9:30 AM BREAK
10:00 AM CH01.09.05
Solid-State Reaction Heterogeneity during Calcination of Lithium-Ion Battery Cathode

Sugeun Jo1, Sungjae Seo1, Subin Choi1, Yijin Liu2, Il Sohn3, Keeyoung Jung4 and Jongwoo Lim1; 1Seoul National University, Korea (the Republic of); 2SLAC National Accelerator Laboratory, United States; 3Yonsei University, Korea (the Republic of); 4Research Institute of Industrial Science & Technology, Korea (the Republic of)

Li-ion batteries, nickel-rich cathodes, synthesis during calcination, phase complex transitions with solid-state reaction, spatial distribution of local chemical compositions within the particles. During solid-state calcination, with increasing temperature, materials undergo complex phase transitions with heterogeneous solid-state reactions and mass transport. Precise control of the calcination chemistry is therefore crucial for synthesizing state-of-the-art Ni-rich layered oxides (LiNi1−x-yCoMnO2, NRCM) as cathode materials for lithium-ion batteries. Although the battery performance depends on the chemical heterogeneity during NRCM calcination, it has not yet been elucidated. Herein, through synchrononster-in-situ structural analyses, gas analysis, X-ray microscopy, mass spectrometry microscopy, we provide a reaction map for Ni-rich layered oxides (LiNi1−x-yCoMnO2, NRCM) cathodes during their calcination, which includes dehydration of the precursors, the insertion of ambient oxygen, and the insertion of solid-state Li2+2O2 – after Li2Co3 thermal decomposition. The temperature-dependent reaction kinetics, the
diffusivity of solid-state lithium sources, and the ambient oxygen determine the favorable aerobic decomposition of particle shell maintaining layered structure while the anaerobic decomposition of the particle core to lithium-blocking Ni-O rocksalt. Additionally, we found that the variations in the reducing power of the transition metals (i.e., Ni, Co, and Mn) determine the local structures at the nanoscale. The investigation of the reaction mechanism via imaging analysis provides valuable information for tuning the calcination chemistry and developing high-energy/power density lithium-ion batteries.

10:15 AM CH01.09.06
Revealing CaH₂-Driven Metal Oxide Reduction Kinetics with In-Situ Transport Measurements

Jinwei Wang\textsuperscript{1,2}, Yijun Yu\textsuperscript{1,2}, Yi Cu\textsuperscript{1,2} and Harold Y. Hwang\textsuperscript{1,2}; \textsuperscript{1}Stanford University, United States; \textsuperscript{2}SLAC National Accelerator Laboratory, United States

Metal hydrides, such as CaH₂, have recently emerged as highly promising reducing agents for facilitating the low-temperature reduction of metal oxides. One unique advantage of hydride reduction is its capability to synthesize metastable materials that are inaccessible through conventional high-temperature reactions. Notably, researchers have harnessed hydride reduction techniques to create unusual NiO\textsubscript{2} square-planar coordination in nickelates to host superconductivity [1]. Beyond the realm of novel materials discovery, metal hydrides also hold substantial potential in applied engineering. For instance, previous studies have shown that CaH₂ can lower the temperature required for gas-phase H\textsubscript{2} reduction of iron oxide, which can benefit clean hydrogen-based ironmaking [2]. Given these promising features, there is a compelling motivation to delve deeper into the mechanisms of the hydride reduction process.

In this study, we investigate the CaH\textsubscript{2}-induced reduction kinetics of metal oxides using epitaxial α-Fe\textsubscript{3}O\textsubscript{4} thin films as a model system. To elucidate the intrinsic reducing capability of CaH\textsubscript{2}, we seal the iron oxide thin-film samples along with CaH\textsubscript{2} in an evacuated quartz tube and analyze the reduction behavior of iron oxide within this closed system. In particular, we have developed an experimental platform that enables real-time monitoring of the CaH\textsubscript{2} reduction process through transport measurements. Using this setup, we have successfully quantified the phase transformation kinetics from iron oxide to metallic iron by continuously tracking the evolution of electrical resistivity in the thin-film sample. Our results demonstrate that CaH\textsubscript{2} alone can effectively reduce α-Fe\textsubscript{3}O\textsubscript{4} into metallic iron within a one-hour reduction treatment at 400 °C, whereas 5% H\textsubscript{2}/Ar (99.999% purity) failed to reduce the sample at identical conditions. These findings can advance our fundamental understanding of the hydride reduction process, opening new avenues to harness this phenomenon for the exploration of emergent materials properties and the development of environmentally friendly engineering applications.


10:30 AM CH01.09.07
The Scanning Transmission Electron Microscope as a Platform for Atomic Scale Synthesis

Ondrej Dyck, Andrew R. Lupini, Christopher T. Nelson, Mina Yoon and Stephen Jesse; Oak Ridge National Laboratory, United States

The scanning transmission electron microscope (STEM), a workhorse instrument in materials characterization, can not only be used to observe dynamic processes with atomic resolution, but also drive and control synthesis with atomic precision. Through custom control of the electron beam position that actively feeds back on image, spectroscopy, and other data streams, it’s possible to use focused beam energy to precisely initiate and interrupt desired transformations. This can be used for generating point defects, drilling and milling materials, changing phase, modifying bond coordination, and positioning dopants. Furthermore, control over the local environment through custom MEMS devices for heating and biasing, in situ evaporators, and laser irradiation, provides means to dose the sample with thermal energy, optical excitation, and reactant or dopant materials to provide the proper conditions for reactions and transformations to occur. Finally, to close the loop, the STEM can then be used in its more traditional characterization modes to image transformation processes as they occur and assess if new functional properties emerge. Presented here are recent results highlighting advancements towards such a “synthescope” [1] including new insights gained by studying the generation and temperature dependent diffusion of beam-generated single vacancies in suspended 2D materials [2], strategies to restrict vacancy diffusion so they can serve as sites for dopant insertion, demonstration of patterning of arrays of dopants [3], and the delivery of dopant atoms to the sample, in situ [2]. Development of this combination of experimental methods provides a window into the dynamic synthesis processes at fundamental length scales and a path towards fabricating materials and devices with atomically precise components for potential quantum information science applications.

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, and was performed at the Center for Nanophase Materials Sciences (CNMS), a U.S. Department of Energy, Office of Science User Facility.


10:45 AM *CH01.09.08
Fabrication Processes of Next-Gen Integrated Circuits through The Lens of In Situ Transmission Electron Microscopy

Utkur Mirsaidov; National University of Singapore, Singapore

Understanding the nanoscale detailed characteristics of chemical and physical processes used in semiconductor manufacturing is critical for scaling and improving the performance of future integrated circuits. Here, I will review the major challenges associated with device scaling and describe how in situ TEM can help in the development of these processes. I will describe how direct imaging of such processes can speed up the implementation of new materials and device architectures to further enable the miniaturization of transistor footprints and improve their performance. Specifically, I will focus on etching and annealing processes used in the fabrication of both transistors and interconnects that link billions of these transistors together and to a power supply. Our study unveils transient nanoparticle shape instability, indicating rapid particle migration, in an oxygen and water vapor environment, contrasting with stability in a vacuum. This underscores the complex interactions between platinum, the alumina substrate, and gases, providing essential insights for the design of improved catalysts for industrial applications.

SESSION CH01.10: Characterization of Catalytic Materials

Session Chairs: Miaofang Chi and Dongsheng Li

Friday Afternoon, April 26, 2024
Room 442, Level 4, Summit

1:30 PM *CH01.10.01
Unraveling Sintering Mechanisms of Precious Metal Catalysts in Diverse Gas Environments

Miaofang Chi; Oak Ridge National Laboratory, United States

Heterogeneous precious metal catalysts offer the highest selectivity and activity in chemical production and combustion by-product reduction reactions. However, their efficiency is hindered by sintering, particularly in high-temperature oxidizing environments such as automotive emissions control. To address this issue, we investigate the sintering mechanisms of platinum on alumina support in various exhaust gas environments at different temperatures using in situ environmental scanning transmission electron microscopy (STEM). We observe that the presence of both oxygen and water vapor significantly accelerates sintering, while water vapor alone has minimal impact. Our study unveils transient nanoparticle shape instability, indicating rapid particle migration, in an oxygen and water vapor environment, contrasting with stability in a vacuum. This underscores the complex interactions between platinum, the alumina substrate, and gases, providing essential insights for the design of improved catalysts for industrial applications.

2:00 PM CH01.10.02

Deformations of hierarchical structures at the atomic scale, especially long-range ones, can significantly enhance their functional behavior, such as catalytic activity. Metastable states or grain boundaries during the synthesis and processing of nanomaterials can introduce and control deformations (strains) in crystal lattices. We design the deformations in the crystal lattice to enhance the catalytic functionality of catalysts, such as TiO2 and platinum-group-based metals, by controlling their synthesis processes of phase transformation and particle aggregation. For example, TiO2 polymorphs have distinct properties that have been widely employed in various applications. It is well known that these polymorphs can transform into more stable phases, such as from TiO2-B to anatase. Here, based on results from semi-in-situ transmission electron microscopy, X-ray atomic pair distribution function, and density functional theory, we will investigate the effects of lattice deformation in crystals on the catalytic activities and their controlling factors. We seek to control deformations in supporting materials and their effect on catalytic materials to uniquely tailor functionalities. These findings suggest that lattice deformations can be designed to advance new functions.

2:15 PM CH01.10.03

Strong Metal-Support Interaction makes Durable Catalysts  
Ji Yang, David Prendergast and Ji Su; Lawrence Berkeley National Laboratory, United States

Liquid organic hydrogen carrier (LOHC) technology is a promising method for hydrogen storage and transportation by using a reversible hydrogenation–dehydrogenation cycle between aromatic compounds and naphthene, such as toluene and methylcyclohexane (MCH). A key issue in this technology is to improve the lifetime of the catalyst for MCH dehydrogenation. Here, we developed a TiO2-supported Pt catalyst (Pt@TiO2) by engineering a unique strong metal-support interaction (SMSI). For the first time, the monometallic Pt@TiO2 catalyst delivers durable MCH dehydrogenation at 350 °C, without any deactivation observed within 500 h. MCH conversion of 94% and toluene selectivity of ~100% are achieved. Detailed electron microscopic and spectroscopic studies, supported by theoretical calculations, reveal that the excellent MCH dehydrogenation performance over Pt@TiO2 is attributed to in-situ generated TiO2–Pt3+ interface induced by optimal SMSI, which immobilizes Pt nanoparticle (NP) onto TiO2 surface and modulates electronic properties of Pt NP. MCH can be thus efficiently dehydrogenated and toluene is easily desorbed on the Pt NP surface. Our results expand the concept of classical SMSI and provide new insights into the rational design of durable supported metal catalysts based on unconventional SMSI.

2:30 PM BREAK

3:00 PM CH01.10.04

Analysis of Defects in Electrocatalysts using Variable Temperature Raman Spectroscopic Analysis of Phase Transition Mechanisms  
Rodney Smith; University of Waterloo, Canada

Defects within solid state materials can dramatically alter material properties, but direct analysis of such defects is particularly challenging. Such analysis is impeded by the low concentrations of defects relative to bulk sites, potential co-existence of multiple defect types in any given material, possibility of dynamic changes during catalysis, and fundamental limitations inherent in every characterization technique. We analyze distortions and defects in solids and interfaces, where changes in structural data for series of samples are monitored as a function of some perturbation. This talk will demonstrate how we have applied variable temperature Raman spectroscopy under controlled environments to analyze phase transitions in solid state materials commonly employed as (photo)electrocatalysts, with particular interest in how defects affect features such as the presence of phase transitions and the temperature at which they occur. Discussion will be focused on the analysis of protons trapped within hematite, a commonly employed photocathode for the oxygen evolution reaction, and the formation of disorder correlated carbonate-containing overlayers on a family of perovskite electrocatalysts.

3:15 PM CH01.10.05

Environmental TEM Observation of Cu/Cu2O Interface-Modulated Methanol Reaction Dynamics  
Meng Li1,2, Matt Curran3, Hao Chu1, Stephen House1,4, Jimmy G. McEver1, Dmitri N. Zakharov2, Wissam Saidi1,5, Goetz Vesper6 and Judith C. Yang1,2; 1University of Pittsburgh, United States; 2Brookhaven National Laboratory, United States; 3Pohang University of Science and Technology (POSTECH), Korea (the Republic of); 4Sandia National Laboratories, United States; 5National Energy Technology Laboratory, United States

Cu-based catalysts are the most widely used commercial catalysts in methanol chemistry due to their cost-effectiveness and high reactivity with methanol. Recent studies on Cu catalyst oxidation states indicate that during the Partial Oxidation of Methanol (POM), Cu catalysts are partially oxidized, producing reactivity and selectivity changes in pertinent reactions. These changes dynamically form metal/metal-oxide (M/MO) interfaces featuring short-lived and high-energy sites, which likely contribute to measured reactivity increases near phase boundaries. However, previous studies on these reaction mechanisms have primarily focused on pure Cu or Cu2O surfaces, rather than investigating impacts on M/MO interfaces.

In this work, using in situ environmental transmission electron microscopy (ETEM) with machine-learning enhanced advanced data analysis and correlated DFT simulations, we investigated the influence of Cu2O/Cu interfacial structures on methanol reduction dynamics. The atomic-resolution reaction dynamics are observed using in situ ETEM under 1 Pa methanol vapor at 300 °C on heteroepitaxial Cu2O/Cu model catalysts. Our observations reveal two-stage reduction dynamics modulated by the structures of Cu/Cu2O junctions: when the Cu/Cu2O interface at a junction is oriented along (100), an anisotropic layer-by-layer reduction occurs at the side facets of the Cu2O island, followed by a Cu2O-to-Cu interfacial transformation along (100). When the Cu/Cu2O interface is oriented along (110), isotropic reduction at both top and side facets of Cu2O islands is observed. Using machine-learning enhanced advanced data analysis, atomic-level size evolution kinetics are extracted. Stochastic trend analysis on island size kinetics suggests two distinct kinetic stages caused by different reaction mechanisms. Using correlated density functional theory (DFT) simulations of MO dissociative adsorption, we found that MOH adsorption energetics favor defect sites at Cu/Cu2O(100) junctions, as opposed to fully coordinated sites on Cu2O(110) surfaces steps or near Cu/Cu2O(110) junctions. As the Cu/Cu2O interface changes during the anisotropic-to-isotropic stage transition, active sites correspondingly relocalize from Cu/Cu2O(100) junctions to Cu2O(110) surfaces steps. Our results emphasize the importance of M/MO interfaceal dynamics during catalytic reactions, and provide new insights towards catalyst design and interface engineering.

Acknowledgements: The authors acknowledge funding from National Science Foundation (NSF) grants DMR-1410055, CBET-1264637, DMR-1508417, DMR-1410335, and DMREF CHE-1534630, and support from Hitachi High-Tech. Technical support from the Nanoscale Fabrication and Characterization Facility in the Petersen Institute of Nano Science and Engineering at the University of Pittsburgh is appreciated. This research used the Electron Microscopy facility of the Center for Functional Nanomaterials (CFN), which is a U.S. Department of Energy Office of Science User Facility, at Brookhaven National Laboratory under Contract No. DESC0012704. J. McEver was supported in part by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists (WDS) under the University of Connecticut Undergraduate Internships Program (SULI).

SESSION CH01/CH03/CH04: Joint Virtual Session
Session Chairs: Yu Deng and Wenhui Wang
Tuesday Morning, May 7, 2024
CH01-virtual

8:00 AM CH01/CH03.01

The Effect Local Residual Stress States on The Internal Pore Growth in Laser-Welded Ti6Al4V  
Wei Sun and Xingrui Jiang; Xi’an Jiaotong-Liverpool University, China

The microm scale local residual stress states in laser-welded Ti6Al4V were characterized with focused ion beam ring-core milling coupled with digital image correlation (FIB-DIC), and its effect on the growth of welding porosity under external loading was investigated by in-situ tension under X-ray computerized tomography (CT). The internal pores were found to preferentially distribute along the fusion zone boundary and the weld centerline. FIB-DIC and X-ray diffraction indicated high-level tension in the vicinity of the fusion zone, balanced by the long-range compression in the base metal. Comparison with stress-free counterparts showed the residual stress significantly prepoons the growth of the pores, whose aspect ratio and volume exhibited observable increments at low applied stresses. On the contrary, the pores without residual tension remained nearly undeformed until the yield point, and the relative tensile strain across the fusion zone showed a similar trend. The results demonstrated that the response of internal welding defects towards external load strongly correlates to the local residual stress states, and highlights the importance of precise measurements of the residual stress states in characteristic regions for applicational titanium laser welds.

8:05 AM CH01/CH03.02
Enhancing ductility is a crucial concern within metal matrix composites. Cu-Pb bronze alloy is a commonly utilized copper-based bearing alloy, and it demands superior mechanical properties and service safety. While copper and lead exhibit excellent ductility, Cu-Pb bronze alloys experience a substantial reduction in ductility due to plastic deformation being concentrated within the low-strength Pb phase. To address this issue, we employed the solid-liquid continuous casting (SLC) method to overlay the Cu-Pb alloy onto a mild steel substrate, significantly enhancing overall ductility. We conducted an in-situ tensile test using a scanning electron microscope (SEM) in conjunction with Digital Image Correlation (DIC) and Electron Back-scattered Diffraction (EBSD) to elucidate the underlying mechanisms. Localized strain is distributed uniformly in the steel layer but concentrated in the Pb phase within the bronze layer. However, this localization is effectively mitigated by the layered structure, as evidenced by the high compressive strain observed in the affected zone at the bronze/steel interface. Larger misorientation angles near the copper grain boundaries indicate that the deformation of copper grains is influenced by the localized strain within the lead phase. The layered structure effectively reduces strain concentration throughout the material and accommodates the deformation incompatibility inherent in Cu-Pb bronze alloys.

8:20 AM **CH01/CH03.03**

**In-Situ TEM Study of Microstructure Evolution in Ferroelectric/ferroelastic Materials under Stress**

Yifeng Ren, Jiayi Li, Zhentao Pang, Jie Wu, Shaojie Fu, Meiyu Wang and Yu Deng; Nanjing University, China

In ferroelectric-ferroelectrics (FMs), stress-induced microstructure such as phase and domain can effectively enhance properties significantly. We prepared free-standing single-crystal BaTiO3 sub-micrometer pillar as a model system to investigate microstructural evolutions in FMs under high stress loading. We directly observed and quantitatively analyzed in situ in a transmission electron microscope with 40-STEM the microstructural evolutions in the pillar under various strain loading (different direction, and rate). We found that dozens of slow compression cycles (strain rate of 10^-2/s, at 520 MPa) can induce multiple-nanodomain and multiple-phase coexistence in BaTiO3. After unloading, the pinned boundaries and domain walls by mobile point defects can stabilize these microstructures, including metastable ones, therefore improve both functional and mechanical performance of FMs. The "brittle" FMs can change to accept functional and mechanical properties under relatively low stress values. Our work elucidates the complex multiscale (from nanometer to unit cell scale) evolution of phase, domain microstructures and their interactions in FMs, as well as the corresponding improvement in properties under the large strain loading. Based on this, we propose a novel method for domain engineering in FMs.

8:50 AM **CH01/CH03.05**

**Raman Spectroscopy: A Versatile Tool for The Studies on The Back-End of The Nuclear Fuel Cycle**

Laura J. Bonales, Jone M. Elerrieta Baigorri, Abel Milena Pérez, Iván Sánchez García, Nieves Rodríguez Villagra and Hitos Galán Montano; CIEMAT, Spain

In recent years, Raman spectroscopy has proven to be a highly versatile characterization technique for nuclear materials research. This sensitive technique possesses, among others, two relevant types of features in the Raman spectrum that allow us to identify the metallic phase. In particular, we show some of the valuable results that can be obtained when applying this technique to: 1) the advanced characterization of nuclear fuels, 2) the evaluation of the spent nuclear fuel behavior under different storage conditions, and 3) the development and monitoring of hydrometallurgical separation processes.

9:05 AM **CH01/CH03.06**

**Variable-Temperature Electron Spectromicroscopy Techniques for Investigating Metal/Insulator Transitions in V2O3 Systems**

Laura Bocher1, Ibrahim Koita1, Tizzi Luiz H. G.1, Jean-Denis Blaziat1, Xiaoyan Li1, Benoît Corraze2, Julien Tranchant2, Marcel Tencé2, Laurent Cario2, Etienne Janod2 and Odille Stephan1; 1Université Paris-Saclay, France; 2Université de Nantes, France

Taming abrupt resistive transitions in functional oxides is a promising approach for developing advanced information processing and storage systems. V2O3 is considered a prototypical system of metal-to-insulator transitions (MITs) where they can be activated under external stimuli such as temperature (T), pressure, or chemical doping [1] but hardly technologically feasible. Recent demonstrations from electric pulses yield MIT in (V1-xCr1/3)xO3 systems with real potential capabilities for non-volatile memories and neuromorphic applications [2]. Hence, understanding the V2O3 electronic phase separation and its local mechanisms governing the insulator/metallic (I/M) domain dynamics across the IMTs remains of interest. However, all these electronic transitions rely on their relationship between structural and electronic degrees of freedom. For instance, when cooled below 160 K, V2O3 presents a symmetry breaking, associated with a large volume change (+1.4%) and an MIT yielding a resistivity change of 7 orders of magnitude. This T-activated MIT has been extensively studied at the macroscopic scale [3] and remains still a perfect arena to probe in situ the V2O3 structural and electronic evolutions at a very local scale. Recently, the microscopic electronic coexistence of I/M domains has been mapped in (V1-xCr1/3)xO3 by in situ scanning photoemission spectroscopy [4], PEEM [5] and nano-IR [6] with 25nm spatial resolution at best. In addition, combined micro-XRD and nano-IR experiments have highlighted competitive mechanisms between structural and electronic contributions during this MIT [6]. These latest investigations also demonstrate the cautions and possible experimental limitations when it comes to accurately mapping the dynamics of mechanisms within regions of interest of a few tens of nm by combining different instruments, hence the need to perform structural and electronic experiments within the same instrument.

Advanced monochromatic electron spectromicroscopy emerged this last decade as real game-changers for nanomaterials characterization. Here we performed in situ monochromated STEM/EELS experiments on the NION CHROMATEM 200 MC with variable-T options under cryo-conditions thanks to a double-tilt HennyZ cryo-holder using MEMS to vary continuously the temperature conditions across the IMTs. For each probed temperature, we associated mapping of relevant spectroscopic electronic excitations (from IR to soft X-ray) with an ultra-high EELS resolution at the nm scale and the local structural features (symmetry and lattice parameters) determined by 4D STEM nano- and microdiffraction. During low-T thermal cycling through the resistive transition, EELS spectra acquired in the low-loss regime present a characteristic signature at 1.1eV only in the metallic phase. Upon cooling, the abrupt MIT was monitored while the coexistence of I/M nanodomains was evidenced upon heating over a few degrees yielding the propagation of the electronic I/M domain wall. 4DSTEM nanodiffraction experiments reveal the local distribution of monoclinic/rombohedral phases coexisting in the insulating domains. The observation of the low-T insulating hexagonal phase suggests an analogous paramagnetic insulating (PI) phase of large volume, as confirmed by the jumps in lattice parameters observed at the transition. These PI-like phases emerge also at the I/M domain wall, as a precursor of the metallic phase.


**SYMPOSIUM CH02**

Utilizing Advanced In Situ/Operando Transmission Electron Microscopy and Spectroscopy for the Investigation of Functional, Energy and Quantum Materials

April 23 - April 26, 2024
Oxides have been widely used for structural applications because of their superior mechanical properties. It has been known that the behavior of GB properties is strongly dependent on the GB characters such as misorientation angle between two adjacent crystals and GB plane, however, such effect has not been clarified yet. In this study, we focus on the behavior of GB properties under external stimuli (Temperature, Photons, etc.) and the influence of dopants on the GB properties. It has been revealed that GB fracture is processed by a cooperative shuffling of atoms in GB ledges along specific routes. We found that GB fracture occurs along the special crystal plane and dislocations are emitted from the crack front. Recently, we have proposed that GB migration behavior in ceramics can be precisely controlled by the aid of the high-energy electron beam irradiation. This electron beam technique was applied to directly visualize the atomic GB migration. It was revealed that the GB migration is processed by a cooperative shuffling of atoms in GB ledges along specific routes. As a result, the GB passed through several different GB structures with low formation energies during GB migration.

### References


### 11:00 AM CH02.01.03

**Cryogenic-Monochromated STEM-EELS Analysis of Symmetry Breaking and Local Ferroelectricity in SrTiO3 Based-Heterostructures**  
**Invited Paper**  
**Invited Distinguished Presenter**

**Yoichi Ikuhara**\(^1\), **Shun Kondo**\(^1\), **Yves Auad**\(^1\), **Daniele Preziosi**\(^2\), **Manuel Bibes**\(^4\), **Jean-Pascal Rueff**\(^5\), and **Alexandre Gloter**\(^1\); **Invited Paper**  
**Invited Distinguished Presenter**

\(^1\)Laboratoire de Physique des Solides Orsay, France; \(^2\)Technische Universität Wien, Austria; \(^3\)Harvard University, USA; \(^4\)IPCMS UMR 7504, CNRS, Université de Strasbourg, France; \(^5\)Unité Mixte de Physique CNRS, Thales, Université Paris-Saclay, France; \(^6\)ICPMR, Sorbonne Université, CNRS, France

The growth of oxide-based electronics in a good pace, and the apt material knowledge obtained by advanced characterization techniques leverages the complexity in designing devices with intriguing properties. Knowledge of the atomic level arrangements in a material system enables us to make atomic level manipulations, thereby tweaking the electronics. This is made possible by one of the most advanced characterization techniques such as the Scanning Transmission Electron Microscopy (STEM). In this, in addition to obtaining a high-resolution image with good atomic contrast, one can have spectroscopic information representative of their electronic states through electron energy loss spectroscopy (EELS). Combining this with controllable external stimuli (Temperature, Photons, etc.) one can study a vast range of electronic and structural states in a chosen material. Some prototypical examples include temperature dependent metal-to-insulator transitions \([1]\), photoduced superconducting transitions \([2]\), etc.

Here we will be focusing on SrTiO\(_3\) (STO) based heterostructures exhibiting incipient ferroelectricity as a result of broken symmetry near the interface \([3]\). Some examples are the AUSTO \([4]\), and Ca-doped STO \([5]\), and even Nd\(_{1-x}\)O\(_x\)STO system that have a metal to insulator transition spanning 150-200K \([6]\). Understanding the electronic origins of it is of paramount importance, and so is studying its variation with external stimuli. STO is an intriguing system that undergoes a cubic to tetragonal antiferrodistortive phase transition below 105K, and undergoes another transition to become a quantum paraelectric below 37K \([7,8]\). The influence of these transitions on the interface properties are of significant interest, and so is studying its variation with external stimuli. STO is an intriguing system that undergoes a cubic to tetragonal antiferrodistortive phase transition below 105K, and even Nd\(_{1-x}\)O\(_x\)STO system that have a metal to insulator transition spanning 150-200K \([6]\).

Our experiments in an Nd\(_{1-x}\)O\(_x\)STO demonstrated significant fine structure variations at the Ti-L\(_{2,3}\) edge, on going from RT to ~110K. It has been previously reported that the cubic to tetragonal antiferrodistortive transition in STO occurs inhomogeneously, where the surface unit cells begin this transition at around ~150K, which possibly spans to the whole STO by ~105K \([10]\). Hence, the fine structure variations we see at around ~110K near the interface could be representative of this transition, thereby altering the interface properties. Characterizing such variations is enabled by high-energy resolution monochromated EELS, in combination with a cryogenic system. The resolution significantly surpasses previous studies reported in this direction, where, in addition a real space mapping of the fine structure variation couldn't be done \([11, 12]\). An investigation in this direction paves the way to better understanding the interesting phenomena such as superconductivity and ferromagnetism that emerges at these interfaces.

**References**


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**Session Chair:** Leopoldo Molina-Luna and Di Zhang

**Session:** Tuesday Morning, April 23, 2024

**Room:** 440, Level 4, Summit
In our relentless pursuit of solutions to advance the decarbonization of our society and economy, hydrogen stands out for its exceptional qualities as a zero-emission fuel, energy storage medium, and chemical feedstock. Nevertheless, the challenge of compact hydrogen storage remains a daunting one in both science and technology. Safe storage of hydrogen, particularly in solid forms such as metal hydrides, offers numerous compelling benefits. However, further improving its storage properties requires a comprehensive understanding of nucleation and growth of metal-to-metal hydride phase transformation at the atomic scale. In this context, real-time visualization of the various steps of the transformation process is essential for a precise and quantitative understanding. For instance, interpreting the hydrogen sorption property of materials, it is crucial to reveal the effect of stress/strain, the role of defects, and intermediate phase evolution during metal-to-metal hydride phase transformation.

In this study, we use MgTi thin films as a model system to study metal-to-metal hydride phase transformation using in-situ Scanning/Transmission Electron microscopy (S/TEM). The phase transition from hexagonal to face-centered cubic in Mg to MgTiHx is tracked through crystal structure changes observed by electron diffraction (ED) and in bulk plasmon resonance detected by electron energy loss spectroscopy (EELS). We also apply in-situ 4D STEM to investigate local structural displacements and strain developed during the process. Moreover, integrated differential phase contrast (DPC) imaging aids in pinpointing hydrogen atom positions within the lattice. By combining these methods, we gain insights into the hydrogenation process and its effects on hydrogen storage properties.

SESSION CH02.02: Exploration of Complex Oxide Heterostructures and Microelectronics Devices via In-Situ Electron Microscopy II

**In-situ Cryogenic and Biasing STEM and EELS for Quantum Materials**

**Shelly Michele Conroy**

University College London, United Kingdom

Understanding how the emergent phases of quantum materials form and behave during operation at the atomic scale is crucial to future quantum technology design. Cryogenic Scanning Transmission Electron Microscopy (STEM) and Electron Energy Loss Spectroscopy (EELS) have emerged as powerful tools, enabling scientists to explore quantum materials under extreme conditions of ultra-low temperatures, vacuum conditions, and applied stimulus such as bias. This cutting-edge combination of techniques integrates the high-resolution imaging and diffraction capabilities of STEM with cryogenic technology and the analytical capabilities of EELS, allowing for the investigation of materials at these low temperature exotic emergent phases, while simultaneously probing their electronic structure.

In this presentation firstly the multi phase effects below room temperature of Fe,II Boracite are investigated using a cryogenic STEM holder with temperature control. We investigate the change in strain, polarisation and domain configuration via 4D-STEM during temperature cycling and thus changing ferroic phases. By switching from 4D-STEM to EELS we can also collect changes in band gap and crystal field splitting. The dynamics of the domain wall topologies within these materials were investigated using in-situ biasing at these various temperatures and phases.

This second presentation will detail how cryogenic vacuum transfer STEM can be used to probe the superconducting phase of a doped Fe(Se,Te) system. Here we show the emergence of nanoscale superconducting puddles by complementary low temperature conducting atomic force microscopy. We could pick out these regions using focused ion beam and with a vacuum transfer system we can do all sample preparation and analysis under vacuum and cryogenic conditions. We reveal the clear changes in physical structure and band gap between the superconducting and high temperature phase using controlled in-situ heating from liquid nitrogen to room temperature.

**In-Operando Optical Tracking of Vacancy Induced Phase Change in Few-nm Thick Ferroelectric HZO**

**Stephan Törbert**

University of Cambridge, United Kingdom

Ferroelectric random-access memories (FeRAM) switching is achieved by ferroelectric switching of dipoles. FeRAMs offer low-energy and faster switching as compared to conventional memory circuits. They excel in power consumption and low-voltage operation when stacked against current-driven contenders. Unfortunately, FeRAMs have been restricted to niche markets due to their limited CMOS compatibility and severe scale issues of the complex ferroelectric perovskite systems. However, the discovery of ferroelectricity in binary oxides gave an impetus for developing a universal memory concept, which may lead to a significant breakthrough in the development of memory devices. Binary oxides generally do not suffer from a “dead layer effect”, which means non-binary oxides, such as perovskites, ineffective for thin film technology. Moreover, high coercive fields inside binary oxides give them considerable resilience toward internal depolarization of the ferroelectricity, crucial to achieving scalability and overcoming the widespread reliability disadvantages of FE material. The underlying reasons for the stable ferroelectricity and distinct switching of FE domains inside binary oxides at an atomic level are poorly understood. Moreover, non-idealities seen upon continuous electronic switching cycles like wake-up and fatigue introduce uncertainties in device performance and endurance. In this work, we present the first proof of the underlying reasons for these non-idealities with cycle-to-cycle tracking of morphologies changes in few-nm thick binary oxide ferroelectric ultra-thin films.

With our Nanoparticle-on-Mirror (NPoM) geometry, we capture for the first time both migration of <1% oxygen ions and material phase change in just 5 nm-thick binary oxide ferroelectric films when under continuous electronic switching and therefore track in real-time and in-operando the nanoscale kinetics of wake-up and fatigue in ferroelectric ultrathin memories. We use in-situ electrical and optical characterizations like darkfield scattering, photoluminescence and Raman spectroscopy to understand the nano-kinetics of the atomic level switching. The tracking of vacancy migration and phase change with the above-mentioned techniques combined with density functional theory (DFT) and finite-difference time-domain (FDTD) simulations provide the first insights into the morphological changes in ultra-thin binary oxide films [1].


**2:45 PM CH02.02.04**

**Unveiling Texture Transfer in Dielectric Thin Films via In Situ Electron Microscopy**

**Robert Winkler**

University of Cambridge, United Kingdom

Transition metal oxide (TMO) dielectric layers are pivotal for applications like field-effect transistors, supercapacitors, and emerging memories such as resistive random access memory (RRAM) [1]. Careful selection of the thin film layer materials and growth techniques in an RRAM device is essential to engineering the desired microstructure via texture transfer to improve performance and reliability [2], [3].

Usually, texture transfer is achieved via epitaxial growth at elevated temperatures, in the case of RRAM, might be more challenging to integrate in current complementary metal oxide semiconductor (CMOS) back-end-of-line (BEOL) processes. Therefore, a question arises if texture transfer is also possible when annealing amorphous HfO2 thin films grown via reactive sputtering. Usually, texture transfer is achieved via epitaxial growth at elevated temperatures, which, in the case of RRAM, might be more challenging to integrate in current complementary metal oxide semiconductor (CMOS) back-end-of-line (BEOL) processes. Therefore, a question arises if texture transfer is also possible when annealing amorphous HfO2 thin films grown via reactive sputtering.

With our Nanoparticle-on-Mirror (NPoM) geometry, we capture for the first time both migration of <1% oxygen ions and material phase change in just 5 nm-thick binary oxide ferroelectric films when under continuous electronic switching and therefore track in real-time and in-operando the nanoscale kinetics of wake-up and fatigue in ferroelectric ultrathin memories. We use in-situ electrical and optical characterizations like darkfield scattering, photoluminescence and Raman spectroscopy to understand the nano-kinetics of the atomic level switching. The tracking of vacancy migration and phase change with the above-mentioned techniques combined with density functional theory (DFT) and finite-difference time-domain (FDTD) simulations provide the first insights into the morphological changes in ultra-thin binary oxide films [1].


References:


**3:00 PM BREAK**
Defect Induced Memristive Switching in Off-Stoichiometric SrTiO$_3$ and CaTiO$_3$ studied by In Situ Transmission Electron Microscopy

Alessandro Mazza$^1$, Quanxi Jia$^2$, Michael Zachman$^3$, Rod McCabe$^1$ and James M. LeBeau$^4$; $^1$Los Alamos National Laboratory, United States; $^2$University at Buffalo, The State University of New York, United States; $^3$Oak Ridge National Laboratory, United States; $^4$Massachusetts Institute of Technology, United States

Dielectric materials, holding charges as capacitors, are vital energy storage components of electronics and power systems. Dielectric capacitors distinguish themselves in features of ultrafast charging/discharging rates, high voltage endurance, and good reliability. Enhancing the relatively low energy densities of dielectric capacitors is essential for their applications in pulsed power equipment. Relaxor ferroelectrics are promising candidates for applications in energy storage. Therefore, considerable effort has been devoted to enhancing the energy storage via composition optimization, defect engineering, and architectural design.

In this talk, we will discuss the strategies of designing interface and domain structure in doped BaTiO$_3$ to achieve relaxor ferroelectrics. In the first part, I will discuss the design of (Ba$_{0.6}$Ca$_{0.4}$)$_3$TiO$_7$ (BCT) and Ba(Ti$_{0.6}$Zr$_{0.2}$)$_3$O$_9$ (BZT) superlattices via a high-throughput combinatorial approach. Well-controlled compositional gradient, superlattice geometry and domain size are explored by scanning transmission electron microscopy (STEM). Ferroelectric and dielectric properties identified the "optimal property point" achieved near the morphotropic phase boundary. Our results have that relaxor-like ferroelectric behavior enhances and the leakage slightly increases with reducing the superlattice periodicity (or with more interfaces). In the second part of the talk, I will discuss our methods to further optimize domain structure and suppress the leakage current in BZT-BCT films via a machine learning approach. Sn has been identified as a good dopant to maintain the rhombohedral/tetragonal phase boundary, reduce leakage current and reduce the domain size below 10 nm for BZT-BCT systems and greatly enhanced relaxor ferroelectric behavior has been achieved. The large polarization and the delayed polarization saturation led to greatly enhance energy density of 80 J/cm$^3$ and transfer efficiency of 85% over a wide temperature range. Such a data-driven design recipe for a relaxor like polar state is generally applicable to quickly optimize functionalities of ferroelectric materials.

4:00 PM CH02.02.06

Defect Induced Memristive Switching in Off-Stoichiometric SrTiO$_3$ and CaTiO$_3$ studied by In Situ Transmission Electron Microscopy

Changmin Liu$^1$, Wahib Aggoun$^2$, Mohamed Abdeldayem$^1$, Alexander Melel$^1$, Houari Aman$^1$, Ijar-Asia Shah$^1$, Thilo Remmel$^1$, Tobias Schue1, Andreas Fiedler$^1$, Jutta Schwarzkopf$^1$, Matthias Scheffler$^2$ and Martin Albrecht$^1$;

$^1$Leibniz Institut fuer Kristallzuechtung, Germany; $^2$Humboldt-Universitaet zu Berlin, Germany; $^3$Thermo Fisher Scientific, Netherlands

In the quest for neuromorphic computing systems that emulate the intricacies of the human brain, the transition of digital memory to an analog state is paramount. A central scientific question revolves around directing materials to incorporate synaptic plasticity. Among the most promising and technologically advanced strategies for achieving this are resistive random access memory (ReRAM) devices. Traditional ReRAMs operate through the stochastic formation and breakage of conductive filaments within an insulator storage medium, making control challenging. This paper presents a novel approach to memristive devices, focusing on single crystalline SrTiO$_3$ and CaTiO$_3$ thin films. By deliberately introducing an A cation deficiency of up to about 16% through metal organic vapor phase epitaxy (MOVPE), we have successfully realized resistive switching without the need for filament formation, achieving on/off ratios as high as 10$^5$. Our investigation integrates various techniques, including electrical measurements, transmission electron microscopy (TEM), and in-situ X-ray studies at a synchrotron, to provide insights into the underlying mechanisms.

Our results suggest that the resistive switching phenomenon in off-stoichiometric films can be attributed to trap-assisted tunneling through Ti antisite defects, which induce a switchable polarization. Crucial parameters such as on/off ratio and retention time depend on the extent of off-stoichiometry. This study presents a comprehensive TEM analysis of these materials, including high-resolution scanning transmission electron microscopy (S-TEM), electron energy loss spectroscopy (EELS), and dynamic in-situ TEM measurements with electrical bias and heating. Our results show that approximately 50% of the V$_{o}$ sites are occupied by Ti and that these antisite defects are responsible for inducing ferroelectric polarization. Differential phase contrast measurements reveal the polarization of these domains. Preliminary in-situ TEM experiments confirm the resistive switching behavior observed in ex-situ electrical measurements.

Furthermore, our in-situ studies suggest that these polar defects combine under bias to form nanopolar domains that are statistically distributed throughout the film. This is visually confirmed by contrast inversion in dark-field images using forbidden reflections, consistent with macroscopic observations in synchrotron experiments. We attribute this contrast inversion to the alignment of off-centered polar defects induced by the applied electric field. Reducing the voltage to 0 V results in a stable state, albeit with the polarization erased, returning the local film to a high-resistance state. These preliminary in-situ I-V measurements confirm our recent findings that resistive switching in Sr-deficient SrTiO$_3$ thin films occurs at significantly lower voltages than those required for filament formation, offering promising prospects for future neuromorphic computing applications.

4:15 PM CH02.02.07

Advanced Phase Plate Fabrication and Thin Film Characterization for TEM Imaging of Biological Samples

Marcus F. Huf$^1$, Mads S. Larsen$^1$, Stephan S. Keller$^1$, Marco Beleggia$^1$ and Paul J. Kempen$^1$; $^1$Technical University of Denmark, Denmark; $^2$University of Modena and Reggio Emilia, Italy

Phase plates (PPs) for transmission electron microscopy (TEM) have been a research field since 2001 [1] and are of continuing interest to enhance contrast and increase resolution when imaging biological samples [2]. The most promising PPs for soft-matter imaging are thin-film-based [3]. These include Volta-, Zernike-, and Hilbert-type PPs. Thin-film PPs are generally fabricated by hand using sputtering tools in a single-device process [4]. These PPs suffer from several limitations that plague their widespread implementation. These limitations include contamination, ease of installation and use, lack of reproducibility, and lack of full understanding and control of the induced phase shift. In this work we use cleanroom processes to fabricate PPs that are reproducible with known parameters. In this manner we can both know and control the induced phase shift. We present the fabrication of both Zernike-type phase plate devices (ZPPs), with an ideal phase shift of $\Delta \phi = \pi/2$, and Hilbert-type PP devices (HPPs), for which $\Delta \phi = \pi$.

In order to achieve this, it is necessary to know the accurate mean inner potential (MIP) of the materials involved. For our work, the most promising thin film materials are silicon nitride and amorphous carbon. MIP values for these materials in the literature vary widely, making it difficult to fabricate a device with the ideal phase shift. The phase shift is related to the mean inner potential $\phi_0$ and the film thickness $t$ (via an electron constant $C_0$) in the following way [5]: $\Delta \phi = C_0 \phi_0 t$. We use ellipsometry and AFM techniques to determine and verify the thicknesses of the thin films. We use electron holography (EH) [6] to measure the phase shift. Using the thickness and phase shift values we can then accurately determine the MIP of our thin films. We can further use this to optimize our devices for optimal phase shift.

In addition to our material characterization, we installed the PPs in the back focal plane of a TEM for enhancing the phase contrast in materials. We will demonstrate the functionality of our phase plate devices via contrast enhancement, using both a test sample made from thin carbon structures on a standard carbon-film TEM grid, and biological samples at cryogenic temperatures.

REFERENCES


4:30 PM *CH02.02.08

In-Situ STEM Studies of Ferroelectric Domains in Free-Standing Thin Films

Tamsin O. Reilly$^1$, Kristina Holsgrove$^1$, Xinping Zhao$^2$, John J. Scott$^1$, Iaro Gaponenko$^1$, Praveen Kumar$^1$, Patrycja Paruch$^3$, Joshua Agra$^2$ and Miryam Arredondo$^1$; $^1$Queen's University Belfast, United Kingdom; $^2$Drexel University, United States; $^3$University of Geneva, Switzerland; $^4$School of Mines, United States

Ferroelectrics are polar materials known for their spontaneous polarization, which can be reversibly switched by applying an external field. As these materials are cooled below their Curie temperature ($T_c$), the resulting domain structure and switching dynamics are driven by boundary conditions, aiming to minimize electrostatic and elastic energy in the system. A particularly interesting aspect of ferroelectrics is the effect that surface chemical species have on the screening mechanism, and its resulting domain structure, and vice versa, how domains affect the surface chemistry. The latter could be exploited to tailor surface reactivity for electrochemical, catalytic,[1-6] and other energy harvesting applications.[2, 7-9]

This study focuses on investigating the thermally induced behavior of ferroelectric-ferroelastic domains in free-standing thin films under different chemical environments using in-situ scanning

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
transmission electron microscopy (STEM) techniques. The similarities and differences between these environments are discussed, along with the associated challenges.

To the best of our knowledge, this is the first time in-situ heating under controlled gas environments has been employed to study ferroelectric-ferroelastic domains. Our findings provide valuable insights into the intricate relationship between important ferroelectric characteristics such as \( T_c \), domain size, etc. and the chemical environment. Furthermore, this work highlights the application of in-situ gas as a powerful tool for dynamically exploring the effects of other external variables such as pressure on polar materials.

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**References**


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**In-Situ Electron Microscopy**

# SESSION CH02.03: Exploration of Complex Oxide Heterostructures and Microelectronics Devices via In-Situ Electron Microscopy III

**Session Chairs:** Leopoldo Molina-Luna and Yaobin Xu

**Wednesday Morning, April 24, 2024**

**Room 440, Level 4, Summit**

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**8:30 AM CH02.03.01**

**High-Resolution Scalar/Vector-Field Electron Tomography Unveiling 3D Topological Spin Textures**

*Xiuzhen Yu*, Nobuto Nakanishi1,2, Yi-Ling Chiew1, Nasoya Kanazawa1, Kosuke Karube1, Yasujiro Taguchi1 and Yoshinori Tokura1,2,3; RIKEN, Japan; 2Thermo Fisher Scientific, Japan; 3The University of Tokyo, Japan

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The emergence of 2D topological spin textures, such as skyrmions in helimagnets, has garnered significant attention in the field of condensed matter physics and spintronics1,2. However, our understanding of nontrivial 3D spin textures remains limited, primarily due to the absence of a high-resolution 3D magnetic imaging technique, especially at lower temperatures below room temperature (RT). While some progress has been made in imaging magnetic twisted structures in 3D through nanotomography3, challenges persist in accurately mapping 3D vector fields and achieving the necessary spatial resolution. These obstacles hinder our ability to comprehensively map 3D exotic spin textures in magnets with topological precision over a broad temperature range. The objective of this study is to develop a high-resolution scalar/vector-field electron tomography microscopy technique that covers a wide temperature range from 95 K to RT, enabling real-space observations of various 3D topological spin textures.

In this study, we introduce scalar/vector-field electron tomography using 3D integrated differential-phase-contour microscopy and discuss its applications. Specifically, we will show vortex pairs on the surface of elliptical skyrmions in an antiskyrmion-hosting magnet at RT and the formation of ‘football’-like skyrmions and their heavy deformations around sample surfaces with varying temperatures in a helimagnet FeGe. This groundbreaking 3D magnetic imaging technique reveals hybrid topological spin textures, including surface spin textures such as vortices and monopoles, providing valuable insights into the topological aspects of various spin textures emerging in topological materials.

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**9:00 AM CH02.03.02**

**Investigating the Resistive Switching Mechanisms of Oxide and Nitride-Based Memristor Devices via In Situ STEM and EELS**

*Di Zhang*, Rohan Dhali1, Matt Schneider1, Chengyu Song2, Sundar Kunwar1, Nicholas Cucinelli1, Hongyi Dou1, Jim Ciston2, John Watt1, Winson Kuo1, Michael T. Pettes1, Haiyan Wang3, Rod McCabe1 and Aiping Chen1; 1Los Alamos National Laboratory, United States; 2Lawrence Berkeley National Laboratory, United States; 3Purdue University, United States

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The resistive-switching (RS) phenomenon observed in a variety of transitional metal oxides is of great research interest since it opens enormous opportunities for the next-generation electronic devices such as nonvolatile memory and neuromorphic computing devices. However, the RS mechanisms for many oxide- and nitride-based memristor devices are still unclear. In this project, we use in situ transmission electron microscopy (TEM) and Electron Energy Loss Spectroscopy (EELS) to investigate the RS mechanisms of different types of memristor devices. The high resolution STEM images captured during the in situ biasing experiment revealed the potential phase transition processes and polarized cations displacements, and the core EELS spectra confirmed the cations valence states change and the oxygen stoichiometry modulation during the RS processes. This study has shined great light on clarifying the RS mechanisms of different types memristor devices, which can be applied to the development of next-generation nanoelectronic devices towards advanced memory and neuromorphic computing units etc.

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**9:15 AM CH02.03.03**

**Breaking Barriers in Oxide Nanoelectronics: Advancements in In Situ TEM Studies**

*Oscar Recalde1, Tianshu Jiang1, Robert Winkler1, Alexander Zintler1, Esmaeil Adabifiroozjaei1, Yevheniy Pivak1, Hector Perez-Garza1 and Leopoldo Molina-Luna1; 1TU Darmstadt, Germany; 2DENsolutions, Netherlands

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In today's microelectronic industry, oxide nanoelectronics are at its core. To gain insights into the dynamic processes within these nano electronic devices at the nano and sub-nanometer scale, in-situ/operando transmission electron microscopy (TEM) has become a vital research avenue. Recent advancements in the integration of microelectromechanical systems (MEMS) within electron microscopes have made it possible to apply various stimuli to samples directly inside the microscope, including electrical biasing.

However, achieving reliable sample preparation for these experiments using focused ion beam (FIB) techniques has been an intricate challenge. Conventional FIB methods have often led to the inadvertent creation of short circuits along the MEMS platforms and TEM devices during sample attachment and electrical biasing. This has obscured the true performance of these devices.

In this study, our innovative FIB sample preparation protocol overcomes these challenges, allowing for the dependable operation of two-terminal oxide devices within the TEM. We have investigated structural changes in materials like SrTiO3-based memristors, Nb-doped lead zirconate titanate (PZNZT) piezoelectric, and BaSrTiO3 ferroelectric, directly correlating these observations with the simultaneous acquisition of current-voltage (I-V) curves. This has facilitated meaningful comparisons with their macroscopic counterparts.

Furthermore, our investigations encompass multi-stimuli experiments, introducing gas nano cells into the equation. Interestingly, we have observed the impact of device oxidation induced by electron beam irradiation that alters the electrical response of a SrTiO3-x and BaSrTiO3 ferroelectric, directly correlating these observations with the simultaneous acquisition of current-voltage (I-V) curves. This has facilitated meaningful comparisons with their macroscopic counterparts.
**Towards Electromagnetic Field Imaging in Materials by Scanning Transmission Electron Microscopy**

11:00 AM  *CH02.03.06*

Divacancy and vacancy-transition metal (v-TM) complexes in silicon carbide (SiC) can form the basis for optically addressable single photon emitters. The convergence of SiC's technological maturity and the compatibility of these qubits with traditional semiconductors has thus sparked considerable interest in these defects. For example, recent quantum coherence measurements of v-TM complex spin states in SiC have underscored the potential of this platform in quantum computing applications. To validate theoretical frameworks and glean insights pertinent to emitter synthesis and stability, atomic resolution electron microscopy offers direct access to their structure and interactions within their local environment.

This presentation will explore the direct observation of individual defects in a SiC film using scanning transmission electron microscopy (STEM) imaging and multislice electron ptychography. We will show how the capabilities afforded by multislice electron ptychography enable us to characterize these defects at a localized level and in 3D without the need for tomography or through-focus methods. Moreover, we will show that conventional methods, such as high-angle annular dark field STEM, can be severely limited for this type of study due to noise and are frequently obscured by surface contamination, damage, and roughness. We will demonstrate that ptychographic reconstructions can directly quantify single defects and defect complexes on a slice-by-slice basis, imparting direct 3D information. This will be explored using simulated ptychographic datasets encompassing an array of defects in various positional configurations. Finally, we will discuss the limitations of capturing three-dimensional structures and the ability to capture small displacements arising from substitution and the formation of v-TM complexes.

**Towards In-Situ Atomic Resolution Scanning Transmission Electron Microscopy**

1:30 PM  *CH02.04.01*

Atomic Resolution Scanning Transmission Electron Microscopy Imaging of The *In Situ* Synthesis of Nanoparticle Catalysts

Sarah J. Haigh1, Yichi Wang1, Nick Clark1, Matthew Lindley1, Thomas Slater2 and Roman Gorbachev1; 1University of Manchester, United Kingdom; 2Cardiff University, United Kingdom

The shape and size of metallic nanoparticle catalysts have been shown to control the activity and selectivity for many chemical reactions. Most industrial catalysts are produced by wet impregnation and calcination, due to the scalable nature of this synthesis technique. However, a greater control of the composition, size and shape of the resulting nanoparticles is highly desirable. Understanding the interactions of metal ions with the surfaces in the wet impregnation solution, as well as better understanding of the drying behavior in hydrogen at elevated temperature would be highly desirable to support the production of the improved industrial catalysts needed to address the current energy emergency.

Our group have been developing in situ 2D heterostructure cells for atomic resolution transmission electron microscopy (TEM) imaging and analysis, using a combination of graphene, hexagonal boron nitride and MoS2 layers to trap liquid and gas pockets and enable new functionality such as liquid-liquid mixing [1]. We have used these 2D heterostructure liquid cells to investigate the dynamic processes that occur at a solid-liquid interfaces as metal ions from solution interact with a solid support at atomic resolution [2]. For example to demonstrate the use of liquid phase imaging to probe the preferred resting sites for platinum atoms on molybdenum disulfide [2].

We have also used in situ gas cell TEM to investigate how the morphology is determined by the impregnation synthesis parameters, as well as how the starting structure and composition determines the evolution of industrial supported nanoparticle catalysts during activation heat treatment [3].

In situ TEM studies are often limited to 2D imaging, especially for highly active nanoparticle systems like PtNi, where the particle composition and morphology can be used tune the performance for the oxygen reduction reaction [4]. We have shown that the single particle reconstruction method, which is widely used in cryogenic TEM imaging of proteins, is a valuable approach to understand the effects of different particle preparation methods on the morphology and structure. We have also shown that the approach averages over particles present in the image with different orientation to build up a tomographic reconstruction at much lower radiation dose than is required for conventional tilt series tomography [5]. We have shown that this opens up the single particle reconstruction technique to allow 3D visualization at different time points during in a synthesis process or catalytic reaction [6]. This approach could be brought to the atomic scale through harnessing the improved imaging performance achievable with new in situ cell designs.


**SESSION CH02.04: Exploration of Catalysts and 2D materials Dynamics via In-Situ/Cryogenic Electron Microscopy**

1:30 PM  *CH02.04.04*

Exploiting Dynamic Processes at Solid-Liquid Interfaces Using In-Situ Transmission Electron Microscopy

 session chairs: Yaobin xu and Di Zhang

Wednesday Afternoon, April 24, 2024

Room 440, Level 4, Summit
Transmission electron microscopy (TEM) now has become one of the most influential techniques in nanoscience and nanomanufacturing characterization fields, which can be used to study the structure, component or valence at sub-angstrom scale. We involved the advanced Cs-corrected STEM to reveal the microstructural evolution of the non-noble catalyst for carbon dioxide hydrogenation. Firstly, we designed a porous Co/C catalyst derived from a novel layered metal-organic framework (MOF) with tunable pore sizes for CO$_2$ hydrogenation. Pointing out the dependence of the durability on the pore size. Secondly, we find the partial loss of catalytic activity of non-noble CoFe alloy catalysts, as exposed to oxygen, can be attributed to the migration of Co element from the core region of CoFe alloy to the surface. The adsortion energy of H for CoFeO$_2$ shell is stronger than FeO$_2$ shell, so it is harder to fully desorb for H in the follow reaction process. Lastly, we revealed the non-noble catalyst structure stability optimization strategies and mechanisms in long-term reaction process for CO$_2$ hydrogenation. The studies above provide a new viewpoint to design high-performance catalyst and modify their structures.

3:15 PM *CH02.04.04
Unveiling Phase Transitions in 2D Layered Materials via Atomic-Scale Cryogenic STEM Miaofang Chi, Haoyang Ni and Hisun-Yin Chao; Oak Ridge National Laboratory, United States
Many quantum materials possess complex electronic phase diagrams where correlated electronic phases, such as superconductivity, magnetic ordering, and charge density waves (CDWs), exist near each other. The proximity of these phases suggests that phase transitions must be understood to establish the microscopic origin for these correlated phases and to use them for applications. These phase transitions have mostly been studied using ensemble-average techniques, lacking real space information of nucleation and growth of these often-competing electronic phases. Nevertheless, such real-space information is essential for applications of quantum materials, which will be at the nanoscale where reduced dimensionality, confinement, local heterogeneities, and defects will greatly modify the phase transitions.

In this talk, I will discuss our group’s efforts on combining cryogenic scanning transmission electron microscopy (cryo STEM) and in situ cryo 4D STEM with in situ transport measurements to study the phase transition of TaS$_2$ in real-space with nanometer resolution as it undergoes a transition from the commensurate CDW (insulating phase) to the nearly commensurate CDW (metallic phase). We directly visualize the nucleation and growth of the NC-CDW phase out of the C-CDW phase and correlate this to the changing transport data. We establish that the phase transition starts at extended defects present in TaS$_2$. We also examine the pulse-induced CDW phase transition in TaS$_2$ and reveal the role of defects and the transition mechanism. Our findings are extended to CDWs in rare-earth tri-tellurides (RTe$_3$) and other layered materials.

4:15 PM CH02.04.06
STEM Imaging of AC Electric Field Driven Non-Centrosymmetric Atomic Displacements in The 2D TMD WSe$_2$ Christopher T. Nelson, Ondrej Dyck, Mina Yoon, Jawaher Almutlaq, Dirk Englund and Stephen Jesse; 1Oak Ridge National Laboratory, United States; 2Massachusetts Institute of Technology, United States
Simultaneous characterization by (S)TEM and application of electrical bias is a powerful platform to study the real-space dynamic electronic couplings at nanoscales: the length scale of interest for many electronic, quantum, and electromechanical materials and processes. Minimum acquisition times across all STEM modes favor in situ electrical bias experiments that are quasi-static for a good signal/noise. Exploring dynamic responses at faster time scales necessitates multi-cycle summation to overcome the shot-noise limits for a coherent source. In this work we utilize this approach to characterize moderate frequency (25kHz) AC electric-field induced response on the atomic structure of a 2D semiconductor WSe$_2$. As tunable 2D direct-gap semiconductors, WSe$_2$ and similar Transition Metal Dichalcogenides show promise for applications in nano- and opto-electronics. Their potential lies in part with a wide library of 2D materials, TMD and otherwise, and a correspondingly large design-space for heterogenous multi-layer engineering. Here we applied an in-plane electric field across a free-standing monolayer WSe$_2$ by biasing across a gap in an overlaid graphene layer. Rolling series short-dwell HAADF images were collected with a custom scan coil controller while an AC 25kHz sinusoidal bias was applied. Atomic structure fluctuations vs applied voltage were determined form a workflow of phase-detection -> averaging -> binning -> and atom position finding using a machine-learning model AtomAI$^2$. Collective atomic motion was removed, observed to be ~0.5 Å/V, owing to beam deflection by long range stray-fields. We observe a small but robust 10% decrease in the CoFe$_3$O$_4$ sample compared to the CoFe$_2$O$_4$ sample. This effect was only observed for datasets collected within the electrode gap and not within the graphene electrode itself. The nominal field concentration within the former and absent in the latter strongly supports this is direct real-space observation of local field induced dynamics, specifically a fixed-frequency optical-photon type dielectric response.

[3] This work was supported by the U.S Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division

4:30 PM CH02.04.07
Endotaxial Polytype Engineering: Enhancement of Incommensurate Charge Density Waves in TaS$_2$ Suk Hwan Sung, Pat Kezer, Nishkarsh Agarwal, Yin Min Goh, Noah Schnitter, Ismail El Bagiari, Hai Sun, Lena Kourkoutis, John T. Heron and Robert Hovden; 1Harvard University, United States; 2University of Michigan, United States; 3Cornell University, United States
Charge density waves (CDWs) are an emergent periodic modulation of the electron density that spans a crystal with strong electron-lattice coupling. CDW phases spontaneously break crystal symmetry, facilitate metal–insulator transitions, and compete with superconductivity [1–4]. At elevated temperatures, many materials exhibit a CDW incommensurate (IC-) with the height symmetry parent phase [5–8]. Unfortunately, the IC-CDWs are inherently weak and disordered. In TaS$_2$, a popular layered CDW material, long-range order has not been demonstrated for the IC-CDW [9–11]. Using new methods of endotaxial polytype engineering [12] we show it is possible to restore long-range order of the IC-CDW phase. Through this process, 2D CDW layers are encapsulated within metallic polytypes to enhance charge order. Furthermore, with restored IC-CDWs we can better understand the nature of disorder in these systems. We show that the IC-CDWs in 1T-TaS$_2$ are hexagonally disordered and undergo a continuous melting as temperature is increased. The hexatic CDW phase retains six-fold orientational order while translation order quickly decays from proliferation of defects with temperature. Here we use endotaxial engineering to enhance CDWs—even at elevated temperatures. The polytype heterostructures consist of monolayers of octahedrally coordinated charge ordered TaS$_2$ embedded within matrices of metallic prismatically TaS$_2$. These endotaxial heterostructures have been shown to raise the critical temperature of the long-range ordered commensurate (C-) CDW phase by 150 K [12].

Surprisingly, long-range order of the IC-CDW phase is significantly enhanced in the polytype heterostructures [13]; in-situ selected area electron diffraction (SAED) of the heterostructures shows sharper and brighter superlattice peaks than the IC-CDW phase in pristine 1T-TaS$_2$. This enhancement of long-range CDW order is accompanied by a marked increase in the in-plane resistivity of the IC phase. The increased intensity is surprising given the number of charge ordered TaS$_2$ layers is decreasing.

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The signature of IC-CDWs in TaS₂ is the presence of azimuthally diffused superlattice peaks decorating bright Bragg peaks in SAEDs. These azimuthally blurred superlattice peaks strongly resemble the structure factor of hexatic phases found in two-dimensional (2D) systems. 2D crystals can melt continuously through intermediate orientationally ordered hexatic phase [14–17]. Similarly, in pristine 1T-TaS₂, the IC-CDW phase is in a hexatic glassy state due to intrinsic disorder. By restoring crystallinity of the IC-CDW, we observe the full hexatic melting process: heating further melts the ordered IC-CDW phase with continuous azimuthal broadening and weakening of superlattice peaks as expected for hexatic phases.

In summary, we demonstrate that polytype engineering can stabilize fragile long-range order in IC-CDW even at high temperatures. The ordered IC-CDW phase melts continuously with hexatic characteristics.

References:


SESSION CH02.05: Poster Session: Utilizing Advanced In Situ/Operando Transmission Electron Microscopy and Spectroscopy for the Investigation of Functional, Energy and Quantum Materials
Session Chairs: Leopoldo Molina-Luna and Di Zhang
Wednesday Afternoon, April 24, 2024
Flex Hall C, Level 2, Summit

5:00 PM CH02.05.01
In-Situ TEM Full Temperature Range Cooling, Heating and Electrical Biasing Sample Holder Calvin A. Parkin, Norman Salmon and Daan Hein Alsem; Hummingbird Scientific, United States

cryogenic cooling of samples during scanning/transmission electron microscopy (S/TEM) has enabled the characterization of various quantum interfaces and phase interactions in strongly correlated systems. Investigation of such quantum properties at the fundamental level has historically been challenging due to inadequate spatial and temporal resolution of characterization techniques as well as inadequate sample stability. Quantum materials must be studied at cryogenic temperatures because many of the relevant properties in these quantum materials only manifest at such low temperatures.

Cryogenic S/TEM sample holders have not only enabled the study of quantum topological insulators in two-dimensional (2D) materials but also atomic resolution observation of battery interfaces, which is traditionally difficult to achieve because they are sensitive to air and prone to electron beam damage at room temperature. However, lack of biasing capability has limited the study of electrical responses in these materials systems. With increasing demand for batteries that function at high temperatures and material phase information across a wide range of temperatures from cryogenic to high temperature, expanded versatility will be required of temperature-controlled in-situ electrical biasing systems. Here, we present a novel in-situ electrical biasing S/TEM holder that simultaneously allows electrical stimulus and high-resolution imaging of a sample in-situ across the full temperature range, from cryogenic up to high temperatures. The holder is exceptionally stable, with drift speeds across the entire temperature range comparable to standard holders at room temperature. Battery processes were demonstrated in a single nanowire system using this holder at near-nitrogen temperature (~170°C) up to room temperature. Electrical biasing was performed on a nanowire sample bridging the electrodes on the biasing chip. A constant current experiment at cold temperatures on the nanowire showed a voltage drop as the reaction proceeds with the growth of a dendrite layer plated on the nanowire's surface. With the new heating capability, such experiments are extended to ~1000°C using heating on the same chip that electrically biases the sample to achieve these higher temperatures. This enables studying the temperature dependence of chemical and microstructural evolution under electrical bias. Far below room temperature where on-chip temperature measurements become increasingly inaccurate, precise temperature control is maintained using a conventional resistance heater and miniature thermocouple at the sample in the TEM holder tip. At intermediate cold temperatures, the on-chip heating/temperature sensing can be combined with tip heating and temperature measurement for precisely controlled rapid heating experiments. For quantum nanomaterials, this enables their synthesis and processing to be studied across a range of different temperatures in the low temperature regime, and their quantum response to electrical biasing to be measured at cryogenic temperatures. Batteries may now be electrochemically cycled at elevated temperature and then returned to cryogenic temperature for imaging, without the need to change holders. The cryo-biasing TEM holder with heating will empower scientists to nimbly investigate structure-property relationships in materials, specifically electronic properties, across the full temperature range. This versatile tool will accelerate the development of the next generation of electronic, quantum, and energy storage materials devices.

5:00 PM CH02.05.02
A Surface Science Investigation of Hydrocarbons Adsorption to a Ru/Al2O3 Catalyst Erin E. Dunphy; University of Colorado Boulder, United States

Hydrogenolysis is an extremely effective method for plastic upcycling. Specifically, Ru-based catalysts supported on metal oxides have shown high reactivity for polyethylene upcycling. Polyethylene hydrogenolysis is an extremely structure-sensitive reaction, where product distribution depends on the size of the adsorbing alkyl chain and the hydrogen availability at the metal oxide support interface. However, surface science studies are required to characterize the structural impact of these dependencies directly.

To study the arrangement of hydrocarbons to the catalyst support, we utilize X-Ray Reflectivity (XRR) and Molecular Dynamics (MD) simulations, and to study the local chemical environment changes of the Ru active site, we utilize Extended X-Ray Absorption Fine Edge Structure (EXAFS). By utilizing hydrocarbons of various lengths (methylene, hexane, dodecane, tricantane, and low-density polyethylene), we will understand preferential adsorption arrangements for undesirable and desirable product species.

We theorize that as hydrocarbon chain length increases, the polymer will adsorb to the support with increased structural order, resulting in increased adsorption potential to the Ru active site. MD simulations of n-dodecane at various temperatures indicate that the preferential adsorption of species parallel to an alumina interface changes, and the application of the distorted crystal model confirms the viability of XRR as an experimental technique, as seen in the attached experiment. EXAFS and XRD data are currently being processed and will yield information about the local relaxation of Ru nanoparticles and the alumina support during species adsorption. This work aims to understand the structure and arrangement of hydrocarbons to the active metal site and the support, thus allowing for fundamental concepts to be unified and expanded upon.

We anticipate our results to inspire future surface science studies to explore how different polymers adsorb to the catalyst surface—ultimately allowing for the creation of catalysts capable of mixed-polymer hydrogenolysis and reduction of energy requirements for polymer upcycling.

5:00 PM CH02.05.03
Luminescence Polarization of Rare Earth Microcrystals under High Pressure Haoran Zhao; Peking University, China

In recent years, the polarization properties of rare earth luminescent materials have attracted extensive attention. The fine spectral splittings generated by the crystal field effect has fingerprint-
like polarization characteristics[1], but its influence factors need to be studied. High pressure is an important protocol to adjust the structure and properties of materials, which can change the unit cell parameters and local symmetry of rare earth luminescent materials, and further affect the crystal field parameters, emission wavelength and intensity[2,3,4]. However, the effect of high pressure on the polarization of rare earth emissions has not been studied. Hexagonal phase NaREF₆, which has an anisotropic crystalline structure, is a decent host material for emission polarization. We studied the emission polarization of NaREF₆ microcrystals under high pressure. Through adjusting the symmetry of crystal structure by high pressure, the influence of crystal structure symmetry on rare earth emission polarization was investigated, meanwhile, the correlation between the direction of emission polarization and the axis of crystal symmetry was analyzed[5]. Taking the 704 nm emission as an example, its polarization degree decreased with the increased pressure, while the polarization direction rotated by 90°. These findings benefit to the in-depth understanding of the mechanism of rare earth emission polarization and are informative for the design of new rare earth polarized luminescent materials.


**SESSION CH02.06: Investigation of Energy Storage Materials via Advanced In Situ/Cryogenic Electron Microscopy**

**Session Chairs: Qianqian Li and Yaobin Xu**

Thursday Morning, April 25, 2024

Room 440, Level 4, Summit

8:15 AM DISCUSSION TIME

8:15 AM CH02.06.01

**Electrochemical Lithium Intercalation & Exfoliation in 2D TMDs and its In-Situ Studies**

Zhiyuan Zeng
City University of Hong Kong, Hong Kong

We developed a lithium ion battery intercalation & exfoliation method with detailed experimental procedures for the mass production of 11 two dimensional TMDs and inorganic nanosheets, such as MoS₂, WS₂, TiS₂, TaS₂, ZrS₂, graphene, h-BN, NbSe₂, WSe₂, SnSe₂ and Bi₂Te₃, among them 3 TMDs achieved mono- or double layer yield > 90%. This method involves the electrochemical intercalation of lithium ions into layered inorganic materials and a mild sonication process. The Li insertion can be quantitatively controlled by monitoring the intercalation rate and finely controlled in the battery testing system, so that the galvanostatic discharge process is stopped at a proper Li content to avoid decomposition of the intercalated compounds. The intercalation strategy can also be used to tune 2D TMDs’ physical and chemical properties for various applications. For example, we developed a one-step coherent functionalization method on MoS₂ nanosheets for membrane fabrication, which exhibited excellent desalination performance. For lithium intercalation mechanism, the state-of-the-art In-Situ Liquid Phase TEM is an ideal technique for identifying the phase changes during intercalation process. With self-designed electrochemical liquid cell utilized, we can directly capture the dynamic electrochemical lithiation and delithiation of electrode in a commercial LiPF₆/EC/DEC electrolyte, such as LiF nanocrystal formation, lithium metal dendritic growth, electrolyte decomposition, and solid-electrolyte interface (SEI) formation. Combining with other in-situ techniques, such as in-situ XAS, XRD and Raman, etc, the underlying lithium intercalation mechanism in TMDs were further investigated, which render us a comprehensive understanding of the intrinsic correlation between the intercalation process and TMDs.

References:


8:30 AM *CH02.06.02

**Seeing the Invisible: Ultrathin (UT) Membrane Chip for Fluidic-Chip Electron Microscopy**

Vinayak P. Dravid
Northwestern University, United States

In the recent decade, in-situ or operando S/TEM utilizing SiNx membrane encapsulated chips to confine fluids for electron microscopy examination has become popular. A great number of prior innovators have shown this to be an effective approach for probing fluid-surface nanostructure interactions and related phenomena or reactions. Such a “closed cell” chip based on silicon nitride (SiNx) membranes as electron transparent encapsulation material, has many practical and technological advantages over the differential pumping environmental TEM (ETEM).

Unfortunately, however, conventional fluid-cells suffer from additional and significant electron scattering from the top and the bottom membranes, which are typically 30-50nm thick to maintain integrity/stability during the operation. Thus, the total thickness of >70-80 nm of the encapsulating membranes imposes many adverse effects on the post electron optics, such as increased chromatic aberrations. More importantly, the is reduced from nominally ~1.0 to 0.3 using a encapsulation. We show that our UT chip increases contrast of typical nanoparticles at sufficient for most high-resolution S/TEM applications on non-electron sensitive materials. Prior innovators have shown this to be an effective approach for probing fluid-surface/nanostructure interactions and related phenomena or reactions. Such a “closed cell” chip based on silicon nitride (SiNx) membranes as electron transparent encapsulation material, has many practical and technological advantages over the differential pumping environmental TEM (ETEM).

We have recently developed a robust, functional and scalable backing support strategy to enable the thinnest possible (<10 nm) SiNₓ encapsulation (without any specific membrane). However, low scattering “thin” membrane is riskily since the mechanical robustness is compromised, resulting in potentially catastrophic failure. Thus, novel design strategies for fabrication of stable ultrathin SiNx membrane are needed.

We have recently developed a robust, functional and scalable backing support strategy to enable the thinnest possible (<10 nm) SiNₓ encapsulation (without any specific membrane). However, low scattering “thin” membrane is riskily since the mechanical robustness is compromised, resulting in potentially catastrophic failure. Thus, novel design strategies for fabrication of stable ultrathin SiNx membrane are needed.

With self-designed electrochemical liquid cell utilized, we can directly capture the dynamic electrochemical lithiation and delithiation of electrode in a commercial LiPF₆/EC/DEC electrolyte, such as LiF nanocrystal formation, lithium metal dendritic growth, electrolyte decomposition, and solid-electrolyte interface (SEI) formation. Combining with other in-situ techniques, such as in-situ XAS, XRD and Raman, etc, the underlying lithium intercalation mechanism in TMDs were further investigated, which render us a comprehensive understanding of the intrinsic correlation between the intercalation process and TMDs.

References:


9:00 AM *CH02.06.03

**In Situ Study of Electrochemical Solid-Liquid Interfaces using Liquid Cell TEM combining with other Advanced EM Techniques**

Haimei Zheng
Lawrence Berkeley National Laboratory, United States

Electrochemical solid-liquid interfaces play a key role in various electrochemical processes relevant to electrocatalysis, batteries, and supercapacitors. The electron and mass transport at the electrochemical interfaces may result in structural modifications that significantly influence the reaction pathways.
Solid oxide fuel cells (SOFC) are a class of solid-state electrochemical conversion devices that produce electricity directly by oxidizing a fuel gas. They consist in an anode-cathode duet separated by a solid electrolyte, i.e., a material conducting oxygen ions. The anode is fed with hydrogen or other fuels whereas the cathode is in contact with air, meaning oxygen. Overall, a SOFC operates thanks to the combined action of two external stimuli: a gaseous environment and temperature. Owing to the recent advances in solid oxide fuel cells (SOFC), we used a single chamber configuration to trigger the operation the cell: the anode and cathode were exposed simultaneously to the oxidizing and reducing gases. Due to a difference in the catalytic activity between the electrodes, \( \Delta \)O2 should reduce at the cathode, while \( \Delta \)H2 should oxidize at the anode, thus leading to a voltage difference between the two terminals.
Materials which are critical for the creation of new technologies to tackle global problems such as climate change are often highly complex, multifarious, and difficult to characterise using standardised techniques. This is particularly the case for electrochemical systems which often contain liquid-solid or liquid-liquid interfaces involving low atomic weight, and mobile elements such as hydrogen, carbon, or lithium. These elements are notoriously challenging to quantitatively characterise in their state of interest. It is essential to gain understandings of the phase, chemistry, and morphology of these systems at multiple length scales to better understand what controls their behaviour and limits their performance. This understanding at fundamental length scales is currently limited due to a lack of high-resolution characterisation techniques which are compatible with both the liquid and solid components of the interface and those which are capable of capturing a dynamic system in its exact state of interest. This lack of understanding has ultimately limited the performance and future development of many liquid-based systems using fundamental atomic-level insights. This has crucially led to understandings of various phenomena within battery research such as dendrite growth and solid-electrolyte (SEI) interface formation remaining elusive from a fundamental perspective.

Liquid microscopy techniques have shown the greatest promise in capturing dynamic nanoscale liquid-based systems in their exact state of interest through techniques such as liquid cell transmission electron microscopy (LCTEM). LCTEM is capable of capturing solution phase static and dynamic processes at high temporal and spatial resolutions, allowing for dynamic nanoscale imaging of various processes in real-time. LCTEM has been used to probe electrochemical processes using unique cell setups allowing for electrical biasing of electrodes within the cell as an electrolytic solution is flowing. While this setup does give unique nanoscale insights into these processes, key problems with respect to spatial resolution and beam-induced effects hinder the necessary sub-nanometre spatial resolution needed to resolve these complex dynamic liquid-based electrochemical systems, particularly those containing light elements. While various strategies have been employed to overcome these problems through state-of-the-art dose limitation techniques and alternative liquid cell setups involving 2D materials, the necessary resolutions have not been achieved under in operando conditions.

The work presented here provides an alternative approach that seeks to combine dynamic liquid microscopy techniques with high-resolution cryogenic microscopy techniques. The emerging field of cryogenic microscopy for material science has been proven capable of capturing a solid-liquid interface in its state of interest through techniques such as cryogenic STEM and cryogenic atom probe tomography (APT). Cryo APT can provide 3D reconstructive reconstructions of frozen nanoscale volumes with sub-nanometre spatial resolutions and has a chemical sensitivity of ppm for all elements including hydrogen, lithium, and carbon. Cryogenic microscopy techniques are however only capable of offering a snapshot of a particular system when a full dynamic understanding is required. This makes dynamic liquid microscopy techniques and high-resolution cryogenic microscopy techniques extremely complimentary.

This work has successfully combined operando LCTEM with cryogenic APT through the use of a cryogenic FIB/SEM, vacuum cryo transfer module technology (VCTM), and an inert glovebox. The combination of these distinct microscopy techniques has allowed for dynamic sub-nanometre understandings of various phenomena within nanoscale electrochemical systems such as dendrite growth as well as SEI growth and formation. This presentation will discuss the workflow needed to realise this combination and the results produced thus far.

Liquid spectroscopy characterisation of initial stages of the SEI layer formation at the Amorphous Si/Electrolyte Interface Andrew Dopilka,1 Jonathan M. Larson2,3 and Robert Kostekci1, Lawrence Berkeley National Laboratory, United States; 2Baylor University, United States

The solid electrolyte interphase (SEI) layer is a crucial component in the function and lifetime of Li-ion batteries; however, the nanoscale mechanism of its growth and evolution are often elusive due to the difficulty in characterising its structure under in situ conditions. Recently, our group has been utilizing nano-FTIR spectroscopy to investigate the structure and composition of battery interfaces with nanometer scale chemical resolution in a nondestructive manner. For instance, this technique was used to probe the graphene/polymer electrolyte interface in situ as well as the liquid/graphene interface thus allowing opportunities to characterize the electrical double layer. The nano-FTIR technique is implemented within an atomic force microscope using a metallically coated tip. By illuminating the tip/sample interface with a broadband infrared laser, plasmonic enhancement occurs at the apex of metallic tip inducing a nanoscopic near-field interaction with the sample. This near-field interaction couples with the infrared active vibrational modes of the sample and creates a change in the amplitude and phase of the backscattered infrared light which can be detected and then separated from the far-field signal with lock-in amplification at the tapping amplitude of the probe. The result is nanoscale, broadband infrared reflection and absorption of the sample with a probing area on the order of the tip radius (~20 nm), far beyond the diffraction limit of conventional infrared microscopy. In this presentation, we will discuss how nano-FTIR spectroscopy is used to characterize and observe the initial formation of the SEI layer at the interface between an amorphous Si surface and a carbonate electrolyte. By fabricating a 25 μm thick, free-standing amorphous Si film and encapsulating electrolyte with this thin layer, the Si can act as a window for the infrared light as well as an electrode to apply potential to the surface and induce electrolyte decomposition. Because of the nanometer scale spatial resolution and sensitivity to the electrolyte components, we observe subtle nanoscale heterogeneities in the electrolyte composition at the interface prior to the polarization of the Si electrode. After polarization of the cell to 0.5 V vs Li/Li⁺, we observe that LiP₆O₁⁶ reacts to form LiF at the surface of the Si and find further inhomogeneity in the formed layer with spatial dependent measurements. Based on the technique’s high chemical sensitivity, spatial resolution, and nondestructive nature, in situ nano-FTIR spectroscopy is anticipated to be an important tool to unravel the elusive nanoscale formation and growth mechanisms of the SEI layer.

This research was supported by the US Department of Energy (DOE)’s Vehicle Technologies Office under the Silicon Consortium Project directed by Brian Cunningham and managed by Anthony Burrell. The work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. This research used resources of the Advanced Light Source from beamlines 2.4, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

References


SESSION CH02.07: Investigation of Energy Storage Materials via Advanced In Situ/Cryogenic Electron Microscopy II
Session Chairs: Qianqian Li and Yaobin Xu
Thursday Afternoon, April 25, 2024
Room 440, Level 4, Summit

1:30 PM CH02.07.01 Microscopic View of Carbon Dioxide Adsorption in Amine-Decorated Porous Silicates for Direct Air Capture Wei-Chang David Yang, Marcus J. Carter, John R. Hoffman, Avery E. Baumann, Christopher M. Stafford and Remu Sharma, National Institute of Standards and Technology, United States

Organic-inorganic hybrid sorbents, based on mesoporous silicates and polymers, are a leading candidate for CO₂ capture under ambient pressure, which takes advantage of the high surface area of the silicates. [1]. An impregnation process allows active functional groups, such as polymer-based alkyl amines, to decorate the internal surface of mesoporous silicates and improve the adsorption-desorption kinetics at a reduced energy expense [2]. The mesopore surface was shown to interact with aqueous polyethyleneimine (PEI) to create the amine-modified sites for CO₂ adsorption [3]. However, the beam-sensitive specimen has limited electron microscopy in measuring these adsorption sites’ structure and chemistry within the nanometer-sized mesopores [4]. In this work, we adopted a new approach that combines in situ cryogenic scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) in an environmental transmission electron microscope (ETEM) to probe the interactions among CO₂, PEI, and mesoporous silicates.

The ETEM is equipped with a monochromated electron source to achieve an EELS energy resolution of up to 80 meV at 80 kV and a custom-built optical spectroscopy system to measure Raman shifts from a ten-micrometer-in-diameter area centered around the electron-beam location [5]. The amine-modified silicates were prepared by impregnating about 60 wt.% of PEI with a molecular weight of 800 g/mol into pristine silicates (e.g., MCM-41). A liquid-nitrogen-cooled holder was used to freeze the amine-modified sample in the ETEM and, therefore, mitigated electron beam damages as monitored with the spatially correlated Raman spectra. We used in situ EELS hyperspectral imaging to benchmark the mesopore surface’s interaction with CO₂ either with or without PEI impregnation. For the pristine MCM-41 mesopores, we obtained carbon K-edge maps based on the distinct π* peak at ≈ 290 eV to show physiosorption in a CO₂

CH02.07.06
3:15 PM
2:45 PM BREAK

We show here that in situ cryogenic STEM-EELS enables the direct observation of CO2 chemisorption and the ability to benchmark the properties and performance of PEI-decorated MCM-41 at the nanoscale. We continue pushing the frontier of understanding the dynamic structure and chemistry in a broad range of beam-sensitive materials with our new approach to elucidate the fundamental principle that leverages adsorption sites for new direct air capture technologies.

References:


1:45 PM *CH02.07.02
Autonomous Characterization for Investigating Cathode Active Materials and Solid-Solid/Solid-Liquid Interfaces in Energy Storage Devices Hualin Xin, Chunyang Wang, Peichao Zou and Yubin He; University of California, Irvine, United States

The characterization of complex energy materials requires detailed structural and functional analysis across multiple length and time scales. While in-situ and operando transmission electron microscopy (TEM) provide dynamic information [1], they can be lacking in resolution and sensitivity to some degree, particularly when studying cathode active materials and solid-solid or solid-liquid interfaces [2-4]. Cryogenic electron microscopy (cryoEM) has successfully filled this gap as a 'freeze-the-moment' technique, allowing for the imaging of dose-sensitive interfaces in a protected environment. CryoEM is particularly well-suited for investigating solid-solid and solid-liquid interfaces in energy materials, where these interfaces play critical roles in determining material properties and performance [4]. By combining cryoEM with an autonomous characterization system, we can overcome the limitations of human operators and improve sensitivity and resolution for these interfaces. This approach has the potential to revolutionize basic energy research, enabling comprehensive investigations of complex materials at multiple length and time scales [5].

References:

[1]s-Tension-Induced Cavitation in Li Metal Stripping, C. Wang, R. Lin, Y. He, P. Zou, K. Kissilgers, Q. He, J. Li, HL Xin, Advanced Materials, (2022)
[5] Supported by the Department of Energy under award no. DE-SC0021204 and the startup funding of HLX.

2:15 PM *CH02.07.03
Real-Space Visualization of Frequency-Dependent Anisotropy of Atomic Vibrations Xingshu Yan1, Paul Zeiger2, Jan Rusz2 and Xiaoqing Pan1,3; 1University of California, Irvine, United States; 2Uppsala University, Sweden; 3University of California, United States

Advancements in transmission electron microscopy (TEM) have revolutionized the study of the interfaces and nanosstructures. Innovations like aberration correctors, pixellated direct electron detectors, and monochromators have enabled atomic-resolution scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS), facilitating investigations into local structure, properties, and dynamic behaviors. Using a space-and-angle-resolved vibrational EELS technique, we have recently observed red shifts and intensity changes in acoustic vibration modes near a single stacking fault in cubic silicon carbide, and nanoscale composition-induced red shifts in Si optical modes in SiGe quantum dots. We also developed a method for differentially mapping phonon momenta revealing the interplay between diffuse and specular reflection. In this talk, I present a novel approach, employing dark-field, monochromated electron energy-loss spectroscopy for momentum-selective vibrational spectroscopy. This technique allows us to map phonon polarization vectors. When applied to centrosymmetric cubic-phase strontium titanate, we discover two types of oxygen atoms with contrasting vibrational anisotropies below and above 60 meV, based on mean-squared dependent thermal ellipsoids provide insights into the thermal and optical behaviors associated with acoustic and optical phonons. The eigenvectors of the density matrix are confirmed by mean-squared displacement analysis. This technique enables the visualization of eigenvectors at multiple scales, and the principle of the use of wavefunction at the nanoscale. We continue pushing the frontier of understanding the dynamic structure and chemistry in a broad range of beam-sensitive materials with our new approach to elucidate the fundamental principle that leverages adsorption sites for new direct air capture technologies.

References:

8:30 AM CH02.08.01
Towards Artificially Intelligent Microscopy of Functional Materials Steven R. Sugarson; Pacific Northwest National Laboratory, United States

Artificial intelligence (AI) promises to reshape scientific inquiry and enable breakthrough discoveries in areas such as quantum computing, energy storage, and advanced manufacturing. While it is now possible to produce materials in almost limitless configurations, engineering of desirable functionality depends on precise control of structure and defects across scales. Complex synthesis pathways can lead to significant deviations from idealized structures, which occur at length and time scales that are challenging to probe experimentally and theoretically. Mastery of materials is therefore predicated on the ability to acquire and act on complex, heterogeneous, and fast-evolving microscopy data streams, a task uniquely suited to emerging AI and machine learning methods. Here I will discuss my research efforts to develop a new framework for materials discovery, leveraging embedded automation, domain-grounded analytics, and predictive control for human-like reasoning. I will show how AI is transforming the present and future of materials discovery and design, allowing us to rigorously manipulate matter for emerging technologies.

9:00 AM CH02.08.02
Elucidating Metal and Oxide Nanoparticle Surface Dynamics through In-Situ TEM and Artificial Intelligence Piyush B. Halai1, Mai Tan1, Adri Marcon2, Matan Leibovich2, Sreyas Mohan3, Yifan Wang4, Carlos Fernandez-Granda5 and Peter A. Crozier3; 1Arizona State University, United States; 2New York University, United States

Nanoparticle systems often show high degrees of instability which are strongly influenced by size and ambient environment. These dynamic structural changes modify material properties such as reactivity, phase changes and catalysis. Atomic-level surface dynamics may play a significant role in defining particle structures and functionalities but characterizing nanoparticle surface structures with high spatial and temporal resolution simultaneously has proven challenging. Transmission electron microscopy (TEM) is a key tool to visualize local atomic structure of nanoparticles. Ultrafast TEM can now achieve picosecond temporal resolution but is limited to a spatial resolution of about 2 nm. Fortunately, modern detectors now provide readout rates in excess of 1000 frames per second, offering the potential to investigate atomic-level structural evolutions with time resolutions down to a millisecond. However, in most situations, the need to limit electron dose rates results in high temporal resolution movies that are dominated by shot noise, which often obscures surface structural dynamics. In order to address this challenge, we propose a fully-supervised AI denoising framework, which enables recovery of atomic-resolution information from such data. The unsupervised deep video denoising framework [1] improves the signal-to-noise ratio (SNR) by a factor of 30 at a spatial resolution of 1 A and time resolution of 10 ms. For this investigation, we explore structural dynamics of metal and oxide nanoparticle particles under combinations of CO2 and O2 at temperatures up to 300°C. The enhanced time resolution reveals that supposedly stable, low-energy surfaces can display highly active dynamics, triggering nanoparticle instabilities resulting in rapid structural fluctuations. The new spatiotemporal capability enabled by the proposed framework dramatically enhances our ability to explore surface dynamics and the evolution of metastable states in nanoparticles at the atomic level, offering new insights into their functionality.

References
2. We gratefully acknowledge the support of the following NSF grants to ASU (OAC 1940263, 2104105, CBET 1604971, and DMR 1840844 and 1920335) and NYU (HDR-1940097 and OAC-2103936). The authors acknowledge HPC resources available through ASU, and NYU as well as the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University.

9:30 AM CH02.08.03
In-Situ Observations of Non-Classical Crystal Growth of Au Nanoparticles on Hematite Xiang Wang1, Sichuang Xue1, Xin Qi2, Duo Song1, Maria Sushko1, Xin Zhang1 and Kevin Rosso1; 1Pacific Northwest National Laboratory, United States; 2Dartmouth College, United States

A significant research gap exists regarding the comprehensive investigation of crystallization mechanisms and facet-dependent stability of atomically precise metal clusters on metal oxide nanoparticles. To address this gap, our study focuses on a detailed examination of the sintering process of gold (Au) on facet-controlled hematite (α-Fe2O3) [104] and [001] nanoparticles through in-situ TEM observation. Our findings reveal the existence of three distinct crystal growth pathways of Au on hematite: Ostwald ripening, particle coalescence, and disordered intermediate-phase-mediated growth, where particle coalescence plays a dominant role in the sintering process. Furthermore, analysis of Au crystal growth kinetics on different hematite facets highlights the important influence of interfacial structure on the process, where hematite [001] stabilizes Au nanoparticles and suppresses their sintering more effectively than [104] facets. First-principles density functional theory calculations and atomic molecular dynamics simulations with enhanced sampling provide valuable support for the crystal growth pathway selection of Au nanoparticles on hematite. Our research significantly contributes to the understanding of metal crystallization on hematite surfaces and offers essential guidelines for selecting hematite supports for heterogeneous catalysts.

9:45 AM CH02.08.04
Interface Strains in 1D and 2D Si/Ge Structures for Quantum Computing Alicja Ruiz-Caridad1, Arianna Nigro1, Nicolas Forrer1 and Ilaria Zardo1,2; 1Universität Basel, Switzerland; 2SNI, Switzerland

During the last decade great efforts were put in the development of materials for quantum computing for its outstanding properties such as high speed, large store capacity and low power consumption [1]. Silicon is the preferred platform for microelectronics infrastructures due to its scalability, low economic costs, harmless for the environment, established fabrication processes and easy implementation of advanced engineering techniques [2,3]. Moreover, silicon is a good quantum material due to its long coherence time of spins of localized electrons and efficient controllability [4]. Germanium is a semiconductor material compatible with silicon. Material engineering of Si-Ge in form of epitaxial planar heterostructures or nanowires lead to enhanced mobility properties for quantum purposes. Despite, strains arising from the 4% mismatch between Ge and Si lattice parameter create defects, these defects hinder mobility. With the purpose to achieve higher mobility, scattering must be minimized by diminishing strains and interface roughness. In this regard, an effective tool to evaluate strains and interface roughness is electron microscopy combined with Raman spectroscopy which allows structural and chemical characterization of samples at the nanoscale. In this work, we grow by chemical vapor deposition (CVD) 2D and 1D structures: (i) planar heterostructure’s composed with variable percentage of Si/Ge barrier’s and a Ge QW; and (ii) Ge-Si core-shell nanowires for quantum computing purposes. In a first step we chemically and structurally localized the Ge and Si by energy-dispersive X-ray (EDX) spectroscopy and scanning transmission electron microscopy (STEM) techniques. Finally, we aim to study strain of the Ge QW and core-shell interfaces by means of geometric phase analysis (GPA) and µ-Raman spectroscopy. High-resolution transmission electron microscope (HR-TEM) images of the samples were performed in a Jeol JEM F200 cFEG TEM/STEM to evaluate roughness of interfaces and defects. GPA is a microscopic technique by TEM based on the signal processing of HR-TEM images and its Fourier transform. For the µ-Raman measurements were performed at 633 nm wavelength in back scattering geometry with the help of a Horiba T64000 double monochromator and a liquid nitrogen-cooled CCD detector. The combination of both methods permits the control, calculation and mapping of strains in different directions (rotation θx, θy, θz and θz) at high precision. By engineering the core-shell diameter ratio in 1D structures and Si/Ge composition of the barriers and Ge QW thicknesses in 2D structures, we proved and measured tensile/compressive strains in the interfaces between Ge QW and SiGe barriers and between core and shell NWs making our material suitable for integration in Si platforms for quantum computing applications.

References

10:00 AM BREAK

10:30 AM CH02.08.05
Advanced In-Situ Electron Microscopy for Energy and Quantum Materials Yimai Zhu; Brookhaven National Laboratory, United States

In this presentation, I will give an overview of our recent work on advanced in-situ microscopy characterization of energy and quantum materials. I will focus on the correlation of electrons, spin and lattice and their degrees of freedom as well as the critical roles of heterogeneity, interfaces, and disorder under external electric, magnetic and photonic excitations to reveal material's response. For response, I will show our cryogenic microscopy study of atomically resolved imaging and electron energy-loss spectroscopy to understand the interface-enhanced superconductivity and of Lorentz phase microscopy to explore the intriguing transformations among various topological chiral spin states including skyrmions under applied electromagnetic fields. Studying spin wave dynamics in nanoscale magnetic architecture under microwave excitation and Li-ion transport mechanisms of battery materials with ionic liquid in operando will also be presented.
Investigation of Dislocation-Controlled Domain Nucleation and Domain-Wall Pinning in Single-Crystal \textit{BaTiO}_3 by Multi-Stimuli MEMS-Based \textit{In Situ} TEM Tianhu Jian\textsuperscript{1}, Fangping Zhuo\textsuperscript{1}, Oscar Recalde\textsuperscript{3}, Yevheniy Pivak\textsuperscript{2} and Leopoldo Molina-Luna\textsuperscript{1}; \textsuperscript{1}TU Darmstadt, Germany; \textsuperscript{2}DENSolutions, Netherlands

Engineering domain walls at the nanoscale to influence macroscopic functional properties presents significant potential in electromechanics and electronics. This potential is particularly apparent in introducing topological defects into functional materials, highlighting the broad possibilities in this area. However, our comprehensive understanding of defect-mediated domain nucleation and domain wall mobility remains limited.

In this work, we achieved well-aligned dislocations with [100]<100> slip systems oriented in the [001] out-of-plane direction in single-crystal \textit{BaTiO}_3. This was accomplished through high-temperature uniaxial compression on a notched sample. Utilizing MEMS-based \textit{in situ} heating and cryo scanning/transmission electron microscopy (STEM), we were able to observe the dislocation-mediated domain nucleation and dynamic interactions between domain walls and these topological defects. These observations spanned a wide temperature range, from -175 °C to 200 °C, covering all phases of \textit{BaTiO}_3 from rhombohedral to cubic, offering high-resolution insights into the electro-mechanical interactions within this ferroelectric material. Furthermore, we explore the direct manipulation of the domain wall motion using \textit{in situ} biasing TEM. Under various stimuli, we observed the pinning of ferroelastic domain walls by these imprinted dislocations, attributed to the stress fields from the dislocations.

Our findings not only deepen the understanding of domain wall engineering in ferroelectric materials but also introduce a novel approach suitable for both advanced nanoelectronics and bulk applications across various temperatures.

Facilitating \textit{In Situ} 4D STEM with Advances in Software for Ultrafast Direct Detectors Barnaby D. Levin, Aziz Aitouchen and Benjamin Bannes; Direct Electron LP, United States

Four-dimensional scanning transmission electron microscopy (4D STEM) involves imaging a diffraction electron beam from a pixellated detector at each probe position of a STEM scan. The resulting information-rich datasets allow multiple types of analyses of a specimen, including high-resolution structural visualization, and mapping of crystal grain structure, molecular orientation, strain, electric and magnetic fields, and more [1]. Typically, 4D STEM involves recording large (several Gigabytes to several Terabytes) 4D datasets to disk to be analyzed with post-acquisition software such as LibetEM [2], py4DSTEM [3], or custom written code. Post-acquisition analysis enables a range of complex data analysis techniques to be applied to the data, but the efficiency of 4D STEM experiments can be severely impacted by the substantial time needed to go from data acquisition to data visualization.

Lack of real-time visualization poses challenges for both main data acquisition, and for the development of automated 4D STEM workflows. However, with ultrafast direct detectors, such as the Celeritas Xs camera, able to acquire data at rates approaching 5 Gigabytes per second, developing real-time 4D STEM analysis software involves its own significant challenges. These challenges are compounded when considering \textit{in situ} 4D STEM, (sometimes referred to as 5D STEM), where the goal is not only to record one large 4D dataset, but multiple large 4D datasets over a period of time so that dynamic processes such as changes in strain, crystal structure, or electric fields in a specimen can be observed [4].

Here, we present a new 4D STEM software platform that aims to address these challenges by leveraging GPU processing for real-time virtual STEM image generation during repeated 4D STEM acquisition. The software is compatible with Direct Electron’s Celeritas Xs, Celeritas, DE-16, DirectView2 and DE-64 cameras, as well as the DE-FreeScan scan generator, and allows the user to stream a series of full 4D STEM datasets to disk, even whilst simultaneously generating a live-view of up to four different types of virtual STEM image. In addition to viewing virtual images and camera frames in the software’s native interface, the system can be controlled via an API, allowing for integration into 3rd-party software, as well as custom software for microscope automation.

Further developments are ongoing to augment this software platform with additional features with the goal of making 4D STEM and \textit{in situ} 4D STEM more accessible techniques for electron microscopists to perform.

References:

Recent Developments of High Energy Resolution X-Ray Spectroscopic Methods for Energy Materials at NSLS-II Denis Leschev and Eli Stavitski; Brookhaven National Laboratory, United States

X-ray absorption spectroscopy (XAS), first used to applied in the field of energy materials, such as catalysts, over 50 years ago, has evolved into an indispensable tool in the arsenal of characterization techniques. XAS is element-specific method which compatible with a variety of sample environments, enabling in situ and operando experiments. An extension of XAS spectroscopy, high energy resolution (HR) X-ray spectroscopy, a collection of techniques which resolves the energy of the fluorescence photons with high accuracy, opened new opportunities in the field [1]. Among these methods is a high-energy resolution fluorescence detection (HERFD) XAS. XAS allows to overcome the limitations of traditional XAS by selectively detecting fluorescence photon within narrow energy band. Another is Valence-to-Core X-ray Emission Spectroscopy (VtC XES) which probes electronic states in the valence band, making it a far more sensitive to subtle electronic changes than the traditional Extended X-ray Absorption Fine Structure (EXAFS). In this contribution we review recent innovations at the National Synchrotron Light Source II (NSLS-II) which can enable applications of HR XAS to energy-relevant systems as well as several examples to demonstrate the advantages of these techniques.

X-ray spectroscopy is a widely used technique in materials science for the study of electronic, magnetic, and structural properties of materials. It involves the absorption of X-rays by a material, which results in the excitation of electrons from inner to outer shells. The energy of the emitted X-rays is characteristic of the material and can be used to determine the electronic structure and chemical composition of the sample.

Recently, there has been a significant increase in the use of high energy resolution X-ray spectroscopy (HERFD-XAS) for studying electronic and magnetic properties of materials. HERFD-XAS allows for the measurement of the energy resolution of the fluorescence photons, which can range from 1 to 100 eV, depending on the technique used. This high energy resolution enables the separation of overlapping absorption edges and the study of subtle electronic changes in materials.

One of the most widely used HERFD-XAS techniques is the use of resonant X-ray absorption fine structure (RXAFS) spectroscopy. RXAFS is a technique that allows for the study of the local electronic structure of materials, such as catalysts, semiconductors, and magnetic materials. It involves the absorption of X-rays by a material, which results in the excitation of electrons from inner to outer shells. The energy of the emitted X-rays is characteristic of the material and can be used to determine the electronic structure and chemical composition of the sample.

Another technique that has gained popularity in recent years is the use of resonant X-ray absorption fine structure (RXAFS) spectroscopy. RXAFS is a technique that allows for the study of the local electronic structure of materials, such as catalysts, semiconductors, and magnetic materials. It involves the absorption of X-rays by a material, which results in the excitation of electrons from inner to outer shells. The energy of the emitted X-rays is characteristic of the material and can be used to determine the electronic structure and chemical composition of the sample.

The use of HERFD-XAS techniques has enabled the study of a wide range of materials, including catalysts, semiconductors, and magnetic materials. The high energy resolution of these techniques allows for the separation of overlapping absorption edges and the study of subtle electronic changes in materials. This has led to a better understanding of the electronic and magnetic properties of materials and has opened up new possibilities for the development of new materials with desired properties.

In addition to the use of HERFD-XAS techniques, there has also been an increase in the use of resonant X-ray absorption fine structure (RXAFS) spectroscopy. RXAFS is a technique that allows for the study of the local electronic structure of materials, such as catalysts, semiconductors, and magnetic materials. It involves the absorption of X-rays by a material, which results in the excitation of electrons from inner to outer shells. The energy of the emitted X-rays is characteristic of the material and can be used to determine the electronic structure and chemical composition of the sample.

There has also been an increase in the use of resonant X-ray absorption fine structure (RXAFS) spectroscopy. RXAFS is a technique that allows for the study of the local electronic structure of materials, such as catalysts, semiconductors, and magnetic materials. It involves the absorption of X-rays by a material, which results in the excitation of electrons from inner to outer shells. The energy of the emitted X-rays is characteristic of the material and can be used to determine the electronic structure and chemical composition of the sample.

In summary, there has been a significant increase in the use of HERFD-XAS techniques in recent years, with new applications in materials science and catalysis. These techniques enable the study of subtle electronic changes in materials and have led to a better understanding of the electronic and magnetic properties of materials. The use of HERFD-XAS techniques is expected to continue to grow in the future, with new applications in materials science and catalysis.

The rapid development of in situ transmission electron microscopy (TEM) has become possible due to advancements of the functionalized microelectromechanical systems (MEMS)-based sample carriers. Nowadays, there exists a great variety of MEMS chips that enable the application of an individual stimulus like thermal, electric, gas, liquid, force, etc. or, usually, a combination of two stimuli. Specifically, multi thermal and electric stimuli have been extensively used to study electronic and energy materials and devices like ferroelectrics, magnetic materials, solid state batteries, thermoelectric, memristors, solar cells and many more.

The study of structure and electrical properties of nano-electronic materials and devices is mainly performed in vacuum. This, however, doesn’t represent real-life working conditions as the presence of oxygen might lead to different behaviour and properties of materials. An environmental TEM can be used to perform an in situ heating and biasing experiments in an atmosphere, but the gas pressure is limited to roughly 20 mbar which still possess a challenge.

In this work we present the development of a new multi-stimuli environmental TEM sample holder. The holder allows the application of thermal and electrical stimuli in ambient environmental conditions. This is achieved through a newly designed dual chip environmental cell with an increased number of contacts. Additional electrodes on the chip are used to prepare a FIB lamella and to characterize the electrical performance of the sample either in 2- or 4-contact mode. Using a newly developed FIB sample preparation procedure, it is possible to prepare contamination-free samples on gas, heating and biasing chips with no electrical short circuits and minimized leakage currents. This development represents a significant step forward towards the realization of real operational conditions inside the TEM offering the potential to further explore and deepen understand of the real properties of nano-electronic devices and energy related materials.
Investigation of Amorphous Silicon Nanoparticles dispersed in Silicon Nitride Passivation Layer for Semiconductor Industry
Filippo Sabatini1,2, 1Politecnico di Milano, Italy, 2ST Microelectronics, Italy

During the formation process of a typical integrated circuit (IC), a passivation layer is deposited to protect the internal semiconductor device after the metallization steps. These passivation layers are typically formed by oxide or nitride layers, most of the time deposited by plasma enhanced chemical vapor deposition (PECVD). As part of my PhD research, in collaboration between Politecnico di Milano and ST Microelectronics, I had to perform extensive characterization of different types of silicon nitride (SiN) in order to optimize its adhesion with an epoxy resin deposited on top of it. During these analysis, I detected the presence of amorphous silicon clusters dispersed within the nitride matrix through the presence of strong photoluminescence (PL) effects observed by Raman spectroscopy characterizations. Photoluminescence effects generally originate from the presence of defects or inhomogeneities of such size as to generate energy quantization. In both cases, electrons in the material, excited by the Raman laser beam, occupy energy levels intermediate to the energy gap and subsequently decay emitting photons that result in the formation of very intense bands in the Raman spectrum, called photoluminescence bands. This phenomenon was most pronounced in SiN samples with higher silicon overstoichiometry, which was intentional by company recipe and confirmed by XRD analysis. The silicon overstoichiometry thus led to spontaneous segregation of amorphous silicon into nanoparticles dispersed in the silicon nitride matrix and this phenomenon is almost nonexistent in samples with stoichiometries closer to equilibrium (%At Si/N equal to 0.75). To corroborate the assumptions made from the photoluminescence phenomenon, it was possible to directly observe the nanoparticles by TEM microscopy in some of the characterized samples.

The presence of these nanoparticles is not only interesting from an academic point of view, but could also have an interesting application aspect: one of the major criticalities of passivation layers is their high fragility, and the presence of inhomogeneous agglomerates could lead to an increase in the toughness of the material due to crack deflection phenomena, which have been studied for years in the field of composite materials. This effect occurs when the crack sliding is delayed by the presence of areas with a different thermal expansion index from that of the matrix: at the interface between these areas occurs the formation of compressive or tensile stress fields which attract or repel the crack tip, forcing it to deflect its path and thus increasing the energy required to slide (hence the toughness of the material). The phenomenon of crack deflection is generally observed in composite materials in which the inhomogeneity has a significant size, comparable to or larger than that of the crack tip. In the case of “Silicon Rich” silicon nitride (the sample with high silicon overstoichiometry), the nanoparticles observed are too small in size to make an effective contribution to the toughness of the material, and for this reason my project has now focused on finding deposition methods that can lead to the formation of larger amorphous silicon agglomerates.

Obtaining a material suitable for the role of a passivation layer that at the same time exhibits high toughness would be a great step forward in the semiconductor manufacturing industry and could solve several crack failure issues that usually form large blocking point in the development of new devices.

2:30 PM DISCUSSION TIME

AFM-SEM Correlative Microscopy Imaging for TEM Grid Mounted Samples
Stefano Spagna1, Kerim Ara1, Will Neils1, Christian H. Schwalb2, Hajo Frierichs2, Sebastian Seibert2, Lukas Stuhn2 and Marion Wolff2, 1Quantum Design Inc., United States; 2Quantum Design Microscopy GmbH, Germany

Microscopists utilizing Transmission Electron Microscopy (TEM) and TEM based Energy Electron Loss Spectroscopy (EELS) in their studies, frequently require the characterization of physical parameters such as heights and cross-sectional shapes of the examined sample1. Because of the typical sub-five nanometer thickness of membranes in TEM grids, Atomic Force Microscopy (AFM) measurements of grid mounted samples are presently challenging and time consuming. In this paper, we present the first truly integrated AFM and Scanning Electron Microscope (SEM) correlative workstation2, which allows imaging of samples directly on a TEM grid, utilizing these two techniques. The highly integrated and easy-to-use AFM-SEM microscopy workstation opens unprecedented measurement capabilities at the nanoscale in challenging geometries. AFM-SEM imaging of TEM grid mounted samples simplifies measurement workflows to yield a higher rate of data output. In addition to topography measurement, the platform allows easy expansion of capabilities, such as elemental analysis via Energy Dispersive X-ray Spectroscopy (EDS). The rich set of AFM modes (Contact, Tapping, Off-resonance, Conductive, Magnetic, and Electrostatic) allows the extraction of various physical properties from the sample.


SYMPOSIUM CH03

In Situ Characterization Methods for Nuclear Materials Applications
April 23 - April 26, 2024

Symposium Organizers
Aurélie Gentils, Université Paris-Saclay
Mercedes Hernandez Mayoral, CIEMAT
Djamel Kaoumi, North Carolina State University
Ryan Schoell, Sandia National Laboratories

* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION CH03.01: Equipment and In Situ Platforms for Characterization of Nuclear Materials I
Session Chairs: Mercedes Hernandez Mayoral and Djamel Kaoumi
Tuesday Morning, April 23, 2024
Room 441, Level 4, Summit
Mosaic is the new name of the platform involving the ion accelerators and the tools of chemical and structural characterization of materials located at JICLab [1]. This includes the JANNUS-Orsay experimental hall, which is in particular known from the community of nuclear materials for the diversity of ion beams that can be produced, as well as the possibilities of in situ characterization of the microstructural evolution of ion implanted or irradiated materials. In situ Transmission Electron Microscopy (TEM) with one or two ion beams can be performed in a large range of temperatures for studies on the nanostadic scale. The damage induced in a single crystal can also be studied through in situ Rutherford Backscattered Spectrometry in Channelling geometry (RBS-C) experiments thanks to the coupling of two ion accelerators. The possibilities, and some limitations, of these two in situ characterization methods currently available at Mosaic will be developed through a few examples of experiments performed on materials of interest for nuclear applications. The Mosaic platform is also in the process of completing its range of in situ tools for the characterization of irradiated materials with the acquisition of an X-ray diffractometer that will be modified for in situ measurements, and that will be available at the beginning of 2026. Examples of future possible experiments will be given along with the characteristics of this X-ray diffractometer.

The MosaIC technical staff, in particular C. Bachelet, C. Baumier, P. Benoît-Lamartine, J. Bourgeois, L. Delbecq, S. Hervé, C. Oriol, F. Pallier, and S. Picard, are gratefully acknowledged for their unfailing assistance during in situ experiments.


11:00 AM +CH03.01.02
Developing a Comprehensive In-Situ Irradiation Testing Facility at Tennessee Ion Beam Materials Laboratory Khalid Hattar and Miguel Crespillo; University of Tennessee, United States

Validating and refining simulation of reactor materials evolution for either next generation fission or fusion energy systems, as well as models to extend the lifetime of current reactor fleet would benefit from controlled experiments in coupled extreme environments. This presentation will highlight the expansion of Tennessee Ion Beam Materials Laboratory (TIBML) from a world-class ion Beam Analysis (IBA) facility based on a 3 MV Tandem Accelerator to a diverse facility designed to understand materials and device evolution in coupled extreme environments. To expand the irradiation environment, the facility will be adding a 300 keV NEC implanter, 20 kV and 5 kV Nonsequitur ion sources, a 30 kV Kimball Physics electron gun, and a Nd:YAG laser from Quantum-Ray with output energies up to 1 J at 1064 nm. The facility is already capable of performing ion irradiation and implantation experiments at temperatures ranging from 30 to 1473 K. In addition, the TIBML facility is developing capabilities to perform in-situ irradiation during photoluminescence, cathodoluminescence, ion beam induced luminescence, Raman, acoustic emission, IBA, nanomechanical testing, and Scanning Transmission Electron Microscopy (STEM). The latter will be done utilizing a highly modified JOEL 2100® that was installed in October 2019. The high tilt polepiece, additional electron beam condenser lens, and LaB6 filament were selected to optimize the characterization of radiation damage. In addition, the STEM was coupled with Nanomegas Automated Crystallographic Orientation Mapping (ACOM) and Theia scientific edge computing systems for machine learning to characterize the impact of radiation damage on phase, orientation, and grain boundary evolution, as well as the size distribution of internal matrix radiation damage, respectively. This presentation will highlight the current status of the TIBML facility development and the initial results of the coupled environment. Finally, this presentation will discuss the potential future opportunities to explore increasingly complex coupled environments in a controlled manner.

11:30 AM +CH03.01.03
Deployment and In-Reactor Testing of an Instrument for Real-Time Monitoring Thermal Conductivity Evolution of Nuclear Fuels Zilong Hua1, Caleb Picklesimer1, Austin Fleming1, David Harley1, Weiyoue Zhou1, Michael P. Short2 and David Carpenter2; 1Idaho National Laboratory, United States, 2Massachusetts Institute of Technology, United States

Thermal conductivity of nuclear fuels directly ties to the reactor safety and efficiency. Because of the microstructure defects generated and evolved in the extreme reactor environment, thermal conductivity of nuclear fuels reduces significantly during the reactor operation. Currently the experimental efforts on understanding such effects are primarily from the post-irradiation-examination (PIE) testing. However, an important type of phonon scatters, point defects, anneal at high temperature after the reactor shutdown and before PIE can be performed. In order to fill this technical gap, we developed an instrument that can perform real-time thermal conductivity measurements in reactor. Here we presented the latest testing results of this instrument in Massachusetts Institute of Technology Research Reactor (MITRR). The final objective is to provide the routine measurements of thermal conductivity of nuclear fuels and materials in reactor. It will make better understandings of the scattering mechanisms between defects and thermal carriers possible, and help predict the fuel performances in reactor.

SESSION CH03.02: Equipment and In Situ Platforms for Characterization of Nuclear Materials II
Session Chairs: Khalid Hattar, Mercedes Hernandez Mayoral and Djamal Kaouni
Tuesday Afternoon, April 23, 2024
Room 441, Level 4, Summit

1:30 PM +CH03.02.01
An In-Situ Platform for Studying Metal Films under Simultaneous Extreme Conditions in The SEM Benjamin K. Derby1, Eric Lang2, Trevor Clark2, Ryan Schoel2, Jon Baldwin3, Darrick Williams1, Michael McBride1, Khalid Hattar2 and Nan Li1; 1Los Alamos National Laboratory, United States; 2Sandia National Laboratories, United States

We report on a novel technique for the in-situ characterization of a sample exposed to ion irradiation in a corrosive medium. A sample chamber has been built that can expose a metal film to a corrosive liquid environment and placed into the environmental scanning electron microscope (SEM) in line with the ion beam accelerator located at the Center for Integrated Nanotechnologies’ (CINT) Ion Beam Laboratory (IBL) at Sandia National Laboratory. In this work, we expose an epitaxial Fe thin film grown on MgO to 6 MeV Fe ions while the sample surface is exposed to pure H2O, 0.1M NaCl, and 0.1M B4Na2O7 solutions. SEM imaging and post-mortem XEDS captured the complex oxide development on the surface over time. This experiment elucidates how the ion beam affected the complex oxide growth in the corrosive media, and how the surface oxide impacts further corrosion processes. This understanding will directly inform the development of new materials required for future nuclear energy sources.

2:00 PM +CH03.02.02
Towards Measuring Hydrogen Dynamics in Yttrium Hydride Moderators James Torres1,2, Alexander Long2, Dale T. Carver2, Sven C. Vogel2, Aditya Shrivastava2, Tyler Smith2, Caitlin Kohner2, Erik Luther2 and Holly Trellue2; 1Oak Ridge National Laboratory, United States; 2Los Alamos National Laboratory, United States

A compact, nuclear microreactor that utilizes low-enriched uranium fuel is a promising solution to meet US demands in remote and decentralized energy grids. Yttrium hydride (YH) is the candidate moderator material for the microreactor design, chosen based on its superior retention of hydrogen at high temperatures. Hydrogen diffusion properties in YH are highly sought after for computer model validation and reactor prototyping. To meet design objectives, the so-called compact dual-zone furnace was developed at the Los Alamos Neutron Science Center (LANSE) with the goal of characterizing hydrogen diffusion in YH samples as a function of applied temperature gradients. Herein, we share our recent progress in technique and hardware developments and provide initial results from recent concentration- and temperature-gradient measurements at LANSE-C.[1]

[1] LA-UR-22-22241

2:15 PM +CH03.02.03
Characterization of The Solid Electrolyte Interphase with Cryogenic Ion and Electron Microscopy Hyeongjun Koh, Eric Detsi and Eric A. Stach; University of Pennsylvania, United States

Characterizing the nanoscale structure and chemistry of energy storage materials is critical due to their significant impact on battery performance. However, conventional sample preparation methods required for high-resolution imaging often fundamentally alter reactive battery components. In this work, the authors employ cryogenic focused ion beam milling (FIB) in a plasma-focused ion beam/scanning electron microscope system to prepare sensitive lithium metal specimens, allowing them to assess potential ion beam damage. Cryogenic transmission electron microscopy reveals that while the lithium itself is not damaged during cryo-FIB milling, lithium oxide shells form around the sample in the instrument chamber, evidenced by diffraction data from thin lamellae prepared at different two thicknesses. Consulting the Ellingham diagram indicates that lithium can react with trace oxygen gas in the FIB/SEM chamber at cryogenic temperatures; notably, liquid oxygen exposure does not contribute to lithium oxidation here. This approach allowed the examination of Li metal batteries with vitrified liquid electrolytes and facilitated the discovery of an elusive solid-electrolyte interphase (SEI).
component, lithium fluoride. This has not been observed when using conventional sample preparation techniques involving rinsing. Furthermore, diffraction data reveals the presence of short-range order at different regions in the SEI structures, presumably influencing and controlling lithium metal growth. Overall, these results highlight the valuable role cryogenic lift-out and cryogenic scanning transmission electron microscopy can play in enabling nano- to atomic-scale characterization of energy storage devices containing reactive materials or solid-liquid interfaces.

2:45 PM BREAK

SESSION CH03.03: In Situ Irradiation and TEM Characterization I
Session Chairs: Aurelie Gentils, Mercedes Hernandez Mayoral and Djamel Kaoumi
Tuesday Afternoon, April 23, 2024
Room 441, Level 4, Summit

3:15 PM *CH03.03.01
Contribution of Raman Spectroscopy to The Understanding of Defect Formation Mechanisms Gaelle Gutierrez, Arthur Georgesco, Claire Onofri-Marroncle and Dominique Gosset; CEA, France

Ion accelerators have been used for decades to study radiation damage in nuclear materials, simulating their behavior in reactors. The diversity of irradiation conditions (ions, energy, fluence, temperature, etc.) is a major advantage of ion beams. This allows for systematic studies aimed at better understanding defect formation mechanisms and the resulting microstructural evolution. Additionally, the very short irradiation times and the handling of non-radioactive samples significantly reduce the cost and duration of experiments compared to reactor irradiations. The coupling of multiple ion beams, the use of heated/cooled sample holders, and the implementation of in situ characterization open the way for real-time observation of microstructure evolution under various extreme radiation conditions. Among these techniques, Raman spectroscopy provides a quick and non-destructive means to monitor vibrational mode evolution. Under irradiation, structural bands evolve, indicating the level of stress and the local structural disorder. Some bands may also disappear, providing information about the level of damage and the type of defects formed.

The JANNUs Saclay platform is equipped with a Raman spectrometer installed in the triple-beam irradiation chamber. This allows for in situ monitoring of vibrational modes when atomic displacements and/or ionizations and electronic excitations are generated within the structure. Studies have thus highlighted the use of Raman spectroscopy in characterizing amorphization mechanisms or phase changes occurring under irradiation [2-4]. In non-amorphizable systems, in situ measurements provide insights into damage kinetics related to the formation of point defects [5]. This paper will focus on several examples illustrating the use of ion beams coupled with Raman analyses to investigate the radiation resistance of current and future nuclear ceramic materials.

References

3:45 PM CH03.03.02
Uncovering Grain Boundary Metastability as a Response to Radiation in FCC and BCC Single Phase Compositionally Complex Alloys Anne Barnett, Emily Hopkins, Mitra L. Taheri and Michael Falk, Johns Hopkins University, United States

Compositionally complex alloys (CCAs) are promising for the future materials of extreme radiation environments, but nuances in unique defect formation and evolution properties have yet to be thoroughly understood. In comparison to their dilute and pure counterparts, both fcc and bcc complex alloys retain chemical order which increases the radiation tolerance due to a convoluted matrix defect bias. This bias profoundly influences grain boundary (GB) metastability under irradiation conditions, resulting in an increase in radiation tolerance with alloy complexity. A combined molecular dynamics and experimental in-situ study is performed to demonstrate GB metastability during point defect bombardment, highlighting the fundamental differences between fcc and bcc alloys in addition to environments with and without local chemical order.

4:00 PM CH03.03.03
Clarifying Phase Instabilities Induced by Irradiation in a FCC-Based FeNiCrMn HEA through In-Situ Irradiation Antoine Dartois1, Maylise Nastar1, Brigitte Décamp2, Anna Fraczkiewicz3 and Estelle Meslin1, 1Université Paris-Saclay, CEA, France; 2Université Paris-Saclay, France; 3MINES St-Etienne, France

Recent studies have highlighted the promising behavior of High Entropy Alloys (HEAs) under irradiation, exhibiting improved swelling resistance [1] and reduced radiation-induced segregation (RIS) [2]. For evident safety concern, they need to maintain high single-phase stability to ensure stable mechanical properties under operating conditions. In this context, our study focuses on the quaternary Fe37Ni34Cr16Mn13. Before irradiation, this high-purity alloy, annealed at 1473 K for 4 hours, is a single FCC phase. However, after heavy-ion irradiation within the JANNuS Saclay facility at 823 K up to 2 dpa, phase instability was detected by means of CTEM (Conventional transmission electron microscopy) and STEM/EDX (Scanning TEM/Energy dispersive X-rays) within a double-corrected Jeol Neo-ARM TEM.

It is well known that irradiation generates point defects – vacancies and self-interstitials – that subsequently agglomerate into dislocation loops, voids or precipitates [3]. Besides, net fluxes of point defects toward sinks lead to RIS potentially leading to radiation-induced precipitation (RIP) [4].

In the current study, phase instability is characterized by the precipitation of nanometer-sized Cr-Mn enriched precipitates. These intragranular precipitates have a spherical shape with an approximate diameter of 10 nm. Their crystallographic structure needs to be examined thoroughly. Considering previous analyses on similar alloys [5], a BCC phase could be expected. The matter balance between self-interstitial atoms (SIAs) and vacancies respectively stored into dislocation loops and precipitates tends to confirm the less dense BCC structure of the precipitates. We hence may expect these precipitates to result from a RIP mechanism explained by the elimination of irradiation-generated vacancies accommodating the volume mismatch between less dense precipitates and the matrix [3].

This phase instability is also correlated with a microstructural evolution. Indeed, both faulted and perfect dislocation loops are formed. According to atom probe tomography (APT) and STEM/EDX analysis, RIS occurs at these radiation-induced defects. Indeed, a strong Ni enrichment and Fe, Mn and Cr depletions, have been detected. An inverse Kirkendall model of atomic fluxes, mediated by vacancies and fitted on tracer diffusion coefficients of the well-known FeCoCrMnNi Cantor alloy, corroborates the identified RIS trend. We highlight a reduced Cr depletions, compared to conventional austenitic steels [6], potentially reducing the irradiation-assisted stress corrosion cracking (IASSC) phenomena.

In order to elucidate the precipitation mechanisms, microstructures exposed to several radiation doses have been compared. First, samples have been irradiated from 0.2 dpa to 2 dpa. Second, an analysis of the microstructure at increasing thicknesses has enabled us to compare various stages of irradiation progress. Indeed, point defects elimination on surfaces is stronger in thinner areas, where effective damage is therefore reduced, whereas this phenomenon is negligible in thicker areas, experiencing a stronger effective damage. On-axis axis STEM imaging shows the formation of a dislocation network, resulting from the interaction of perfect loops as well as a decrease of the density of both Frank loops and precipitates with increasing depth.

To further investigate the precipitation mechanisms, in-situ irradiations are essential. These will be conducted inside a TEM in November 2023 within the JANNuS-Orsay facilities, to track both the microstructural evolution as well as the precipitation using electron diffraction spots signal produced by the formation of Cr-Mn precipitates.

References
In recent times, High-Entropy Alloys (HEAs) or Multi Principal Elemental Alloys (MPEAs) have been attracting much attention as new structural materials for nuclear reactor in-core applications due to their structural stability and excellent mechanical properties. However, their microstructural behaviour under irradiation still requires special attention. Particularly, the impact of specific chemical elements on the irradiation response of the alloys still needs to be evidenced and is at the core of this NSF funded project. The current work compares the radiation behaviour of CrFeMnNi, Al_{0.3}CrFeMnNi and Al_{0.8}CrFeMnNi alloys. The alloys, which were prepared through Plasma Spark Sintering (SPS), were irradiated in-situ in a Transmission Electron Microscope (TEM) using 1 MeV Kr^{+} ions up to 10 dpa at room temperature (RT) and at 300 °C. Since the starting microstructure depends not only on the composition but also on the way of processing, thorough pre-irradiation characterization of all the three alloys was carried out using X-Ray Diffraction (XRD) and TEM which showed the formation of (BCC+CPC) phases in major proportion. Addition of Al resulted in an increase in the proportion of BCC phase along with the formation of NiAl based ordered phase. At RT, with increased irradiation dose, the phases with more uniformly distributed elemental composition showed the dynamic formation and annihilation of irradiation induced defects. However, the Cr-segregated phase in the (Al_{0.3}CrFeMnNi) alloy showed amorphization behaviour with increasing irradiation dose. At RT, the alloys did not show the formation of voids or Radiation induced Segregation (RIS). However, at 300 °C, the alloys showed the formation of voids at doses around ~5 dpa. Also, Ni segregation at the void/matrix interfaces has been observed in the Al_{0.8}CrFeMnNi alloy at 300 °C. Overall, the void formation was observed to depend on the local chemistry and temperature of irradiation. Additionally, irradiation at 300 °C also resulted in Radiation Induced Precipitation (RIP) in these alloys, the existence of which were confirmed through extensive post-irradiation TEM diffraction analysis, which showed low intensity crystalline spots and streaks around the major diffraction spots. The Cr-rich phase in Al_{0.8}CrFeMnNi alloy showed the formation of nano-crystalline features. The Ni-rich phase showed the formation of nano-crystalline features. The Ni-rich phase showed the formation of nano-crystalline features. The Ni-rich phase showed the formation of nano-crystalline features.

\[ \text{SESSION CH03.04: In Situ Irradiation and TEM Characterization II} \]

\[ \text{Session Chairs: Aurelie Gentils, Mercedes Hernandez Mayoral and Djamel Kaoumi} \]

\[ \text{Wednesday Morning, April 24, 2024} \]

\[ \text{Room 441, Level 4, Summit} \]

\[ \text{8:45 AM} \]

**CH03.04.01**

**Dislocation Loop Evolution in Ni-Based fcc Model Alloys by In-Situ Self-Ion Irradiation at High Temperatures**

\[ \text{Marie Lopez-Prost}^{1}, \text{Kan Ma}^{1,2}, \text{Brigitte Décamps}^{3}, \text{Liangzahao Huang}^{4}, \text{Maylise Nastar}^{5}, \text{M.A. Belgouz}^{6}, \text{Anna Fraczkiewicz}^{7}, \text{Robin Schaüblin}^{8}, \text{Philippe Vermaux}^{9} \text{and Frédéric Prima}^{10} \]

\[ \text{1Université Paris-Saclay, CEA, France; 2University of Birmingham, United Kingdom; 3CNRS, Université Paris-Saclay, France; 4Ecole Nationale des Mines de Saint Etienne, France; 5ETH Zürich, Switzerland; 6Sorbonne Université, France; 7ChimieParisTech, PSL Research University, CNRS, France} \]

Austenitic Stainless Steels (ASSs) are foreseen as cladding material for next generation reactors even though their swelling under irradiation will limit the fuel burnup. Solute elements, such as titanium and carbon, efficiently reduce this swelling but the mechanism is still ambiguous.

Here we focus on the effect of a progressive addition of titanium on the microstructure evolution of nickel at small irradiation dose and on the loop interaction during irradiation. Nickel is considered as a model alloy for ASSs (same crystallographic structure). Pure Ni and nickel alloyed with various percentages of titanium (xi ranging from 0.4% to 1.2% by mass), are in-situ irradiated at 450°C and 510°C within a Transmission Electron Microscope using the JANNuS-Orsay facility. The in-situ microstructural evolution and dislocation loop characteristics are finely analyzed in function of specimen composition and doses. We reveal a strong impact of micro-alloying on: microstructure: loop nature, growth rate, formation thickness, density, Burgers vector and mobility. A direct correlation of Frank loop morphology and nature is observed. Finally, a temperature-dependent critical Ti content for Frank loop nature is highlighted and discussed.

**9:15 AM**

**CH03.04.02**

**Investigation of Grain Growth in Nanocrystalline Oxide Thin Films during Irradiation and Heating using In-Situ TEM**

\[ \text{Dmitrii Kreto}^{1}, \text{Tiffany Kaspar}^{2}, \text{Benjamin K. Derby}^{3} \text{and Djamel Kaoumi}^{4} \]

\[ \text{1North Carolina State University, United States; 2Pacific Northwest National Laboratory, United States; 3Los Alamos National Laboratory, United States} \]

Grain growth, which occurs at elevated temperatures and under irradiation is manifested by an increase in the average grain size, a decrease in the number of grains, and a decrease in grain boundary area. Nanocrystalline metals having very small sizes and high GB densities are of interest to the nuclear materials community not only for their improved mechanical properties but also for their radiation resistance, since grain boundaries are effective sinks for radiation-induced defects, ultimately impacting the radiation tolerance of nanocrystalline materials against net defect accumulation. However, even if nanocrystalline metals present increased radiation tolerance at the nanoscale, irradiation-induced grain growth is responsible for grain enlargement and annihilation of these benefits. While the literature shows several studies on this particular topic of grain growth in nanocrystalline metals, very little focus was put on grain growth in nanocrystalline oxides, especially under irradiation. The scarce available literature focuses on fuel oxides. In this work, grain growth kinetics was studied in Fe_{2}O_{3}, Fe_{3}O_{4}, Cr_{2}O_{3} which are nanocrystalline oxides, especially under irradiation. The scarce available literature focuses on fuel oxides. In this work, grain growth kinetics was studied in Fe_{2}O_{3}, Fe_{3}O_{4}, Cr_{2}O_{3} which are nanocrystalline oxides, especially under irradiation. The scarce available literature focuses on fuel oxides.

Through real-time TEM/STEM imaging, we explore the intricate processes taking place within zirconium alloys, such as Excel alloy, Zr-2.5SnB and Zircaloy as they are subjected to ion irradiation. We observe and analyze the complicated changes in microstructure, including a-type and c-type dislocation formation, defect accumulation, and phase transformations. These microstructural changes have a direct bearing on the material's mechanical properties and dimensional stability, making this research crucial for the nuclear industry.

This presentation highlights the invaluable contribution of in-situ TEM techniques in providing real-time, atomic-scale observations of zirconium alloy behavior during irradiation, paving the way for enhanced material design and reactor safety.

**9:45 AM BREAK**

**CH03.04.03**

**Unveiling The Microstructural Evolution in Irradiated Zirconium Alloys Through In-Situ Transmission Electron Microscopy**

\[ \text{Zhongwen Yao; Queen's University, Canada} \]

Understanding the impact of irradiation on the microstructure of zirconium alloys is critical for ensuring the safety and reliability of nuclear reactors. In this presentation, we applied in-situ transmission electron microscopy (TEM) as a powerful tool to unravel the dynamic evolution of zirconium alloy microstructures during irradiation or after irradiation.

Through real-time TEM/STEM imaging, we explore the intricate processes taking place within zirconium alloys, such as Excel alloy, Zr-2.5SnB and Zircaloy as they are subjected to ion irradiation. We observe and analyze the complicated changes in microstructure, including a-type and c-type dislocation formation, defect accumulation, and phase transformations. These microstructural changes have a direct bearing on the material's mechanical properties and dimensional stability, making this research crucial for the nuclear industry.

This presentation highlights the invaluable contribution of in-situ TEM techniques in providing real-time, atomic-scale observations of zirconium alloy behavior during irradiation, paving the way for enhanced material design and reactor safety.

**10:45 AM**

**CH03.05.01**

**Real Time Monitoring of Defect Evolution and Relaxation by In-Situ Positron Annihilation Spectroscopy**

\[ \text{Farida Selim}^{1}, \text{Adric Jones}^{2}, \text{Thaighang Chung}^{2}, \text{Matthew Chancey}^{3}, \text{Riley Ferguson}^{3}, \text{Peter Hoesemann}^{4}, \text{Yongqiang Wang}^{5}\text{and Blas P. Uberuaga}^{1} \]

\[ \text{1Arizona State University, United States; 2Bowling Green State University, United States; 3Los Alamos National Laboratory, United States; 4UC Berkeley, United States} \]
In-situ measurements during irradiation are critical to monitor material response to irradiation in real time; several in-situ techniques with remarkable capabilities have been developed to address this and examine material structure, properties, and performance under extreme radiation environments. In-situ TEM has been particularly powerful in monitoring the microstructural changes and growth of cavities in real time during irradiation. However, revealing the mechanisms governing early formation of defects and their evolution in extreme environments requires measuring defects on all length scale from atomic- to meso-scale. Positron annihilation spectroscopy (PAS) is uniquely sensitive to atomic scale defects revealing their density and structure even in the very early stages of damage and has been shown to be an effective tool to probe vacancies and stresses in nuclear and structural materials [1,2].

Here we report the first in-situ PAS (iPAS) measurements during high energy ion irradiation. The measurements reveal that vacancies are formed and their number increases during collision cascades without change in structure or clustering. However, vacancies are shown to coarsen, and their structure substantially change during relaxation after ceasing irradiation. The trend is shown to dominate in the low irradiation regime and the defect density increases linearly with irradiation time up to 0.1 dpa. In higher regime above 1 dpa, vacancies are formed and coarsen during collision cascades. Further, iPAS during annealing reveals the various recovery stages of induced radiation and the defect type involved in each stage. Lastly, we will discuss how iPAS may shed the light on the mechanism behind some interesting phenomena such as radiation induced vacancy injection in multi-phase materials that we recently observed in Fe / FeO bilayers.

This work was funded as part of FUTURE (Fundamental Understanding of Transport Under Reactor Extremes), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences.


2:15 PM CH03.05.02
In situ Performance of Non-Volatile Memory under Mixed Radiation Environment Chaitanya Sharma and Juan Nino; University of Florida, United States

Nonvolatile memory technologies have paved the way for in-memory computing, eliminating the constant need to move data between storage and processing units. This reduces the von Neumann bottleneck and can significantly boost a system's effective floating operations per second (FLOPs). However, their performance evolution under irradiation from cosmic rays, solar storms, neutrons, and other secondary sources has not been extensively studied. To explore device degradation, we developed a testing apparatus at the University of Florida training reactor (UFTR) to perform in situ electronic measurements under varying gamma and neutron radiation profiles. The 6" diameter cylindrical setup fits inside one of the reactor beam ports and includes a Pelletier thermal controller coupled to a 4-terminal electrical microprobe with variable radiation shielding. To delineate different radiation beam environments, specifically gamma rays, thermal, epithermal, and fast neutron, shielding materials such as borated polyethylene, standard polyethylene, and lead are used. Here, we demonstrate the platform's effectiveness by examining self-directed channel (SDC) memories, ferroelectric capacitors (FeCAPs), and resistive random-access memory (ReRAM) devices both in volatile and non-volatile configurations (i.e., 1T-1R and 1R). The experiments were conducted within the temperature range of -30°C to 120°C across a range of reactor power levels from 1W to 10KW with a total flux of 2.035 x 10^8 particles/cm^2 at 100KW. We will further discuss radiation effects pertinent to various memory architectures, evaluating on device failure induced under radiation and total ionizing dose.

2:30 PM BREAK

3:30 PM CH03.05.04
Beam-On Effects during Irradiation of Nuclear Materials Michael P. Short; Massachusetts Institute of Technology, United States

In situ characterization methods for nuclear materials performance hold enormous promise for faster discovery of nuclear materials science, radiation effects, and down-selection of optimal alloys for nuclear power applications. Advancements in combining traditional irradiations and post-irradiation examination with new, rapid analysis tools promises, and will be shown in this talk, to hasten data throughput by up to 1000x compared to purely traditional methods. Particular emphasis on building robust inference models, whereby properties of ultimate interest are tightly correlated to those which are more readily measured by in situ techniques, will be made via illustrative examples of nuclear materials discovery, down-selection, and optimization. We specifically focus on utilizing in situ ion irradiation transient grating spectroscopy (ITGGS) for prediction of high-temperature superconductor performance during irradiation, rapidly exploring nuclear alloy compositions for fusion structural and functional materials, and sorting materials that resist to major degradation modes such as void swelling. Finally, we will present a call to collaboration and requests for input from the community, on how to best build robust and easy-to-use TGS systems to help others establish similar in situ capabilities of their own.

SESSION CH03.06: In Situ Electrochemical Methods
Session Chairs: Mercedes Hernandez Mayoral and Djamel Kaouni
Thursday Morning, April 25, 2024
Room 441, Level 4, Summit

8:30 AM CH03.06.01
Understanding Oxidation Mechanism using In Situ Analytical Transmission Electron Microscopy Eric Presta1, Giacomo Bertali2, Duc Nguyen-Manh1, Joven Lim1, Anicha Reuban3, Andrey Litovsky1 and Grace Burke4; 1UK Atomic Energy Authority, United Kingdom; 2University of Manchester, United Kingdom; 3Forschungszentrum Juelich, Germany; 4Idaho National Laboratory, United States

Environment-sensitive behaviour of materials encompasses a broad range of degradation phenomena in metals and alloys. The interaction of metallic materials with the environment is of fundamental importance in understanding a material's performance in "real world" applications. Of particular significance is the effect of liquid and/or gaseous environments on the material of interest. The ability to visualise the localised changes associated with oxidation in gaseous environments and dissolution reactions in liquids coupled with qualitative STEM-XED spectrum imaging and analysis is now providing unprecedented opportunities for real-time observations that can lead to improved mechanistic understanding of nanoscale oxidation, and localised dissolution/corrosion.

In this presentation, we will discuss the application of in situ gas microscopy to understand the oxidation behaviour of metallic materials using open cell and closed cell system. For the closed system, two 30 nm thick Sn electron transparent membranes are used to contain up to 1 bar atmospheric pressure from the vacuum of the TEM columns. We have applied the Protocips in situ platforms to examine gaseous environmental interactions in structural alloys such as Ni-base alloys (Alloy 600) and tungsten. The Protocips Atmospheric system interfaced with a FEI Titan G2 200 kV S/TEM equipped with X-FEG and Super X (4 SDDs) or a JEOL NeoARM 200kV wide gap pole piece cold FEG and Dual-EDS system has been successfully used in a variety of gaseous environments. Open cell experiments were performed on a Hitachi H-9500 TEM operating at 300 kV and fitted with an add-on gas injection system for windowless environmental conditions up to ~0.1 Pa at the sample.

Critical to any in situ experiment is the preparation of representative electron-transparent samples, so as to provide a valid link with bulk behaviour. Electron-transparent specimens were prepared using the hybrid method [1]. These specimens can then be attached to an Atmospheric heating chp with Pt. A series of examples will be discussed that are related to the detailed study of bulk material behaviour including localised oxidation reactions pertinent to stress corrosion cracking in Ni-base alloys as well as the study of oxidation of tungsten alloys. The successful experiments using the gas reaction cell system in a variety of H2-containing environments at elevated temperatures can be further refined to assess variables such as H2 and O2 partial pressures, and can also be used to assess localised reactions in 1 bar gas over a range of temperatures of interest and thus provide insight at the nanoscale about diffusion-induced grain boundary migration, internal oxidation, and the role of carbides in preferential oxidation. Similarly, S/TEM imaging and Electron energy loss spectroscopy (EELS) was used for ex situ and in situ study of the oxidation of self-passivating tungsten alloys using. Mapping the elemental distribution of W, Cr, Y at the nanoscale shows that Cr-rich grains undergoes Cr/W phase separation exhibiting characteristics of spinodal decomposition, which is in good agreement with first-principles modelling predictions. Similar Cr/W phase separation was observed at grain boundaries. The in situ (S/TEM) oxidation shows that the Cr-rich grain exhibiting Cr/W phase separation are oxidized first and formed a dense Cr oxide, providing a stable oxide layer. Additionally, in the vicinity of the yttria precipitates present at grain boundaries or grain triple junctions the oxide growth is reduced in the initial stage of oxidation. Inhomogeneity in the layer oxidation could lead to localised failure of the oxide layer, such as delamination of the protective oxide layer.

9:00 AM CH03.06.02
In Situ Sample Thickness Monitoring in Simultaneous Irradiation-Corrosion Experiments Franziska Schmidt1,2, Matthew Chancey1, Hyesim Kim1 and Yongqiang Wang2; 1Los Alamos National Laboratory, United States; 2University of California, Berkeley, United States

Irradiation-corrosion experiments have recently become a popular approach to studying the simultaneous effects of both extremes on materials. Each individual experiment requires extensive
To develop aging techniques, representative cement cylinders were aged in 100% CO2 atmosphere at room and elevated temperatures for varying durations of time. The pore structure and radiolysis, chloride ion attack, entrapped gasses (methane, carbon dioxide), and interfacial corrosion between the steel casque and cementitious barrier. This work details a preliminary approach to developing reliable characterization techniques of corrosion mechanism in concrete, particularly those specific to DGR conditions such as high pressure, high temperature, temperature cycling, etc. These phase changes showed clear signatures in the EDX-XRD study of the interface's role in the mechanisms of steel corrosion.

Molten fluoride salts have been proposed to be excellent candidates as primary reactor coolant and liquid fuel in a Molten Salt Reactor (MSR) due to their advantages of high thermal conductivity, low viscosities, high boiling points and high specific heats. However, the corrosion of structural materials in molten fluoride salts is a great challenge that prevents the successful fruition of MSR. In most corrosive environments, materials derive their corrosion resistance by the formation of a protective oxide scale and/or passive films. However, these oxide films are chemically unstable in high temperature molten fluoride salts and cannot provide protection of materials from corrosion. An understanding of in-situ dissolution rate and corrosion mechanism of oxide film in fluoride salt is significantly important for the development of MSR.

In this work, coupons of 316L stainless steel (SS) were pre-oxidized in hot air and then immersed in molten FLiNaK salt at 700 °C for electrochemical experiments. The impedance of oxide film on 316L SS as a function of exposure time were investigated using in-situ electrochemical impedance spectroscopy (EIS). The oxide resistance and capacitance under different exposure time were compared. The results show that the resistance of the oxide film decreases with increasing the exposure time, due to the dissolution of the Fe and Cr elements into the molten FLiNaK salt. After experiments, the structures of the oxide film were characterized and compared.

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Molten fluoride salts have been proposed to be excellent candidates as primary reactor coolant and liquid fuel in a Molten Salt Reactor (MSR) due to their advantages of high thermal conductivity, low viscosities, high boiling points and high specific heats. However, the corrosion of structural materials in molten fluoride salts is a great challenge that prevents the successful fruition of MSR. In most corrosive environments, materials derive their corrosion resistance by the formation of a protective oxide scale and/or passive films. However, these oxide films are chemically unstable in high temperature molten fluoride salts and cannot provide protection of materials from corrosion. An understanding of in-situ dissolution rate and corrosion mechanism of oxide film in fluoride salt is significantly important for the development of MSR.

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An understanding of in-situ dissolution rate and corrosion mechanism of oxide film in fluoride salt is significantly important for the development of MSR.
Recrystallization Behavior of Laser Powder Bed Fused 316L Stainless Steel by In-Situ Annealing Yanling Ge1, Zaqing Que1, Witold Chrominski2, Maciej Zielinski2, Kimmo Kaunisto1 and Ivona Jozwik1; 1VTT Technical Research Centre of Finland, Finland; 2National Center for Nuclear Research, Poland

Laser powder bed fusion (LPBF) addition manufactured (AM) 316L stainless steel (SS) shows superior mechanical and corrosion properties due to its heterogeneous microstructure. The recrystallization behavior of LPBF stainless steel is a key knowledge for application of AM material in nuclear sector. The two unique microstructure features of AM 316L, dislocation cellular structure and nanoscale oxide inclusions, are important controlling factors on recrystallization behavior and annealing structure. The recovery and recrystallization of LPBF 316L SS are analyzed with differential scanning calorimetry (DSC). The evolution of microstructure is studied with in-situ x-ray diffraction (XRD) and in-situ electron backscattered diffraction (EBSD) in scanning electron microscopy (SEM). The detailed dislocation network evolution and nanosized oxides interaction with grain boundaries during annealing are studied with in-situ transmission electron microscopy (TEM).

Heterogeneous Grain Boundary Corrosion in Ni-Cr Alloy Exposed to Molten Fluorinated Eutectic Salts under Applied Potential Sean Mills1,2, Ho L. Chan3, Nathan Biederbirs4, Minsung Hong1, Elena Romanovskiaia5, Chaitanya Peddeti1, Laurent Capulong6, Mark Asta7, John Scully3, Peter Hosemann3 and Andrew M. Minor1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States; 3University of Virginia, United States; 4Los Alamos National Laboratory, United States

Structural materials used in nuclear reactor environments are exposed to coupled extremes such as irradiation, high temperature, and corrosion which act synergistically to degrade their performance. Integral features of these processes are that defects produced under irradiation directly limit or accelerate the corrosion rates. Moreover, in molten-salt reactor environments, previous experimental work has shown that Cr de-alloying is strongly coupled to the microstructure evolution of these alloys. Connecting corrosion attack with alloy microstructure such as grain boundaries and accumulating point defects is imperative to understanding underlying mechanisms. However, it is challenging to predict how varied alloying elements, salt species, and nanoscale point defects interact with one another to lead to the failure of materials, as the multiscale nature of these reactions is hidden. Until recently, the capabilities to directly measure vacancies, interstitials and black spot damage have been limited to bulk techniques such as positron annihilation spectroscopy or x-ray diffraction measurement of lattice parameters. The recent developments in 4D-STEM with high-speed direct electron detectors and atomic resolution STEM provide an opportunity for potentially mapping point defect distributions at the nanoscale and their associated strains, both of which have far-reaching implications for potential development of complex irradiation / corrosion damage.

Active corrosion mechanisms are investigated in a model Ni80Cr20 metal alloy exposed to molten LiF-NaF-KF eutectic (FLiNaK) at 600°C. When a critical applied potential of 2.1V is reached, this enables both Cr and Ni dissolution and the formation of salt-filled corrosion channels at grain boundaries. For post-corrosion characterization, we implement microscale techniques such as energy dispersive spectroscopy (EDS) and electron backscatter diffraction (EBSD) to uncover variations in morphology and composition that are tied to non-uniform corrosion damage. This grain boundary corrosion mechanism is connected to a pure Ni de-alloyed region that forms within the salt-filled cavity. These findings are supported by phase-field modeling that describes an infiltrating salt-filled corrosion channel between two grains where Ni dissolves preferentially and re-forms on the opposing grain. This is attributed to the redox potential that is modified by the interfacial energies between grains. Building off the conditions that promote grain boundary corrosion and de-alloying, we conduct an in-situ experiment to track local changes in structure, morphology, and transport of species within a pre-fabricated salt-filled corrosion channel. The sample is annealed in the TEM at elevated temperatures (350–900°C via MEMS heating + biasing holder) to simulate typical molten salt reactor operating conditions. Further, we perform simultaneous EDX-STEM and 4D-STEM to correlate changes in structure and composition that result from surface diffusion or by bulk lattice diffusion in response to non-uniform corrosion.

This extensive study aims to fundamentally improve the understanding of complex corrosion processes and provide a new pathway for engineering materials designed in future nuclear energy systems. The project is part of FUTURE Energy Frontiers Research Center (EFRC), which aims to study how the coupled extremes of irradiation and corrosion work in concert to modify the evolution of materials by coupling experiments and modeling that target fundamental mechanisms.

Complement In Situ Microscopy with Multimodal Synchrotron Experiments in the Characterization of Radiation Damage Jason R. Trelewicz, Cormac Killeen, Yang Zhang, Spencer Thomas and David J. Srouster; Stony Brook University, United States

The formation of gaseous defects during irradiation due to, e.g., transmutation or ion implantation, involves a transition from defect clustering to the nucleation of bubbles and its biasing to various microstructural sinks such as grain boundaries. In situ microscopy techniques are limited in their ability to resolve the behavior of sub-nanometer helium clusters during the incubation stages of bubble formation while common X-ray techniques such as X-ray diffraction (XRD) provide information specifically pertaining to changes in the lattice parameter in the presence of such defect clusters. In this study, a region of reciprocal space accessible via wide angle X-ray scattering (WAXS) is identified that allows for the direct probing of sub-nanometer helium clusters irresolvable through transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) and only indirectly quantified by an XRD lattice parameter analysis. Using WAXS, we demonstrate that during carbon implantation with 400 MeV C ions, in which the films’ thermal conductivities reveal significant enhancement after ion irradiation, up to a factor of 3, depending upon the preirradiation composition [2]. Films with higher initial hydrogen content provide the greatest increase, which is complemented by an increased stiffening and densification from the irradiation process. This enhancement in vibrational transport is unique when contrasted to crystalline materials, for which ion implantation is known to produce structural degradation and significantly reduced thermal conductivities. At solid/solid interfaces, we also observe this ion irradiation-induced increase in thermal conductance. We experimentally demonstrate this increase in thermal conductivity (TBC) by ion irradiating Gallium Nitride to produce near interface point defects. GaN is bombarded with varying doses of C+, N+, and Ga3+ ions, with a maximum target near-interface defect density of 2%. We show an increase in the measured Al/GaN TBC. Our results show an increased level of scattering within the affected material, which assists in the thermalization between interfacial and bulk vibrational modes and decreases TBR. This is in contrast to conventional formalisms, where scattering across the interface is said to dominate thermal transport.

Bi-Directionally Tuning the Thermal Resistance of Materials and Interfaces with Irradiation-Induced Defects Patrick E. Hopkins; University of Virginia, United States

Materials in radiative environments (e.g., nuclear reactors, spacecraft, research instruments, among others) are subject to unique forms of damage. The microstructural damage results in a change in electron and phonon scattering rates in materials, which typically leads to a reduction in thermal conductivity. For example, in a study focused on silicon wafers irradiated with an array of ions (C2+, N2+, Al2+, Si2+, P2+, or Ge2+), we demonstrate that an increase in ion dose results in a significant reduction in thermal conductivity (up to an order of magnitude reduction) of the silicon within damaged region [1]. These reductions in thermal properties are general predicted based on the displacements-per-atom (dpa). While dpa and resulting defects lead to reductions in thermal conductivity in crystalline materials, we observe the opposite trend in thermal conductivity of amorphous materials and thermal boundary conductance across interfaces. For example, we demonstrate the ability to increase the thermal conductivity of amorphous solids through ion irradiation, in turn, altering the bonding network configuration. We report on the thermal conductivity of hydrogenated amorphous carbon implanted with C+ ions, in which the films’ thermal conductivities reveal significant enhancement after ion irradiation, up to a factor of 3, depending upon the preirradiation composition [2]. Films with higher initial hydrogen content provide the greatest increase, which is complemented by an increased stiffening and densification from the irradiation process. This enhancement in vibrational transport is unique when contrasted to crystalline materials, for which ion implantation is known to produce structural degradation and significantly reduced thermal conductivities. At solid/solid interfaces, we also observe this ion irradiation-induced increase in thermal conductance. We experimentally demonstrate this increase in thermal conductivity (TBC) by ion irradiating Gallium Nitride to produce near interface point defects. GaN is bombarded with varying doses of C+, N+, and Ga3+ ions, with a maximum target near-interface defect density of 2%. We show an increase in the measured Al/GaN TBC. Our results show an increased level of scattering within the affected material, which assists in the thermalization between interfacial and bulk vibrational modes and decreases TBR. This is in contrast to conventional formalisms, where scattering across the interface is said to dominate thermal transport.


3:00 PM *CH03.07.04 BREAK
3:30 PM *CH03.08.01
Investigating Dislocation Loop Nucleation and Growth under Stress by In-Situ TEM in Al Daphné Da Fonseca1, Thomas Jouard1, Fabien Onimus1 and Frederic Mompiou2; 1CEA, France; 2CEMES-CNRS, France
Irradiation creep occurs both under stress and irradiation flux, even at moderate temperature, has a profound impact on mechanical properties in structural materials. For instance, it leads to deleterious permanent deformation in austenitic steel vessel internals in pressurized water nuclear reactors. Although this phenomena has been documented in the 70’s and 80’s, experimental and theoretical investigations proposed have never found consensus so far. It was proposed that irradiation would contribute to dislocation climb but the role of anisotropic growth of irradiation loops was the subject of debates and contradictory results. From early microstructural observations, showing a bias in the development of Frank loops in austenitic steels, two models have emerged. They postulate that the applied stress biases either loop nucleation or their growth which lead to different loop populations density and size. Experimental results, provided by post-mortem TEM observations at high doses, were not able to discriminate clearly between the two models, while in-situ observations carried out in high voltage microscopes reported opposite trends.

To gain knowledge in these phenomena, we studied loop nucleation and growth during in-situ TEM experiments under stress and irradiation at low doses. To that purpose, we take advantage of the low energy displacement threshold of aluminum, to both irradiate and observe samples at the same time, in-situ in a conventional transmission electron microscope. We show that close to the elastic limit, almost only interstitial Frank loops are formed in the [111] planes normal to the tensile direction. Deep learning and tracking approaches were used to follow the kinetics and distribution of loops during these experiments. They reveal that loop growth is in average linear with time, i.e. with electron fluence, but with numerous cases of stagnation or accelerated growth. More importantly, we demonstrate that the anisotropy of loop population is determined at early stage, probably at the nucleation, and that the growth kinetic only plays a minor role in the development of the observed loop population. These findings echo simulations performed both at atomic scale for the nucleation processes (molecular dynamics Frenkel-pair accumulation), and at mesoscale (Object Kinetic Monte-Carlo) for elastic-diffusion mechanisms of loop growth.

SESSSION CH03.08: Computational and Simulation Tools Helping in the Interpretation and Management of In Situ Characterization Data
Session Chairs: Aurelie Gentils and Mercedes Hernandez Mayoral
Friday Morning, April 26, 2024
Room 441, Level 4, Summit

4:00 PM *CH03.08.02
Investigating Localized Deformation in Irradiated Stainless Steels through TEM In Situ Straining Experiments Silvia Guerra1, Marta Navas1, Jia-Chao Chen2, Shavkat Akhmadaliev3 and Mercedes Hernandez Mayoral1; 1Centre for Energy, Environmental and Technological Research, Spain; 2Paul Scherrer Institute, Switzerland; 3Helmholz-Zentrum Dresden-Rossendorf, Germany
This research focuses on comprehending the processes occurring in austenitic stainless steels during the initial stages of deformation that can lead to localized deformation, and the impact of irradiation in the deformation modes of the material.
To achieve these goals, the methodology employed in this study deals with performing in-situ straining experiments at the interior of a Transmission Electron Microscope (TEM). These experiments offer direct insights into the microstructural processes that occur in real time during sample deformation. This includes the observation of phenomena like nucleation and movement of dislocations, the interaction between dislocations and defects as well as early stages of defect-free channel formation. These in situ straining experiments were conducted as interrupted tests, and the resulting microstructure was characterized by means of SEM/EBSD and TEM before and after each in-situ experiment in order to observe the evolution of the deformation in each sample and compare them.

The material under study is the AISI-316L, because due to its high corrosion resistance and good mechanical properties, it is a recurrent material in the construction of internal components of nuclear power plants. Two irradiation conditions have been studied, (1) with helium ions and (2) with iron ions, and each of them along with the non-implanted material, have been characterized.
A systematic study of the irradiated and deformed microstructures has been carried out with the aim to identify, describe, and classify features generated after interrupted testing and assess the influence of the irradiation conditions studied. Results will be presented and discussed.

8:30 AM *CH03.09.01
Advancements in Real-Time Quantification for In-Situ Materials in Extreme Environments Kevin G. Field1,2, Hangyu Li1, Kai Sun1, Robert Renfrow1, Matthew Lynch1, Ryan Jacobs3, Aidan Pilny4, Benjamin Eftink5, Dane Morgan6 and Chris Field1; 1University of Michigan, United States; 2Theia Scientific, LLC, United States; 3University of Wisconsin–Madison, United States; 4Los Alamos National Laboratory, United States
In this talk, we discuss our recent developments on integrating automated detection of defects1–5, stereomicroscopy6,7, edge-computing8, and in situ ion irradiations to form a high-throughput, limited-bias workflow for studies on materials in extreme environments. Materials in extreme environments has been identified as a key research challenge for the materials community9, where radiation at elevated temperature, as well as stress, is one facet of the materials in extreme environments paradigm. Experiments on radiation-temperature effects are highly complex and dynamical, where defects are nucleated and can move in 1D and 3D with changes in their size, morphology, character, and can be annihilated. We discuss the application of machine learning to form a backbone for a high-fidelity, rapid quantification architecture that can perform 2D-projection and 3D visualization of defects and analysis of these complex dynamical events per frame and in near real-time fashion. We show that performance of deep learning methods, such as Mask R-CNN and You Only Look Once (YOLO), demonstrate performance levels that are at or exceed human performance with inference times below 100 ms. We see that such high-level model performance persists even when trained using physics-based synthetic datasets. We explore the application of deep learning coupled to tracking algorithms, such as DeeplSORT, ByteTrack and BoT-SORT, to track hundreds of defects during extreme exposures, including during in-situ transmission electron microscopy (TEM) ion irradiations of several FeCrAl alloy variants on edge and near-edge computing devices. Then, we will show how object detection and tracking can be coupled with 2-tile stereomicroscopy via the Obtain3D code package10 to form 3D reconstructions allowing for detailed 3D analysis such as pair distribution evolution of defects and 1D/3D diffusion of slow-moving defects under irradiation. The capabilities of this ensemble for high fidelity quantification are realized through a platform that couples a modern web application (webapp) hosted on edge or near-edge computing devices that is seamlessly coupled with a state-of-the-art in situ TEM ion irradiation facility. This platform enables real-time application of the algorithm ensemble and corresponding graphical displays and overlays from the in situ video feed during irradiation providing for in operaendo microscopy. The edge-device with a hosted webapp platform, termed TheiascopeTM, has been demonstrated for in situ TEM ion irradiations. It will be shown the platform is system agnostic (both in hardware and experiment) allowing for immediate feedback of materials evolution when exposed to extreme environments in other imaging systems such as scanning electron microscopy. We will conclude the discussion with recent improvements and thinking on extending the overall presented framework and advances to automated microscopy experimentation through integration with microscopy vendor software APIs.

Materials within nuclear reactors undergo irradiation that results in adverse microstructural changes, including the formation of point defects, defect clusters, voids, dislocation loops, segregation, and precipitation. The Intermediate voltage electron microscope (IVEM)-Tandem Facility at Argonne National Laboratory is a user facility for in situ TEM study of the radiation effects on material microstructures. It interfaces a 500 kV accelerator and a 20 kV helium ion source to a 300 kV Hitachi H-9000AR TEM, allowing real-time microscopy under dual-beam ion irradiation damage/implantation with well-controlled conditions including specimen orientation, temperature, ion type, ion energy, dose, dose rate, applied strain. In situ TEM has unique capabilities to characterize the dynamic process that cannot be obtained with ex situ experiments.

Our previous study in IVEM observed voids growing or shrinking in nickel at various temperatures from 525 °C to 650 °C under 1 MeV krypton ion irradiation with a flux of 6.3x1011 ions/cm² s⁻¹. Initially, 6 samples underwent irradiation at 600 °C to achieve a damage level of 0.5 dpa, which resulted in the formation of voids with an average size of about 15 nm within the TEM foil. Subsequently, the temperature was individually adjusted to 525 °C, 550 °C, 575 °C, 600 °C, 625 °C, and 650 °C. Following this temperature adjustment, irradiation continued for an additional 1 dpa. The stability of the voids at these new temperatures was monitored through in situ TEM in regions where the foil thickness was approximately 100 nm. A total of about 5000 frames of videos were recorded. We applied deep learning-based semantic segmentation model (IoU score = 0.8135) to automatically analyze the videos and showed that voids shrink at low temperatures and grew at high temperatures under irradiation, unlike 575 °C (~0.5 TM).

This presentation will focus on the behavior of small Kr-containing bubbles, which had a size smaller than 10 nm. Unlike larger, immobile voids, these small bubbles are mobile under irradiation. Notably, the bubbles were often found trailing along with the irradiation-induced dislocations loops. The movement of those bubbles was confined to the path where dislocation loops expanded or shrunk. For bubbles not associated with dislocations, on the other hand, their movements appeared to be random. Besides, while large voids tended to grow steadily at temperatures above 575 °C, the bubbles were unstable, switching between growth and shrinkage. The behavior of individual bubbles may be affected by its own unique surroundings such as voids, bubbles, dislocations, and concentration of point defects. Understanding how these individual bubbles behaved exhibited heterogeneous behavior and added up contributing to the resultant macroscopic property requires tracking capability.

We developed an automated tracking system using Trackpy, and showed that, in average, void stability increases with void size, while void mobility decreases with void size. Nonetheless, there is significant variability in growth or mobility across voids of the same size and for the same void at different times. Besides, the analysis allows us to identify the threshold size at which bubbles transition from instability to steady growth. The temperature dependence on the bubble stability and mobility will also be discussed.

Kinetics Governed by Elastic Bias in In-Situ Electron Irradiated Aluminium: A Coupled Experimental and Modeling Study Camille Jacqueline, Thomas Jourdan, Maylise Nastar, Chu Chun Fu and Estelle Meslin; CEA Saclay, France

In this study, we investigate the direct in-situ formation of nanometer-scale radiation damage, including voids and loops, using a High-Resolution Transmission Electron Microscope (HRTEM). We observe a size-dependent effect on the shape of cavities induced by electron irradiation, with non-truncated and cross shapes appearing at sizes below 2 nm, while larger sizes exhibit truncated shapes, consistent with DFT-based-equilibrium shapes. This effect is explained by our multi-scale modelling, considering the effects of finite size and network discretization on void shapes. The observed dispersion in cavity shape during their growth and shrinkage is primarily influenced by magic numbers, determined by geometry and network frustration. Additionally, not only the voids but also loops were followed in-situ. Loops grow until they attain the surface, while voids go through periodic growth and shrinkage. We demonstrate that the evolution of both objects is linked and governed by elastic bias. The unexpected void shrinkage is attributed to the change of the main sink for the elimination of interstitials. Void growth occurs when the main sinks for interstitials are the strongly biased dislocation loops, generating a stronger vacancy flux towards voids. Conversely, cavity shrinkage occurs when the loops are absent, and the main sinks for interstitials are the foil surface, generating a stronger interstitials flux towards voids. We reproduce accurately this phenomenon through Object-Kinetic Monte Carlo (OKMC) modelling.

Automated Defect Detection in Electron Microscopy of Radiation Damage in Metals Dane Morgan1, Ryan Jacobs1, Ayaj Annamareddy1, Matthew Lynch2 and Kevin G. Field2; 1University of Wisconsin–Madison, United States; 2University of Michigan–Ann Arbor, United States

In this talk, we discuss our recent work on automating detection of defects in electron microscopy images of irradiated metals relevant for advancing the capabilities of in situ defect characterization of nuclear materials [1-5]. Radiation response of materials is a critical design constraint for future nuclear fusion and fusion materials. Electron microscopy is widely used to explore defects in crystal structures, but human tracking of defects can be time-consuming, error prone, unreliable, and is not scalable to large numbers of images or real-time analysis. In this work, we apply a multi-scale modeling approach to find the location and geometry of different defects in irradiated alloys, such as dislocation loops, black dot interstitial cavities, and voids. We explore multiple deep learning methods and generally find performance approaching or equivalent to human accuracy. We explore multiple avenues of assessment, including the use of canonical classification metrics like precision and recall of specific defect identification (F1=0.8), accuracy of microstructurally-relevant defect properties (e.g., average defect area density and size distribution ≈10% fractional errors), and accuracy of macroscopic engineering properties such as hardening (10-20 MPa errors, or about 10% of total hardening) and swelling (≈0.3% swelling errors). These results suggest that specific images can have significant errors, but averaging over many images yields quite good results. We explore convergence of the results with number of training samples, finding that certain defect types are significantly less well detected, likely due to both their having reduced sampling and greater variability, as well as labeling and model limitations for small size features. Finally, we discuss recent efforts using synthetic data to improve object detection model training and reduce the need for a large corpus of labeled experiments. We explore both deep learning approaches to create synthetic dislocation loop images and physics-based electron dynamical simulations to create synthetic cavities. We generally find that the use of synthetic data is a practical path toward generating new training data essentially instantaneously, leading to improvements in object detection model performance.


10:00 AM BREAK

10:30 AM *CH03.09.05
A Comprehensive Study on The Kinetics of Defect Formation and Interaction Coupling In-Situ TEM with Deep Neural Networks Kory D. Burns1, Caitlin Kohner2 and Khalid Hattar2; 1University of Virginia, United States; 2Los Alamos National Laboratory, United States; 3The University of Tennessee, Knoxville, United States

Simulating reactor conditions inside a transmission electron microscopy (TEM) gives insight into the rate of defect formation and survivability of materials in the environments in which they were designed to perform. Efforts to fully encapsulate dynamic processes occurring in a material have been challenging, owing to the large volume of information collected from an individual experiment and multiple interactions occurring simultaneously. Hereby, deep neural networks emerge as a suitable method to extract complicated information from input images and output useful analytics that help understand the physics of a reaction. This talk discusses strategies for handling a range of datasets from in situ TEM experiments that span different material systems, imaging conditions, and irradiation conditions to predict the stability of materials. Emphasis will be placed on developing end-to-end process flows equipped with generating synthetic data to learn feature representations of images, pattern recognition to highlight hidden trends in the data, and overall implications for the development of nuclear materials characterization.

11:00 AM CH03.09.06
Investigation of Extended Defect Evolution in UO2 and ThO2 during Ion Irradiation and Post-Irradiation Annealing Marat Khafizov1, Joshua Ferrigno1, Mutaz Alshannaq1, Md
A rate theory model is applied to analyze the kinetics of extended defect evolution revealed by in-situ transmission electron microscopy characterization during ion irradiation and post-irradiation annealing of uranium dioxide (UO$_2$) and thorium dioxide (ThO$_2$). The objective is to investigate mechanisms governing dislocation loop growth, unfauling of Frank loops, and extended defect coarsening. In-situ characterization of krypton ion irradiated ThO$_2$ reveals that loop growth is limited by the mobility of cation interstitial and loop nucleation is influenced by the mobility of both cation and anion interstitials. Similar conclusion has been obtained from ex-situ characterization of proton irradiated ThO$_2$. Additionally, we determined that during in-situ experiments utilizing TEM lamellae it is important to include surface as a sink for both extended and point defects. Observed extended defect coarsening under in-situ annealing is best described by coalescence mechanism resulting from migration of extended defects. This detailed understanding of extended defect evolution allows to improve assessment of physical properties important for nuclear fuel performance analysis. The established procedure also allows to infer point defect concentration, which are more impactful in determining several physical properties, such as thermal conductivity and atomic diffusion.

SYMPOSIUM CH04

Characterization of Materials Dynamics
April 23 - May 9, 2024

Symposium Organizers
Yuzi Liu, Argonne National Laboratory
Michelle Mejía, Dow Chemical Co
Yang Yang, Brookhaven National Laboratory
Xingchen Ye, Indiana University

* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION CH04.01: Understanding Material Dynamics in Multimodalities
Session Chairs: Yuzi Liu and Xingchen Ye
Tuesday Morning, April 23, 2024
Room 443, Level 4, Summit

10:30 AM CH04.01.01
Operando, Multimodal Characterization of Bimetallic Catalysts with Electrons and X-Rays
Alexandre Foucher$^{1,2}$, Nicholas Marcella$^{2,3}$, Jennifer Lee$^{4,5}$, Daniel Rosen$^{6}$, Ryan Tappero$^{7}$, Christopher B. Murray$^{8}$, Anatoly Frenkel$^{2,3}$, and Eric A. Stach$^{9}$

Alloyed nanoparticles are of increasing interest in many applications, most notably as heterogeneous catalysts. Alloying allows the tuning of composition and structure to increase functionality, most specifically reactivity and selectivity. However, harsh, reactive environments can induce changes in the structure and composition of these materials in unexpected ways, which can inhibit their performance. These materials also present a significant characterization challenge: they are tiny (from single atoms to particles of 10 nm) and can also be heterogeneous in size, composition, and structure.

I will describe how we have developed a new approach to characterize catalysts using so-called 'operando' methods to take measurements. At the same time, the materials are 'in a working condition': i.e., in a reactive environment performing their function. We use a microreactor system compatible with imaging, diffraction, and spectroscopy, using electron, photon, and x-ray probes. The presentation will describe how this multimodal approach can provide unique insights into the dynamic changes in these complex systems as they function.

There will be two specific applications. In the first portion, I will show how we can exploit an innovative colloidal synthesis method to produce highly monodisperse Cu-Pt alloy nanoparticles with a Pt-rich shell and Cu-rich core; the intermetallic CuPt phase formed after annealing shows enhanced and stable catalytic activity for CO oxidation compared to pure Pt nanoparticles or the fresh Cu-Pt particles with a Pt-shell. This synthesis route allows control over Cu-Pt nanostructures, demonstrating Cu-Pt alloy's promising catalytic properties. In the second portion, I will show how Ni-Cu alloy nanoparticles undergo compositional and morphological changes during redox cycles that simulate catalytic reactions; specifically, while Cu segregates in the fresh catalyst, oxidation at 400°C leads to restructuring into hollow particles with heterogenous Ni-Cu composition, explaining the deactivation observed for conversion of biomass-derived 5-hydroxymethylfurfural over NiCu/C.

11:00 AM CH04.01.03
Understanding Particle-Mediated Growth Pathways by using Advanced Transmission Electron Microscopy and X-Ray Scattering Techniques
Xin Zhang$^{1}$, Xiaoxu Li$^{1}$, Yining Wang$^{1}$, Jianbin Zhou$^{1}$, Sebastian T. Mergelberg$^{2}$, Tuan Ho$^{2}$, Lili Liu$^{1}$, Honghu Zhang$^{3}$, Ruipeng Li$^{1}$, Mark Bowden$^{1}$, Ping P. Chen$^{1}$, Maria Sushko$^{1}$, Carolyn Pearce$^{1}$, and Kevin Rossol$^{1}$
Pacific Northwest National Laboratory, United States; Sandia National Laboratories, United States; Brookhaven National Laboratory, United States

Particle aggregation involves the phenomenon of oriented attachment (OA), where crystalline particles join together by attaching to specific crystal faces with lattice matching, is a prevalent mechanism in crystal growth and has been extensively utilized in the development of hierarchically structured crystalline materials, which has been applied to catalysts, energy storage, environmental conservation, biological medicine, etc. Using a combination of advanced transmission electron microscopy (TEM) and small-angle X-ray scattering/wide-angle X-ray scattering (WAXS) techniques and computational methods, we are investigating these phenomena for several metal oxide systems and their relationship to interfacial structure in vacuum and water vapor. Here we discuss three cases. In the first, we use high-resolution TEM and scanning TEM (STEM) to explore the aggregation behaviors of hematite nanocrystals with different exposed facets including [001], [012], [104] and [116]. The experimental data indicates that hematite nanoparticles aggregation-based crystallization is orientation dependent (along the [001] direction), not relies on exposed facet. We then compare the results to the predictions of density functional theory (DFT) to relate the behavior to surface interactions. In the second case, we report the
formation of gibbsite mesocrystals in pure water. By evaporating the suspension of monodisperse gibbsite nanoparticles with a diameter of around 100 nm, plate-like mesocrystals with a diameter of up to a hundred micrometers were formed. The single crystal XRD pattern and SAXS/WAXS of the mesocrystals matched that of bulk gibbsite crystal along the specific zone axis, indicating well-aligned particles in the monocrystals. Further analysis through scanning electron microscopy (SEM) and TEM revealed a hexagonal columnar superstructure. Moreover, the in situ liquid phase TEM was conducted and observed the OA of a few gibbsite nanoparticles in pure water, and the result matched well with ex situ characterizations. The MD simulation was used to investigate the energy-structure relationship for the sliding motion of two co-planar gibbsite nanoplatelets along the (010) direction. The results indicated that to obtain the first perfectly aligned configuration, sliding in the (010) direction exhibits a smaller energy barrier than sliding in the (100) direction (0.89 vs. 2.49 kcal/mol). In the third case, the measurement of anisotropic forces between rutile TiO2 (001) nanocrystals as a function of their azimuthal orientation and surface hydration extent using a combined environmental TEM-atomic force microscopy (AFM) technique. At tens of nanometers of separation, the attractive forces are weak and show no dependence on azimuthal alignment nor surface hydration. At separations of approximately one hydration layer, attractive forces are strongly dependent on azimuthal alignment and systematically decrease as intervening water density increases. Measured forces closely agree with predictions from Lifshitz theory and show that dispersion forces are capable of generating a torque between particles to align them.

SESSION CH04.02: Advanced Characterization of Energy Materials
Session Chairs: Tianyi Li and Xianghui Xiao
Tuesday Afternoon, April 23, 2024
Room 443, Level 4, Summit

1:30 PM *CH04.02.01
Origin of Structural Degradation in Lithium Layered Oxide Cathode
Luxi Li1, Tongchao Liu1, Ian Robinson2, Ross Harder3 and Wonsuk Cha1; 1Argonne National Laboratory, United States; 2Brookhaven National Laboratory, United States; 3University College London, United Kingdom

Li and Mn-rich (LMR) layered oxide cathode materials can substantially increase battery energy density by facilitating both cation and anion redox reactions. However, the cathode materials suffer from continuous voltage decay over the charge/discharge cycles and results in capacity loss. Coherent X-ray Diffraction (CXD) techniques are invaluable for investigating the morphology, structural and strain information in crystalline specimens under in-situ and operando conditions [1-2]. In this presentation, Li2MnO2·(1/4)CO3·(1/4)O2 is used as a benchmark to explore the origin of structural degradation in LMR cathode materials [3]. In-situ CXD techniques are used to visualize the strain accumulation in the charging process that leads to an abrupt oxygen loss to release the lattice strain. In the meanwhile, a new phase with a trace quantity is observed from the microbeam diffraction that supports the hypothesis of oxygen loss. These results highlight the significance of lattice strain in the voltage decay mechanism and will inspire a wave of efforts that seek novel solutions for eliminating this issue.


2:00 PM *CH04.02.02
X-Ray Nano-Scale Spectroscopic Imaging on Battery Research – A Case Study
Xianghui Xiao1, Dong Hou1, Feng Lin2 and Zhengrui Xu3; 1Brookhaven National Laboratory, United States; 2University of Louisiana at Lafayette, United States; 3Virginia Tech, United States

Chemical reaction heterogeneity is ubiquitous at both interparticle and intraparticle scales during battery cycling. Spectroscopic imaging provides position-dependent chemical state information that is directly related to the chemical reaction heterogeneity in the samples. Transmission X-ray Microscope has been widely used in battery research as a spectroscopic imaging modality. Simultaneously, it also provides morphological structure information. In this paper, we will present a case study of the characterizations of two types of high-Ni NMC cathode materials that have different primary particle arrangement patterns. They show distinct performances at room temperature. Nonetheless, the thermal stabilities of these two types of materials are inverse compared to their electrochemical performances. The chemical state distributions and morphological structures at the single particle level show consistent evolution behaviors as the observations with neutron diffraction. The results help to reveal the fundamental mechanisms that cause the differences. The case demonstrates the capability of TXM as a spectroscopic imaging tool and its applications in battery research.

2:30 PM CH04.02.03
Boosting the CO2 Uptake of MgO-Based Sorbents using Na2CO3 as Nucleation Seeds: Mechanistic Insights via In Situ Synchrotron XRD
Annelies Landuyt1, Dong Hou1, Ian Robinson1,2 and Ross Harder1; 1Argonne National Laboratory, United States; 2University of Chicago, United States

MgO-based CO2 capture materials suffer from continuous voltage decay over the charge/discharge cycles and results in capacity loss. Coherent X-ray Diffraction (CXD) techniques are invaluable for investigating the morphology, structural and strain information in crystalline specimens under in-situ and operando conditions [1-2]. In this presentation, Li1.2Ni0.13Mn0.54Co0.13O2 is used as a benchmark to demonstrate the mechanism behind this phenomenon via in-situ synchrotron XRDR measurements (1 s resolution), revealing that Na2CO3 rapidly (within seconds) transforms into Na2Mg(CO3)2, the co-promotion of MgO with Na2CO3 and NaNO3 is a facile, inexpensive and highly promising strategy for improving MgO–based CO2 capture sorbents.


2:45 PM CH04.02.04
Depth-Profiling Spectroscopic Investigation of The Activation Mechanism of LiMn2O4: Micro-SORS Method
Wang-Hyo Kim1, Myeong-Hee Lee1, Byung-Man Kim2 and Tae-Hyuk Kwon1; 1Usan National Institute of Science and Technology, Korea (the Republic of); 2University of Cambridge, United Kingdom

Lithium manganese oxide (LiMn2O4, LMO) stands out as a promising material for lithium-ion batteries due to its high thermal stability, low cost, abundance, and environmental compatibility. However, the dynamics of LMO’s behavior in electrode is still unknown. In this study, we explore LMO as a storage electrode in photo-electrochemical batteries (PRB) using non-invasive depth-profiling techniques, specifically micro-spatially offset Raman spectroscopy (micro-SORS). We delve into the Raman profiles of LMO layers, examining their variations based on depth after galvanostatic charging and discharging cycles of PRB. During these cycles, the oxidation state of manganese species shifts from Mn3+ to Mn4+, accompanied by a phase transition from cubic to tetragonal. This transition results in increased capacity. To unravel this mechanism, we analyze depth-dependent Raman profiles corresponding to the phase transition throughout charging and discharging cycles. To validate our micro-SORS findings, we employ X-ray absorption fine structure (XAFS) and X-ray absorption near edge structure (XANES) techniques, confirming both oxidation states and phases. The XAFS and XANES data reveal the activation of an irreversible charged state (Li2Mn2O4, L2MO) over repeated charging-discharging cycles. By integrating micro-SORS analysis with this information, we pinpoint the specific site of activation in the electrode, elucidating the capacity increment mechanism through tracking this activation process.

3:00 PM BREAK

3:30 PM *CH04.02.05

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Developing Automation and In-Situ Capabilities for X-Ray Scattering towards Autonomous Lab-At-Beamline Ruipeng Li; Brookhaven National Laboratory, United States

X-ray scattering is a unique tool for revealing material structures, spanning from the atomic level to hundreds of nanometers. Its broad probe range and flexibility make it invaluable for in-situ and operando studies across various materials research fields. The development of the in-situ capabilities, coupled with technological advances in light sources and detectors, have increased our ability to explore complex material processing, resulting in vast amounts of data in more intricate parameter spaces.

In this presentation, I will discuss recent developments in in-situ capabilities at the Complex Materials Scattering (CMS) beamline of NSLS II, as well as our journey toward automation and autonomous exploration of materials. I will also outline our strategy to integrate automation, advanced data analysis, in-situ capabilities, and other characterizations to develop the beamline into an autonomous lab-at-beamline.

4:00 PM *CH04.02.06
Advancing Research with Combined Synchrotron Techniques at 7-BM NSLS II Lu Ma; Brookhaven National Laboratory, United States

At the 7-BM, NSLS II, we've developed combined synchrotron techniques for materials characterization, particularly X-ray absorption spectroscopy (XAS)/X-ray diffraction (XRD) and XAS/Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). These combined approaches yield numerous advantages including comprehensive analysis, real-time monitoring, and the maximization of data yield during valuable beamtime. Notably, their integration often reveals unexpected material properties and bridges gaps across varied research areas.

The combination of XRD and XAS offers an all-encompassing perspective on material structure/properties. XRD examines phase identification, crystal structure, and other microstructural properties, while XAS studies the electronic configurations, oxidation states, and the intricacies of local coordination.

With XAS elucidating details of the catalyst structure and DRIFTS offering a snapshot of surface interactions and molecular dynamics, this combination proves to be a powerful tool for gaining a comprehensive view of catalytic reactions.

Leveraging these integrated techniques at the 7-BM NSLS II, we not only enhance our understanding of material properties but also set the stage for future innovations in diverse research fields.

4:30 PM CH04.02.07
Designing The Next Generation Silicon/Graphite Anodes for Lithium-Ion Batteries: From The Nanoscale to The Macroscale Benjamid Rezen, Sofia Marchesini, Carmen Lopez, Andrew Wain, Rudra Samudjar, Ken Mingard, Vivian Tang, Helen Jones, Daniel O'Connor, Giannis Chatzopoulos and Andrew Pollard; National Physical Laboratory, United Kingdom

Reaching net-zero emissions and transitioning to widespread electrification of vehicles have emerged as key challenges for ensuring a sustainable future. Central to these goals is the critical role played by energy storage systems, which are pivotal in enabling the efficient utilisation and distribution of renewable energy. The advancement of energy storage technologies, particularly in the realm of lithium-ion batteries, holds the key to mitigating the challenges posed by intermittent renewable energy sources. Moreover, electrification of the transportation sector, primarily through electric vehicles, is fundamental to reducing greenhouse gas emissions.

The operating range for electric vehicles is determined by the energy density of the battery, which, in the case of anode materials, is directly correlated to their lithium storage capacity. While traditional graphite anodes have a theoretical capacity of 360 mAh/g, silicon has a much larger theoretical capacity (3600 mAh/g) and silicon-based lithium-ion batteries have therefore emerged as a promising technology. However, silicon anodes suffer from large volume expansion (up to 300 %) during cycling, which causes a drop in capacity. Recent industrial advances allowed for the development of silicon/graphite composite materials with limited volume expansion and increased capacity. However, while these materials showed improved electrochemical performance, little is understood on the physicochemical mechanisms underpinning these improvements. The successful advancement of this technology necessitates a thorough understanding of intricate phenomena such as particle cracking, volume changes on various length scales (from pouch cell level down to individual particles), and the formation of solid electrolyte interphase (SEI) layers.

Herein, we employed a suite of complementary physical and chemical characterisation techniques using both post-mortem and operando methods, across a range of length scales, from pouch cells down to individual particles observed at the nanoscale. Collaboration with an industrial supplier of these anodes and cells allowed the elucidation of the material degradation phenomena and the correlation to their electrochemical cycling performance.

This work highlights the significance of integrating multiple characterisation methods to unravel the underlying degradation mechanisms in silicon-based anodes, paving the way for the design and engineering of efficient silicon and graphite anodes, thus propelling the evolution of lithium-ion battery technology.

4:45 PM CH04.02.08
Evaluations of Reaction Heterogeneities in Battery Electrodes upon Fast Charging using Operando Focused Beam X-Ray Diffraction Tianyi Li, Donal Finegan and Kamila Wiaderek; Argonne National Laboratory, United States, 2National Renewable Energy Laboratory, United States

Recently, the use of thick electrodes in lithium-ion batteries has drawn extensive attention as it effectively promotes cell-level energy density by reducing the fraction of inactive components such as separators and current collectors. However, the spatially non-uniform reaction can easily arise within a thick electrode design due to the sluggish electrolyte transport. Understanding the heterogeneous reaction and preventing it is happening are therefore critical as it may result in inferior rate performance, fast capacity degradation, and even safety hazards. This study aims to experimentally evaluate the reaction heterogeneities in thick electrodes by employing operando focused beam X-ray diffraction (XRD). We will compare the traditional graphite anode with laser ablated sample in full cells upon 6C fast charging, therefore, quantitatively assessing the degree of reaction along the depth direction in electrodes under operational conditions. A detailed comparison between the experiments and simulations will help us better understand the origin of reaction heterogeneities in electrodes and guide the design of battery materials and structures in the future.

5:00 PM CH04.03.01
Grand Canonical Monte Carlo Simulation with MOF-303 and Metal-Coated MOF-303 Jeongho Ag and Kunoh Chng; Kyung Hee University, Korea (the Republic of)

Managing Xe/Kr radioactive novel gas generated from spent nuclear fuel is critical for both environmental and human radiation protection. While numerous experimental methods applied to find effective adsorbent, the computational simulation can help minimize experimental costs and help pre-screening effective materials. The Grand Canonical Monte Carlo (GCMC) Simulations are used to explore selective adsorptions at Metal-Organic Frameworks(MOFs). This study aims to use GCMC to select MOFs that have a large capture capacity and selective adsorption of gaseous radionuclides emitted from spent nuclear fuel such as Xe/Kr. Among the MOFs, MOF-303 shows improvement it’s total uptakes and selectivity when it doped with metal such as Cu. Through GCMC calculations, the effect of Cu doping on the gas adsorption of MOF-303 was evaluated, and the effects on the capture capacity and selectivity changes were quantitatively analysed.

5:00 PM CH04.03.02
Excited-State Dynamic in Thiophene/Phenylene Co-Oligomer Nanocrystals Andi Marwanti Panre, Hitoshi Mizuno, Tomomi Jinio and Hiroaki Katsuki; Nara Institute of Science and Technology, Japan

Thiophene/phenylene co-oligomer (TPCO) nanocrystals (NCs) hold strong promise for nano-environment photoluminescence probes, qubits, and quantum light source. Their optical properties show considerable versatility and flexibility depending on the size of the nanocrystals. This adaptability enhances light emission efficiency, making them a promising choice for improving organic light-emitting diodes (OLED) technology, especially as active layers. To extend the potential applications of these nanocrystals, it is essential to investigate how the size of nanocrystals is related with the excited state relaxation and photoluminescence (PL) dynamics. For example, we expect the excited state lifetime for smaller NCs should be affected by the enhanced spatial overlap of electron and hole states. In the present study, we observe the transient absorption spectrum in NCs of 5,5′-bis(4-(cyanoarylphenyl)-4-yl)-2,2′-bithiophene (BP2-CN). BP2-CN NCs with an average size of 75 nm were prepared by the precipitation method, which show strong yellow emission centered around 555 nm. The size-dependent steady-state optical properties were elucidated through the measurement of absorption and PL spectra. In comparison to vapor-deposited films, the BP2-CN NCs water dispersion displayed shifted in the 0-1 and 0-2 absorption bands, attributed to lattice softening (surface effect) and quantum effects. Additionally, PL lifetime measurements yielded a decay time of 1.33 ns at an excitation wavelength of 400 nm. The transient absorption signal in the yellow-emitting BP2-CN NCs is characterized by three exponential decays with 0.65 ps, 2.3 ps, and 75 ps components. These time constants shed light on relaxation processes, including electron trapping, intra-band relaxation, and non-radiative decay. Photoinduced absorption bands (PA, ΔΔT < 0) appeared at 670-700 nm from the
Atomic Spatiotemporal Characterization of Light-Emitting 2D Materials by Cathodoluminescence and Femtosecond Photoluminescence Spectroscopies

Our findings will give a clue on the photophysical processes within these co-oligomer NCs, providing valuable insights for potential applications in optoelectronic devices and photonics, especially in OLED development.

5:00 PM CH04.03.05
Atomic Spatiotemporal Characterization of Light-Emitting 2D Materials by Cathodoluminescence and Femtosecond Photoluminescence Spectroscopies

Our results show the formation of hydrogen species H\(^+\), H\(_2\), H\(_3\) and hydrides ZrH\(_2\), ZrH\(_3\). The evolution of the relative abundances of H\(^+\), H\(_2\), H\(_3\) depends on the surface field estimated from the Zr\(^2+\)/Zr\(^3+\) ratios, as seen in previous studies on other materials[2]. This is not the case for the hydrides which overlap with the Zr isotopic species. In this contribution we will discuss the quantification of hydrogen and zirconium hydrides and their dependence on the field.

5:00 PM CH04.03.06
Photoluminescence of Up-Conversion Nanoparticles with High Spatial Resolution

The emerging realm of two-dimensional (2D) materials has introduced remarkable advancements in the fields of optoelectronics and photonics. To harness the full potential of these materials, a comprehensive understanding of their light-emitting characteristics at atomic spatiotemporal scales is indispensable. Cathodoluminescence (CL) integrated within a scanning electron microscope (CL-SEM) or scanning transmission electron microscope (CL-STEM) is capable of conferring material properties with sub-nanometer spatial and spectral resolutions, surpassing the limitations of traditional photoluminescence (PL) techniques employed by the Abbé diffraction limit. Furthermore, time-resolved photoluminescence (TRPL) spectroscopy enables the characterization of ultrafast electron-hole recombination dynamics through the up-conversion technique, employing ultrashort excitation and gating laser pulses. In this context, our specifically designed sample holder and spectrometer, integrated with the high-resolution Hitachi S5500 SEM and equipped with sample loading chips featuring ultrathin windows, are aimed to develop an atomic-resolution hyperspectral CL-SEM/STEM imaging system. Additionally, in conjunction with our homemade ultrafast TrPL setup, the ultimate goal is to investigate the electronic and optical characteristics of 2D materials at the atomic scale, encompassing both spatial and temporal dimensions.

5:00 PM CH04.03.07
Multi-Modal Synchrotron X-Ray Techniques for Visualizing 3D Brittle Fracture

Every grain in the material had unique stress and strain tensors at each load that were not identical to the applied stress. Crack propagation characteristics such as its speed and path (intragranular or intergranular) were influenced as the crack interacted with these grains and complex micromechanical stress states. Because of the DCDC geometry, the crack could be grown a short distance, and then the loading could be paused along with the crack extension, creating a near-in-situ state for analysis. By using u-CT and HEDM scans in this load-controlled state, the relative extension of the crack with the increase in loading could be monitored, while also providing information on what features and grains in the microstructure caused the crack to slow down, arrest its propagation, or divert its direction of extension. We have found that certain grain orientations and accompanying stress tensors acted as barriers to crack extension and forced the crack either to change directions or to pause and accumulate enough stress concentration energy to advance. These findings can be used to inform computational methods and predictive models for future studies of brittle fracture.

5:00 PM CH04.03.08
Thermal Stability of Calcium Carbonate and its Relationship with The Crystalline Growth of The Mineralized Phases Present in Chicken Eggshells

The application of a uniaxial compressive load caused a crack to pop in to a length on the order of 100 um, and the crack was grown to over 1 mm by the application of further compressive load. The studied material was aluminum oxynitride (AlON), a cubic ceramic with randomly oriented anisotropic grains on the order of 100 um. The Rotational and Axial Motion System (RAMS) [1] at the 1-ID beamline of the Advanced Photon Source at Argonne National Laboratory was used to carefully grow the crack and conduct these experiments. The sample being investigated was machined into the double-cleavage drilled compression (DCDC) geometry with parallelepiped dimensions of 18 mm x 1.4 mm x 1.4 mm and a hole diameter of 0.42 mm. The application of a uniaxial compressive load caused a crack to pop in to a length on the order of 100 um, and the crack was grown to over 1 mm by the application of further compressive load.

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Biomineralization processes in nature are associated with a structural control carried out by biomolecules (DNAs, proteins, and polysaccharides). There are two biomineralization processes, which are usually used by living organisms in terms of producing biominerals: (1) organic matrix-mediated biominalerization, known to be a highly regulated and homogeneous process; (2) biologically induced biominalerization, where mineralization deposits occur definitely and heterogeneously. However, little structural information is known about the macromolecules that constitute and act in the living organisms in these processes, since the level of structural organization of biominerals is often hierarchical in different structural orders to produce a final structure with a unique morphology with properties that until now have not been reproduced by man. Among the processes mediated by a membrane, like in diatoms, of which the importance of biological entities is appreciated, there is a rigid and porous cell wall called a frustule composed of amorphous silica. It also appears in bones comprised mainly of calcium phosphate, and in eggshells whose percentage of calcium carbonate can vary depending on the species. However, there is a lack of a universal model that will allow us to obtain information about these two biomineralization processes. Therefore, this poster presentation will be focused on using the mineral phase and the membranes of the eggshells from chickens that are with a controlled diet (industrial sale) and those that are free (organic) as a model to differentiate the calcification, ensuring its permeability to stabilize the amorphous mineral part. By the thermal stability analysis, we will be able to obtain information on the process of formation of the eggshells as well as on the change that occurs in the membrane during the formation of crystals. The topographical analysis was performed via X-ray diffraction (XRD) and scanning electronic microscopy (SEM). The investigation has an important impact in the fields of biological and materials properties, which would provide an effective understanding of the biomineralization processes. Additionally, this research will also allow us to know how to mimic them since most of the studies carried out are focused on immunohistochemical studies on the formation of the chicken eggshell.

5:00 PM CH04.03.11
Effect of Phase Transition caused by Different Treatment Process on Mechanical Properties of Powder Metallurgy Titanium Alloys Jie Wu; Institute of Metal Research, Chinese Academy of Sciences, China

The microstructural evolution and mechanical properties of powder metallurgy Ti-22Al-24Nb-0.5Mo prepared by combination of hot isostatic pressing, ring rolling, and heat treatment were investigated. Ring rolled and solution treatment in the (α + B2 + O) region led to the refinement of grain size and long lath O phase and α2 phase mostly located at the grain boundaries. Aging treatment in the (B2 + O) region caused the occurrence of peritectoid reaction B2 + α + O → O owing to the segregation of the Nb element and refined the acicular O phase. The mechanical properties of PM alloys varied with the size and volume fraction of O phase and α2 phase. The long lath O phases improve the elongation and acicular O precipitates are benefit to the elevation of alloy strength.

5:00 PM CH04.03.13
A Micro Mechanical and Chemical Analysis of a New Vitrified Rock Material for use in Environmental Sustainability Eve Meltzer and Herbert Einstein; Massachusetts Institute of Technology, United States

Extraction of the energy available via geothermal heat in the Earth could provide substantial contributions to U.S. energy needs long-term. However, there are major technical and economic limitations with the current technology available for Enhanced Geothermal Systems (EGS). I work on a new technology in the field of EGS that uses a millimeter (MM) wave gyrotron, which allows for more efficient ultra-deep drilling. The gyrotron heats rock to temperatures ranging from 1500 to 3000°C, transforming the rock into its liquid state. Upon cooling, the new material solidifies around the circumference of a well bore hole, creating a vitrified lining.

I have conducted an in-depth micro-mechanical and chemical analysis of the vitrified material from the melting and re-solidifying of basalt. Basalt is an igneous rock that forms from the solidification of molten lava and primarily consists of minerals such as plagioclase, feldspar, pyroxenes, and olivine. And thus, when heated, the elements within these minerals go through transformation processes; this includes the formation of iron oxides as well as the possible reduction of iron. To do my study I used a combination of experimental methods including Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), optical imagery, micro-and nano-indentation, and Raman spectrometry. These experiments allow me to quantify the micro- and nano-scale properties. The presence of mineral phase changes and elemental differences in the basalt pre- and post-melting are evident and thus understanding these differences can give insight into the future use of this material in the field of EGS, sustainable mineral extraction, and beyond.

SESSION CH04.04: Dynamics Study by X-ray
Session Chairs: Tao Sun and Tao Zhou
Wednesday Morning, April 24, 2024
Room 443, Level 4, Summit

8:00 AM CH04.04.01
Modulation Excitation Coupled with X-Ray Absorption Spectroscopy for Probing The Restructuring Dynamics of Surface Species in Bimetallic Nanocatalysts Prahlad Kumar Routh

Rational catalyst design guided by a combined theoretical-computational-experimental approach has recently allowed the development of a “dynamic catalyst” using dilute alloy components. These bimetallic nanocatalysts possess dual functionality with a minority metal as the active element and a majority element as a less reactive environment to impart selectivity. Furthermore, the composition and pretreatment of these nanocatalysts can be used to selectively tune the active species on surface. Such dynamic restructuring of surfaces creates a complex behavior of these dynamic catalysts, under operando conditions in response to the changes in reactive environment. A notable challenge is the detailed understanding of the structure and evolving composition of catalytic species on nanoparticle surfaces during reactions. In-situ X-ray absorption spectroscopy (XAS) is a potential tool to elucidate this, but its efficacy is hampered by the dilute and varied nature of active sites. However, the dilute nature of the active sites, heterogeneity associated with nanoparticles as well as active sites, and the ensemble nature of XAS itself, presents significant challenges in sensitivity to active species.

In this work, we addressed these challenges by enhancing XAS sensitivity with a modulation excitation approach, focusing on 30% Pd-Au supported bimetallic nanocatalysts. We applied a modulation excitation approach to the X-ray absorption spectroscopy (ME-XAS) by inducing structural changes in the 30% Pd-Au supported bimetallic nanocatalysts (ca. 6 nm in diameter) via the gas (H2 and O2) concentration modulation and resolved the structure and kinetics of different surface species with time resolution. We demonstrated that ME-XAS dramatically improves the sensitivity towards surface species in bimetallic alloys – the active species in dynamic catalysts. We isolated the minor contributions (3-7 at. %) of different surface species, such as Pd-Au ensembles and Pd oxides, from the total XAS data and discovered that they respond dynamically to the periodic modulation conditions. During the oxygen pulse, the formation of surface PdOOx species dominates over the bulk-to-surface segregation of Pd. During the hydrogen pulse, Pd dissolution within the Au host drives the oxide decomposition. Such direct experimental measurement of the active species in various catalytic systems has been a challenge, given the heterogeneity associated with these active sites and the absence of a technique which can selectively measure the active species and its dynamic evolution as the reaction conditions progress. This work provides an experimental pathway to not only study the dynamic nature of active species but also enables designing non-equilibrium states of dynamic catalysts. The methodology and findings presented herein can be applied to a broad class of multicomponent nanomaterials and processes involving the active minority species, for which the ensemble-average spectroscopy data are dominated by spectators.

8:15 AM CH04.04.02
In-Situ/Operando Bragg Coherent X-Ray Diffraction Imaging for Visualization of Nanoscale Structural Evolution Worasuk Cha,
Argonne National Laboratory, United States

In the last two decades, Bragg Coherent X-ray Diffraction Imaging (BCDI) has become a powerful non-destructive 3D characterization tool for features in nanoscale [1]. Because of unique sensitivity to lattice, BCDI has been employed on various nano-sized materials such as metal, metal oxide, and mineral, to reveal 3D map of lattice distortion and strain distribution. Adding in-situ and operando approaches to BCDI enables to address scientific questions on physics, chemistry, and materials science in recent years.

In this talk, I will introduce current state-of-art of BCDI and recent experimental results on in-situ and operando BCDI. Annealing effect on gold grains on thin films [2], relaxation of strain inside quantum materials such as nanodiamond and silicon carbide [3, 4]. Strain and defect in battery materials [5] and in catalysts [6] will be discussed. In addition, some estimates of BCDI in the near future will be discussed.

The unique imaging power of nano-focused synchrotron hard x-rays can be harnessed to provide non-destructive methods for 3D visualization of crystallographic phase and strain in solid-state materials. This gives access to understanding extremely subtle lattice perturbations (<10^-4 d/c) near optically active defects or interfaces within fabricated heterostructures that can be located potentially microns away from surfaces without sectioning the sample. The use of time-resolved coherent synchrotron illumination synchronized to external stimuli can further augment this approach to understand exciton-driven energy flow and dynamic structure-function relationships across broad classes of classical and quantum materials for energy. Current work and future directions enabled by the near-term completion of diffraction limited storage rings such as the Advanced Photon Source Upgrade (APSU) and correlative data synthesis with quantitative electron microscopy methods will be explored in the context of recent results.

9:00 AM *CH04.04.04
Coherent Acoustic Wave Propagation in Two-Dimensional Metal Halide Perovskites Peijun Guo; Yale University, United States

I will discuss our recent efforts on the development of spatiotemporal optical imaging techniques to examine coherent strain waves in quasi-two-dimensional (2D) metal halide perovskites (MHPs). Specifically, I will describe our experiments performed on a variety of 2D MHPs with different number of octahedral layers, where the experiments employ hyperspectrally-resolved pump and probe pulses and cover a unique nanosecond-to-microsecond time range. The effects of the choices on the halides and the organic cations will be discussed as well. If time permits, I will also discuss our results on the self-trapped excitons in double perovskites examined by optical-pump x-ray diffraction experiments.

10:00 AM *CH04.04.06
Keyhole Dynamics in Laser Powder Bed Fusion Additive Manufacturing Tao Sun; Northwestern University, United States

Laser powder bed fusion (LPBF) is the most extensively used metal additive manufacturing technology due to its unique capabilities in building parts with high geometric complexity and fine features. During the LPBF process, sparks (i.e., sputtered particles) can be observed following the laser scanning path, indicating the presence of high-velocity vapor arising from the melt pool. Indeed, strong metal vaporization occurs in LPBF, resulting in recoil pressure that creates a depression in the melt pool, often referred to as a keyhole. The keyhole is an important dynamic structural feature in LPBF as it influences energy coupling, metal melting mode, and defect generation. Without a keyhole, the laser is absorbed by the metal surface only once, with significant amount of energy being reflected away. In contrast, with the presence of a deep keyhole, multiple laser absorption events occur, significantly increasing laser absorption efficiency. The laser melting mode can shift from conduction to transition, stable keyhole, and then unstable keyhole as the energy input increases. When the conduction mode is applied, lack-of-fusion voids may be generated during the build. An unstable keyhole condition also leads to porosity.

Keyhole porosity is a major defect that hinders the widespread adoption of laser-based metal additive manufacturing technologies. With simultaneous high-speed synchrotron X-ray imaging and thermal imaging, coupled with multi-physics simulations, we discovered two types of keyhole oscillation in laser powder bed fusion of Ti-6Al-4V. Amplifying this understanding with machine learning, we developed an approach for detecting the stochastic keyhole porosity generation events with sub-millisecond temporal resolution and near-perfect prediction rate. The highly accurate data labeling enabled by operando X-ray imaging allowed us to demonstrate a facile and practical way to adopt our approach in commercial systems.

9:45 AM BREAK

10:30 AM CH04.04.07
Gas Pore Formation in Powder Bed Fusion Kai Lin Lyszak, Erin B. Curry, Lauren A. Gorman, Donal Sheets, Lukas Lasig and Jason Hancock; University of Connecticut, United States

Additive manufacturing (AM) of metal materials based on powder bed fusion technology is widely used now in many industries. A known limitation of this type of manufacturing is the formation of gas pores in bulk material arising from stochastic events related to melt pool instability or vapor depression. Here we present a combined X-ray imaging and infrared pyrometry study of pore formation in repeated adjacent tracks, and quantify the correlations of pore positions and sizes for a common material (Aluminum 6061) of interest in AM as a function of its laser processing conditions. We find both in cases that an existing pore in one track often catalyzes the formation of another pore in a consecutive track at the distance of closest approach. In a raster scan strategy commonly used to construct bulk material, this phenomenon has the result of forming perforations, or lines of pores transverse to the scanning direction in a rastered patch. If controlled, this effect can be eliminated to improve the yield strength of the build, or exploited to create programmable failures for specific purposes.

Distribution A. Approved for public release: distribution unlimited. (AFRL-2023-5001) Date Approved 10-10-2023.

10:45 AM CH04.04.09
Operando XAS-XRD Reveals Structural Dynamics in CoPt Nanoparticles under Dry Reforming of Methane Conditions David Niedbalka, Marcel Janak, Diana Piankova, Paula Abdala and Christoph R. Müller; ETH Zurich, Switzerland

Gaining insight into how the geometric and electronic structure of (mono)metallic nanoparticles is modified through the addition of a second metal (bimetallic nanoparticles) and how such structural changes affect in turn their catalytic properties is crucial for the rational advancement of catalysts. Further, as the structure of a catalyst is often dynamic ex-situ characterization methods may be insufficient to describe the active phases of a catalyst. Therefore, operando studies are key to correlate a catalyst’s structure to its performance while relying at the same time on well-defined model systems.

The dry reforming of methane (DRM) is a reaction that converts CH4 and CO2 into a synthesis gas at 600-1000 °C and is typically catalyzed by transition metals such as Ni, Co, or Pt. However, such monometallic catalysts often suffer from deactivation due to particle growth, carbon deposition, and/or oxidation.

In this study, we investigate SiO2-supported, bimetallic CoPt nanoparticles and their monometallic counterparts (CoPtSiO2, CoSiO2, and PtSiO2) for the DRM. Prior to the catalytic DRM tests, all catalysts were activated in-situ in a H2/N2 mixture (1-2 h). The bimetallic CoPtSiO2 catalyst shows superior activity and stability under DRM conditions (800 °C and 1 bar, CH4:CO2 ratio = 1, space velocity = 30,000 ml g^-1 h^-1) in comparison to its monometallic counterparts. Specifically, while Pt/SiO2 showed the lowest CH4 conversion (10%), Co/SiO2 underwent deactivation, resulting in a decrease in CH4 conversion from 30% to 15% within 120 min. Conversely, Co/Pt showed a stable conversion of 35% CH4 conversion over 6 h.

To elucidate the structure of the active phase in CoPt/SiO2 under DRM conditions, and to probe structural dynamics, we conducted operando experiments using combined synchrotron X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD). Co K-edge and Pt L3-edge XAS analysis shows that in CoPt/SiO2 during in-situ activation Co and Pt become both fully reduced to their metallic states. We further observe differences in the Co K-edge and Pt L3-edge XAS features of CoPt/SiO2 when compared to Co/SiO2 or Pt/SiO2, possibly due to a charge transfer between the metals, orbital hybridization in the CoPt alloy and/or a change in the local structure of Pt and Co. The Rietveld analysis of the acquired XRD data after in-situ activation at 800 °C indicates the formation of two types of CoPt alloys: an ordered (intermetallic) CoPt (52%) and a random CoPt alloy (48%). Interestingly, upon switching to DRM conditions (800 °C, CH4:CO2 ratio = 1) XRD analysis revealed an instantaneous transformation of the intermetallic phase into a random alloy. This phase transition was also evidenced in the Pt L3-edge XAS data but did not change the electronic structure/oxidation state of Co (i.e., Co-K edge remained invariant prior to and during DRM). In contrast, under DRM conditions, Co/SiO2 underwent a partial oxidation showing the stabilization of the metallic state of Co through its alloying with Pt. This stabilization, combined with changes in the electronic/local structure and site isolation that very likely suppresses coking on Pt, contribute to the superior activity of CoPt/SiO2 compared to Co/SiO2 and Pt/SiO2.

We also observe a phase transition from a random to intermetallic alloy during the cooling down to room temperature of the reacted catalyst, underscoring the significance of operando characterization in capturing dynamic changes and identifying the catalytically active phase.

(1) Nakaya, Y.; Furukawa, S. Chem. Rev. 2023, 123 (9), 5859-5947.
The novel ultrafast Transient Liquid Assisted Growth (TLAG) method [1-3] is an outstanding opportunity to fabricate low-cost, high throughput epitaxial superconducting YBa$_2$Cu$_3$O$_y$ (YBCO) films using scalable methods. However, the fast kinetics of this non-equilibrium process require in-situ techniques to understand its growth mechanism and determine key process parameters. A specialized instrumentation was developed to allow investigating the dynamics of TLAG process based on in-situ monitoring of the precursors reaction, intermediate phases evolution and final products of the YBCO growth by in-situ XRD at synchrotron radiation sources at acquisition times from 2 - 100 ms/frame. This setup allows to control the key parameters of growth of the YBCO by TLAG, this includes the temperature, partial oxygen pressure, total pressure and the heating rate, as well as to perform very fast changes in total and partial oxygen pressures. Additionally, Mass Spectrometry measures the gaseous products of the reaction. Furthermore, the resistance is measured in-situ throughout all the growth process providing valuable information on the growth rate of the superconducting phase. The installation is placed in a movable rack that allows its use in different synchrotron facilities and all the equipment is time synchronized. All of the acquired data during the combined experiments is advancing our understanding of the non-equilibrium growth mechanism and pinpoints the direction to the optimal conditions for ultrafast epitaxial growth of YBCO reaching up to 1000 nm/s.

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SESSION CH04.05: Self-assembly
Session Chairs: Yuzi Liu and Michelle Mejia
Wednesday Afternoon, April 24, 2024
Room 443, Level 4, Summit

1:30 PM *CH04.05.01
Peering into the Self- and Directed-Assembly of Nanoparticles [Honeycom Fan, Sandia National Laboratories, United States]

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

Sandra National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

2:00 PM CH04.05.02
Design of Open Systems using Aqueous Polymer Solutions causing Meniscus Splitting Phenomena [Reina Haigwan and Kosuke Okeyoshi; Japan Advanced Institute of Science and Technology, Japan]

Self-organization is a process commonly observed in soft matter and in spontaneous phenomena of life. Extracting and reproducing in vitro the physicochemical conditions is an important step beyond designing “life-like” materials having smart responses to environmental change. The behavior of polymeric solutions is known as viscous fingering. We have reported “meniscus splitting”[1], in which the pattern formed on a substrate is developed into a millimeter-scale spatiotemporal structure. This is a non-equilibrium phenomenon in the controlled evaporation of polymer solution that splits the air-water interface into multiple regions. Drying an aqueous polymer dispersion from one interface in a limited space causes the polymer to precipitate at a specific position, driven by capillary forces. Also, the deposited polymer membrane has an oriented structure and becomes a functional material such as a humidity actuator[1]. However, the specific spatiotemporal changes at the interface observed in the meniscus-splitting phenomenon have only been shown using some biopolymers, and the regulatory factors toward the universalization are unclear.

In this study, we demonstrate that meniscus splitting can happen with chemical species independence, and it is a universal phenomenon, through the experiment. Polyacrylic acid (PAAc), polycrylamide (PAAm), and polyvinyl alcohol (PVA) were used as synthetic vinyl polymers for the demonstration. The effect of different molecular weights on the interfacial behavior was pronounced, indicating that molecular weights with appropriate viscosity are necessary for membrane formation. PAAC and PAAm exhibited a splitting pattern like that of the polysaccharides reported previously. On the other hand, PVA did not form vertical membranes, but rather horizontal ones. This difference is thought to be due to the reactivity of water, and PVA’s propensity to form intra- and intermolecular hydrogen bonds. When the relative humidity was adjusted, vertical membrane was also formed for PVA as well as for the other chemical species. Furthermore, we attempted a mathematical analysis of the spatiotemporal changes in the specific interfacial shape observed during the drying process. To understand the transformation of the interface the characteristic interface curves were fitted by a hyperbolic curve or an elliptic curve. Through the fitting evaluation, it was suggested that the interface curves transformed from a hyperbolic curve to an elliptic curve during the splitting.

Reference:

SESSION CH04.06: Surface and Chemistry
Session Chairs: Lixi Li and Yang Yang
Wednesday Afternoon, April 24, 2024
Room 443, Level 4, Summit

3:30 PM CH04.06.01
Electronic Characterization of 9A-GNR on H:Si(100) using a Scanning Tunneling Microscope [Abigail Berg1, Mamun Sarker2, Anshual Saxena3, Narayana R. Aluru3, Alexander Sinitskii2 and Joseph Lyding1; 1University of Illinois at Urbana-Champaign, United States; 2University of Nebraska–Lincoln, United States; 3The University of Texas at Austin, United States]

We present the electronic characterization of a new solution-synthesized type graphene nanoribbon (GNR). The GNR was synthesized with two different precursors to form coves along the length of an N=9 armchair GNR. The GNR also contains two different functional end groups, -NO2 and -NH2, with each synthesized to attach to the two different precursors. Atomically precise graphene nanoribbons with functional end groups have the potential for further modification and integration into complex electronic structures. We use the dry-contact transfer (DCT) method to exfoliate the GNRs onto hydrocarbon passivated Si(100) in a room temperature ultra-high vacuum (UHV) scanning tunneling microscope (STM). The bandgap and density of states are
Gibbsite (α-Al(OH)₃) is naturally abundant and plays a vital role as a raw material in various industrial applications. Furthermore, it constitutes a significant portion of the solid components in aqueous systems and industrial waste. Our study uses a new approach for investigating the role of diffusion in modifying laser-pretreated adhesive joints. Scanning electron microscopy (SEM) was utilized to observe the effects of heating on surface morphology. To illustrate the effect of various parameters on the surface morphology, we performed experiments under different conditions. The results show that heating at temperatures above 1000°C leads to a significant change in the surface texture, with a decrease in the roughness and an increase in the crystallinity of the surface. Consequently, the mechanical properties of the adhesive joints were improved, with an increase in the bond strength and a decrease in the failure rate. This study highlights the importance of understanding the diffusion processes in laser-pretreated joints and provides insights for improving the durability and reliability of adhesive bonds.
In this contribution several examples of a dynamic use of APT will be reported: (i) the formation of molecular ions in silicon carbide, with its consequences on spatial and compositional accuracy of APT reconstructions[2], (ii) the microscopic assessment of single reactions involving molecular hydrogen adsorbed at the surface of III-N materials [3] and (iii) the field-dependent formation of hydride molecules in III-N materials. The perspective extension of these dynamic APT approaches to other materials and surface chemical reactions will finally be discussed.

SiO$_2$ is one of the most important dielectric materials used as gate insulators and interlayer films in nanoelectronic devices. Although the density of SiO$_2$ has been evaluated by the Si-O-Si stretching vibration peak using IR (infrared spectroscopy) [1] so far, there is no established technique to evaluate the density distribution in the nanoscale area. In this work, we develop a technique for nanoscale evaluation of SiO$_2$ using STEM (scanning transmission electron microscopy) – EELS (electron energy loss spectroscopy). While there are a number of reports on vibrational spectra measured by STEM-EELS [2,3], a method for density evaluation using EELS has not been established yet. We found differences in the stretching vibration peaks reflecting the density between SiO$_2$, with different atomic structures: α-quartz (2.648 g/cm$^3$) and silica glass (2.2 g/cm$^3$). The dependence of the stretching peak on the thickness of the STEM specimen was investigated in detail by experiment and spectral calculation using a dielectric model.

IR spectra showed that the FWHM (full width at half maximum) of the stretching peak was larger for silica glass than for α-quartz. This corresponds to lower density in the silica glass as a result of greater variation in the Si-O-Si bond angle [3]. We also measured vibrational EELS spectra using STEM with a nanometer resolution and a high energy resolution of 16 meV (FWHM of the zero-loss peak). The FWHM of the stretching peak for silica glass was observed to be 5 meV larger than that for α-quartz, which is consistent with the IR results. On the other hand, simulations based on the Kröger formula [4] showed the experimental stretching peaks reflect both surface scattering and bulk scattering. This simulation suggests the specimen thickness is a key factor when comparing the different samples, because the contribution of surface scattering strongly depends on the specimen thickness. Thus, to establish our evaluation method by STEM-EELS, we investigated in detail the dependence of the stretching peaks on specimen thickness in the range of 30 nm to 100 nm. By comparing the FWHM of the samples with the same specimen thickness, we confirmed that there is a significant difference of more than 4 meV in the stretching peaks between silica glass and α-quartz for all the thicknesses.

We prepared α-quartz locally amorphized by electron irradiation for a longer duration (~50,000 times longer) than the vibrational EELS measurements, and investigated its density using the established evaluation method. As a result, the amorphized α-quartz was found to be denser than silica glass and to have the same density as α-quartz. This suggests that the atomic number of α-quartz is maintained during the amorphization under the low electron current (~10 pA) irradiation, which does not cause significant atomic desorption. These results indicate that vibrational EELS using STEM is a promising technique for local density analysis of SiO$_2$.


9:30 AM BREAK

10:00 AM CH04.07.05
Dynamic Atomic-Scale Fundamental Mechanisms of the Initial Stages of Cu Oxidation Revealed by Environmental Transmission Electron Microscopy

Jürgen C. Yandl1,2, Meng Li2, Matt Curran3, Linna Qiao3, Dmitri N. Zakharov1, Guangwen Zhou1 and Wissam Saidi5,2; 1Brookhaven National Laboratory, United States; 2University of Pittsburgh, United States; 3Pohang University of Science and Technology, Korea (the Republic of); 4Binghamton University, State University of New York, United States; 5NETL, United States

Surface oxidation is an important process for corrosion, which costs a few percent of the U.S. Gross Domestic Product (GDP) each year. Much is known about oxygen interaction with metal surfaces and the macroscopic growth of thermodynamically stable oxides. At present, however, the transient stages of oxidation - from nucleation of the metal oxide to formation of the thermodynamically stable oxide - represent a scientifically challenging and technologically important terra incognita. These issues can only be understood through a detailed study of the relevant microscopic processes at the nanoscale in situ. We have previously demonstrated in situ transmission electron microscopy (TEM) that the formation of epitaxial Cu$_2$O islands during the transient oxidation of Cu(100), (110), and (111) films bear a striking resemblance to heteroepitaxy, where the initial stages of growth are dominated by oxygen surface diffusion and strain impacts the evolution of the oxide morphologies. To deepen our understanding of the atomic-scale dynamic processes of Cu$_2$O island formation on Cu during oxidation in situ, we are currently using copper-coated high-resolution environmental TEM (ETEM) and atomicistic theoretical simulations. As an example of this approach, preferential monolayer-by-monolayer growth along Cu$_2$O(110) planes was noted instead of along Cu$_2$O(100) planes. Correlated Density Functional Theory (DFT) simulations on the surface and diffusion energies during Cu$_2$O growth on various CuO$_2$ surface orientations and terminations were carried out. Our DFT results show that monolayer formation of Cu$_2$O along Cu$_2$O(110) was both thermodynamically and kinetically preferred over that of Cu$_2$O(100) during Cu$_2$O growth, which explains the observed phenomena. These results shed new light on the epoxide oxide growth mechanism and provide a deeper understanding of the dynamic processes involved in initial oxidation, which will ultimately help to precisely predict, design, and control nanostructured oxide growth for either corrosion-protection or creating nano-oxides for their functional properties. Furthermore, advancing hardware and software for enhancing in situ experiments will be discussed. We gratefully acknowledge support from the National Science Foundation (NSF), including NSF-CMMI 1905647, NSF-DMR 1410055, 1508417, 1410335. This research used the electron microscopy resources of the Center for Functional Nanomaterials (CFN), which is a U.S. Department of Energy Office of Science User Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

10:30 AM CH04.07.06
Enabling sustainable chemical manufacturing with atomically-optimized photocatalysts

Jennifer A. Dionne; Stanford University, United States

Chemical manufacturing is critical for industries spanning construction, plastics, pharmaceuticals, food, and fertilizers, yet remains among the most energy-demanding practices. Optical excitation of plasmons offers a route to more sustainable chemical synthesis. Plasmons create nanoscopic regions of high electromagnetic field intensity that can modify electronic and molecular energy levels, enable access to excited-state dynamics, and open new reaction pathways that are impossible to achieve under typical conditions. Further, plasmons can be efficiently excited with sunlight or solar-driven LEDs, for sustainable chemical transformations.

Here, we present our research advancing plasmon photocatalysis from the atomic to the reactor scale (see Figure 1). First, we describe advances in in-situ atomic-scale catalyst characterization, using environmental optically-coupled transmission electron microscopy. With both light and reactive gases introduced into the column of an electron microscope, we can monitor chemical transformations under various illumination conditions, gaseous environments, and at controlled temperatures, correlating three-dimensional atomic-scale catalyst structure with photo-chemical reactivity. Then, we describe how these atomic-scale insights enable optimized reactor-scale performance. As model systems, we consider three reactions: 1) acetylene hydrogenation with Ag-Pd catalysts; 2) CO$_2$ reduction with Au-Pd catalysts; and 3) nitrogen fixation with AuRu catalysts. Here, Au/Ag acts as a strong plasmonic light absorber while Pd/Ru serves as the catalyst. We find that plasmons modify the rate of distinct reaction steps differently and that reaction nucleation occurs at electromagnetic hot-spots – even when those hot-spots do not occur in the preferred nucleation site. Plasmons also open new reaction pathways that are not observed without illumination, enabling both high-efficiency and selective catalysis with tuned bimetallic catalyst composition. Our results provide a roadmap for how atomically-architected photocatalysts can precisely control molecular interactions for high-efficiency and product-selective chemistry.

11:00 AM CH04.07.07
Structural Studies of 2D Perovskites for Catalyst Support Applications by Environmental Transmission Electron Microscopy

Dmitri N. Zakharov; Brookhaven National Laboratory, United States

Two-dimensional perovskites gained traction for applications in various optoelectronic and sensor devices. Another potential application for this class of material is as a catalyst support, as epitaxial relationships between catalyst and support can be utilized to gain control over catalyst active sites in catalyst activity studies. Nanosheets of Sr$_2$Nb$_3$O$_{10}$ (SNO) with two-beam conditions show contrast from grain boundaries of misoriented grains. Planar defects (PD) running at an angle to the imaging plane reveal alternating contrast. Some areas show excited with sunlight or solar-driven LEDs, for sustainable chemical transformations. Further, plasmons can be efficiently excited with sunlight or solar-driven LEDs, for sustainable chemical transformations.
Ultrafast transmision electron microscopy (UEM) methods have become a new frontier in materials science due to the ability to follow dynamics on time scales down to hundreds of femtoseconds with nanometer spatial resolution. Imaging on ultrafast time scales reveals nonequilibrium metastable states of matter, phonon transport pathways in materials, and plasmon dynamics. This presentation will overview some of these ultrafast methods, and provide examples of how they have been used to enable new understanding of materials.

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

MeV Electron Time-Resolved Total Scattering for Material Dynamics Xiile Wang; SLAC National Accelerator Laboratory, United States

The MeV electrons produced by the photocathode RF gun made it feasible for MeV ultrafast electron scattering [1-2]. MeV ultrafast electron scattering became a new frontier in ultrafast science due to its capability of following dynamics on femtosecond scale with the high spatial resolution and sensitivity [3-4]. Furthermore, MeV electrons experience less multiple-scattering, and possess "real" flat Ewald-sphere; MeV ultrafast electron diffraction (MeV-UED) is an ideal tool to explore both structure and dynamics using total scattering technique. Total scattering has been explored by X-ray and Neutron scattering communities to study energy materials, the time-resolved total scattering enabled by MeV-UED make it feasible to image structure dynamics and energy transfer in 2-D heterostructure [5] and revealing the intricate relation between dynamics and function of 2-D perovskite [4].

I will discuss many advantages of MeV electron for total scattering. MeV electron total scattering not only produces stronger diffraction signal and sensitive to the structure change, but also has less background and no geometric correction. Furthermore, we have experimentally demonstrated that MeV electron total scattering is capable of probing both electronic and nuclear structure dynamic [5]. MeV-UED enabled the first ultrafast operando [6] and in-situ [7] experiments.


Capturing Laser Induced Dynamics of Materials via Ultrafast Transmission Electron Microscopy Volkan Ortalan; University of Connecticut, United States

Recent developments in instrumentation have made it a very exciting time to perform both fundamental and applied research in the electron microscope. In-situ microscopy is moving forward at a rapid pace with the development of gas/liquid stages that permit reaction processes to be imaged and analyzed at atomic resolution. Moreover, the development of nanosecond and faster photoemission electron sources offers the chance to move the high spatial resolution world of electron microscopy into the ultrafast world of materials dynamics. Conventional in-situ TEM coupled with ultrafast TEM can be utilized to gain a fundamental understanding of dynamic processes occurring in materials. The combination of these capabilities allow for vast improvements of in-situ TEM studies limited by video rate in that many processes span multiple time and length scales. Ultrafast in-situ electron microscopy promises to answer challenging questions in the fields ranging from materials science and chemistry to nanoscience and biology. In this presentation, examples of ultrafast electron microscopy studies will be presented for selected systems. Short lived transient processes involved in dynamic processes in materials will be discussed to obtain new insights. Additionally, the potential of novel in-situ stages for various data acquisition schemes to push the envelope of ultrafast electron microscopy for the investigation of materials will be discussed.

High-Speed Imaging Techniques for Imaging High-Jitter Dielectric Breakdown Noah Hopkins1, Kathryn Sturges1, Jonathan E. Barney2, Brian L. Beaudoin2, Ariana Bussio3, Ashley E. Hammell1, Samuel Henderson1, James Krutzler1, Joseph P. Lichhardt1, Alexander H. Mueller2, Karl Smith2, Bryce Tappan2 and Timothy W. Koehl1,2,1University of Maryland, United States; 2Los Alamos National Laboratory, United States

Imaging mechanically induced dielectric breakdown, which operates on ultra-short timescales, poses a formidable challenge. A significant hurdle in this endeavor is breakdown initiation jitter, where even a tenth of a microsecond of timing deviation can frustrate imaging efforts. Our initial attempt to use a gigahertz frame rate camera to record dielectric breakdown initiated by an exploding bridge wire detonator was hindered by pronounced initiation jitter.

To surmount this obstacle, we developed an innovative optical image delay line apparatus to mitigate the effects of breakdown jitter on imaging performance. In this presentation, we delve into the design and performance of this optical delay line apparatus, showcasing its transformative impact. The integration of the optical delay line increased image capture success rate from 25% to 94%. Moreover, it facilitated superior temporal resolution. Beyond its applicability in the realm of dielectric breakdown, this technique holds promise for imaging other high-jitter, ultra-fast phenomena.

Imaging Quantum Coherence using Electron Wavepackets Ido Kaminer1 and Giovanni Maria Vanacone2; 1Technion, Israel; 2The University of Milano-Bicocca, Italy

Until recently, work in quantum optics focused on light interacting with bound-electron systems such as atoms, quantum dots, and nonlinear optical crystals. In contrast, free-electron systems enable fundamentally different physical phenomena, as their energy distribution is continuous and not discrete, allowing for tunable transitions and selection rules. Free electrons also enable unique capabilities in microscopy and spectrosocopy that are otherwise inaccessible.

Recent theoretical and experimental breakthroughs involving quantum interactions of free electrons spawned an exciting new field: free-electron quantum optics. We developed a platform for exploring coherent electron-electron interactions at the nanoscale, and used it to demonstrate the coherent interaction of a free electron with quantum statistics of photons. This platform enables new pathways toward using free electrons as carriers of quantum information. Concepts of quantum optics with free electrons also promote new modalities in electron microscopy. We recently demonstrated the first instance of coherent amplification in electron microscopy. Specifically, we present an algorithm-based microscopy approach that uses light-induced electron modulation to demonstrate the coherent amplification effect in electron imaging of optical near-fields. We provide a simultaneous time-, space-, and phase-resolved measurement in a microdrum made from a hexagonal boron nitride membrane, visualizing the sub-cycle dynamics of 2D polarization wavepackets therein. Our experiments show a 20-fold coherent amplification of the near-field signal compared to conventional electron near-field imaging, resolving peak field amplitudes of few kV/m.

Our vision is to develop a microscope that can image coherence, going beyond conventional imaging of matter to also image the quantum state of matter and probe quantum correlations between individual quantum systems.

**Uncovering Microscopic Interactions in Skyrmion Hosts via Lattice Dynamics**

CH04.08.08

4:30 PM DISCUSSION TIME


**References:**

Work at BNL was supported by the DOE-BES-MSED under the grant DE-SC0012704.

**In this presentation, several of our research examples are selected to highlight the characterization of materials dynamics in strongly correlated systems. I will focus on ultrafast phenomena and charge-lattice and spin-lattice correlations. For instance, I will show:**

1) A new two-color scheme based on near-field electron microscopy (PINE), one for temporal gating, the other for pumping to achieve nm-spsp/atemporal resolution, ultrastable dielectric response and insulator-to-metal transition in nanowires [1]; 2) quantitative diffraction and diffuse scattering analysis to capture the photoinduced ultrafast atom dimerization and rotation dynamic pathways [2] and the evolution of optical and acoustic phonon population in charge-density-wave materials [3] using VE-UED; and 3) study electromagnetic wave propagation in interrogated comb device that is widely used as an antenna or sensor in mobile platforms [4] and observe spin wave dynamics under microwave excitation using the GHz electron pulser we developed at BNL. The ability to probe material dynamics responses under RF excitations has promising applications for qubit devices and quantum information science.

Work at BNL was supported by the DOE-BES-MSED under the grant DE-SC0012704.

**References:**


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**New Approaches of Ultrafast Electron Microscopy for Quantum Materials**

Yimei Zhu; Brookhaven National Laboratory, United States

In this presentation, several of our research examples are selected to highlight the characterization of materials dynamics in strongly correlated systems. I will focus on ultrafast phenomena and charge-lattice and spin-lattice correlations. For instance, I will show: 1) A new two-color scheme based on near-field electron microscopy (PINEM), one for temporal gating, the other for pumping to achieve nm-spsp/atemporal resolution, ultrastable dielectric response and insulator-to-metal transition in nanowires [1]; 2) quantitative diffraction and diffuse scattering analysis to capture the photoinduced ultrafast atom dimerization and rotation dynamic pathways [2] and the evolution of optical and acoustic phonon population in charge-density-wave materials [3] using VE-UED; and 3) study electromagnetic wave propagation in interrogated comb device that is widely used as an antenna or sensor in mobile platforms [4] and observe spin wave dynamics under microwave excitation using the GHz electron pulser we developed at BNL. The ability to probe material dynamics responses under RF excitations has promising applications for qubit devices and quantum information science.

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**References:**


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**Uncovering Microscopic Interactions in Skyrmion Hosts via Lattice Dynamics**

Andi M. Barboux1; Myung-Geun Han1; Fernando Camino1; Chuhang Liu1; Mario Cucco2; Yimei Zhu1 and Claudio Mazzoli1; 1Brookhaven National Laboratory, United States; 2Consiglio Nazionale delle Ricerche, Italy

NSLS-II’s Coherent Soft X-ray (CSX) beamline has world leading coherent soft x-ray flux and, as such, can provide insight to materials traditionally studied with either neutrons or electron microscopy (EM). In other words, bulk versus neara-surface, respectively. The highly tunable CSX beamline can close this gap since “bulk-like” and EM specific free-standing films are readily investigated using soft x-ray resonant elastic scattering (REXS). Capitalizing on this capability, we turn to study interacting skyrmions. Most skyrmion hosting materials are conducting metal alloys (the B20 metals), and these materials do exhibit interesting skyrmion lattice dynamics. However, Cu2OSeO3 (CSO) offers an interesting comparison since it is a vastly different material, being an insulator and exhibiting magnetoelectric coupling – which are attractive properties for devices. We will present new findings associated with skyrmion lattice (SLL) dynamics in CSO. Recently reported rotational dynamics of the SLL are currently thought to be induced by either thermal gradients [1] or magnetic field gradients [2]. By combining coherent X-rays and REWS, we can interrogate the structure and dynamics of rotating and non-rotating SLL points in a highly controlled manner. In collaboration with LTEM researchers, we are able to expand our findings with complementary LTEM experiments.


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**Identifying Degradation Mechanism in Cathode Materials for Lithium Batteries with Precession Electron Diffraction**

Hyungcheol Shim1; Young-Woon Byeon2; Seungmin Hyun1 and Jae-Pyoung Ahn2; 1Korea Institute of Machinery and Materials, Korea (the Republic of); 2Korea Institute of Science and Technology, Korea (the Republic of)

Due to the explosive growth of the electric vehicle market, recently, attention to lithium ion batteries (LIBs) is increased. The specialty of automotive applications is promoting the development of long-life batteries based on material technology. Developing a reliable LIB begins with understanding the mechanism of degradation of the material. In other words, based on the degradation mechanism of the material analyzed from accurate and various angles, we can propose a design method of robust material that is one step further.

In this study, we tried to analyze the cause of the deterioration of cycling characteristics for Li(Ni1/3Co1/3Mn1/3)O2, which is mainly used as a cathode material for LIBs, by precession electron diffraction (PED). In other words, we wanted to know the causes of degradation in the whole system by analyzing the material properties at a single crystal in nanoscale. For the analysis of extremely small ranges of materials, we analyzed the degradation mechanism of the material in the sub-10nm range using Precession Electron Diffraction (PED) techniques. The PED method can reduce the dynamic diffraction phenomenon according to the thickness of the TEM sample, so that the diffraction intensity can be quantified within a very small range. By using the PED technique based on nano-sized electron beams, we were able to map the structural change of Li(Ni1/3Co1/3Mn1/3)O2 material in a single crystalline unit over a long period of electrochemical cycles.

It is known that the main cause of the decrease in LiB’s capacity over the electrochemical cycles is the formation of an electrochemically irreversible rock salt phase inside the cathode material. However, the PED analysis showed that we could identify the existence of new metastable phase that had not discovered before. In other words, accelerated testing results revealed new unstable phases due to cation migration and found that the presence and distribution of these phases had a decisive effect on LiB’s electrochemical degradation. In addition, the quantitative relationship between the strain and phase transition also could be derived. Therefore, based on these results, we expect that PED based on nano-sized electron beams can add new perspectives to the analysis of the degradation mechanism of materials for LIBs.

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**Unveiling The Distribution and Dynamic Behavior of Multi-Valent Chromium Ions in Li(SiC1−xInx)O2:Cr Phosphors via In-Depth X-Ray Characterization**

Yi-Ting Tsai and Mu Huai Fang; Research Center for Applied Sciences, Academia Sinica (RCAS), Taiwan

Cr3+-doped inorganic compounds have played an important role in the development of near-infrared optical materials. However, the presence and distribution of multi-valent Cr ions remains unclear. In this study, we examined a series of Li(SiC1−xInx)O2 phosphors doped with Cr3+ using X-ray techniques from National Synchrotron Radiation Research Center. Through high-resolution synchrotron X-ray diffraction, we identified two closely related phases within Li(SiC1−xInx)O2. Ramon spectra also confirmed distinctive scattering patterns for the two end-members of the compositional range, consistent with our XRD results. Further investigation using Cr K-edge X-ray absorption near edge structure and extended X-ray absorption fine structure techniques revealed the prevalence of Cr6+ ions in the initial samples. However, a significant shift occurred towards Cr3+ dominance upon water washing. We also used X-ray fluorescence and
5:00 PM CH04.09.05
Unraveling the Interfacial Behavior of Double Functionalized Silica Nanoparticles at Oil-Water Interfaces: Insights from Atomic Force Microscopy, In Operando Ultrasmall and Small-Angle and X-ray and Interfacial Rheology Measurements Ahmed W. Almasaeq1, Sohaib Mohammed1, Bashayer Aldakkan1, Nikolaos Chalmpes1, Antonios Koulopoulos1, Georgia Potsi1, Gheesha Gadikota1, Mazen Kanj2 and Emmanuel P. Giannelis1; Cornell University, United States; King Fahd University of Petroleum and Minerals, Saudi Arabia

Tuning interfacial interactions of emulsions is of utmost importance in addressing hydrocarbon contamination of water resources and facilitating sustainable synthesis and processing of organics across different industries, such as energy recovery, pharmaceuticals, and the food industry. In this comprehensive study, we investigated the assembly of colloidal stable silica nanoparticles (NPs) at the oil-water interface, employing a novel double functionalization strategy. The NPs were functionalized with a blend of two silanes, one based on a quaternary ammonium group and the other combining primary and secondary amine groups, thereby endowing them with a positive charge. By modulating the charges on both the NPs’ surface groups and the oil phase, either by pH adjustments or the addition of electrolytes, we controlled the assembly and behavior of the emulsion. The careful combination of tunable charge and specifically chosen silane coupling agents provided the NPs with outstanding colloidal stability, which is significant for practical applications.

To evaluate the colloidal stability of the NPs, we conducted accelerated Space-Time Extinction Profiles (STEP®) measurements in brine solutions up to 60,000 ppm containing monovalent and divalent electrolytes to prepare model emulsions up to 60 °C. Remarkably, even under these harsh conditions, the NPs displayed exceptional stability. Assembly of the NPs at the oil-water interface can be controlled by balancing the pH or in the presence of electrolytes. Specifically, at pH 9 or in high salt concentrations, the interfacial tension (IFT) was substantially reduced from 35 nN/m to 5 nN/m and 2 mN/m, respectively.

To gain further insights into the interface properties of the emulsion, we used Ultrasmall/Angle-X-ray scattering measurements, which unequivocally confirmed the presence of nanoparticles at the interface. Moreover, we found a correlation between the time-dependent scattering profiles and the dynamics of the growth of the interfacial film. To explore the nanomechanical characteristics of the interface, Atomic Force Microscopy (AFM) was employed. Notably, in the presence of the NPs at pH 9, the stiffness of the interface was substantially lower compared to acidic and neutral conditions, in brine or at pH 9 the assembly leads to jamming, reminiscent of an elastic membrane characterized by high dilatational and storage moduli.

Leveraging the jamming phenomenon, we demonstrated the efficacy of our approach in forming oil droplets, thereby showcasing its potential for oil spill remediation. Additionally, our method facilitated the preparation of highly moldable and printable oil-in-water emulsions, presenting novel opportunities in various applications in the fields of environmental remediation, catalysis, drug delivery, food technology, and oil recovery.

5:00 PM CH04.09.07
Effects of Topological Parameters on Thermal Properties of Single-Walled Carbon Nanotubes by Molecular Dynamics Simulation Lida Naimi and Zhong Hu; South Dakota State University, United States

Due to their enhanced properties, carbon nanotubes (CNTs) are increasingly used in various industrial sectors. Specifically, the thermal conductivity of these materials is affected by heat transfer mechanisms across multiple scales, leading to a complex relationship between the effective response and the microscopic characteristics of the material. Due to their high thermal conductivity, CNTs have applications in various fields including electronics, materials science, and thermal management. They are incorporated into composites, films, and other materials to enhance their thermal performance. In this topic, the thermal properties of single-walled carbon nanotubes (SWNTs) are investigated using molecular dynamics (MD) simulation. The effects of the chirality, diameter, and length of SWNTs on the thermal properties were studied using the reverse non-equilibrium molecular dynamics (RNEMD) method and the carbon-carbon based Tersoff interatomic potential based on the Large-scaled Atomic/Molecular Massively Parallel Simulator (LAMMPS). The SWNTs studied have tube lengths of 5, 10, 15 and 20 nm, respectively.

The thermal conductivity follows a law. The exponent B is insensitive to the chirality of the CNT; B at room temperature is about 0.89 and 0.69 for zigzag and armchair CNTs, respectively. Although thermal conductivity increases with increasing the chirality angle, and armchair SWNTs have higher thermal conductivity than zigzag CNTs, the effect of chirality on the thermal conductivity for longer CNTs decreases. Therefore, for longer length SWNTs, the thermal conductivity of the zigzag is greater than that of the armchair ones. Through research on SWNTs of different diameters, it was found that at the same chirality angle, the thermal conductivity of SWNTs decreases with the increase in diameter, while SWNTs with greater chiral angles exhibit higher thermal conductivity than those of the same diameter. The thermal conductivity follows a law, and the exponent B is insensitive to the chirality angle of the CNTs; B of zigzag and armchair CNTs at room temperature are about 0.43 and 0.26, respectively. In addition, the thermal resistance at the CNT’s interfaces was studied as a function of the nanotube spacing, overlap, and length. The simulation results were compared with the experiments and simulation results from the literature which are in agreement. The presented approach can be applied to study the properties of other advanced materials.

5:00 PM CH04.09.08
In-Situ Electron Channeling Contrast Imaging of Local Deformation Behavior of Lath Martensite in Low-Carbon Steel Shuang Gong and Junya Inoue; University of Tokyo, Japan

This study reveals the dislocation dynamics that control the local deformation behavior of lath martensite in low-carbon steel using a combination of in-situ tensile Electron Channeling Contrast Imaging (ECCI) and X-ray based Convolutional Multiple Whole Profile (CMWP) fitting methods.

Lath martensite, characterized by distinct anisotropy in its local deformation behavior, poses challenges for its ductility in engineering applications. Unveiling the local dislocation dynamics driving this behavior is crucial for material optimization. Recent studies using X-ray and neutron diffraction line profile methods have successfully employed the CMWP fitting method to probe the macroscopic evolution of dislocations in this material. Building on the foundation of this innovative approach, this study presents an integrative use of advanced X-ray analysis and in-situ tensile ECCI, which allows for microscopic direct observation of dislocation motion dynamics, directly linking them with the macroscopic evolutions.

By capturing X-ray diffraction patterns before and after a specific elongation threshold, and applying CMWP fitting, the study accurately determines the dislocation density, character, and arrangement within the lattice. The analysis meticulously tracks the behavior of dislocations, identifying intra-lath crystallographic slip and boundary sliding as the two primary deformation processes. The onset of dislocation movement signifies the commencement of microscopic yielding. As the stress applied to the material increases, a transition to macroscopic yielding is observed, characterized by the ability of dislocations to navigate through and overcome densely packed dislocation walls within the laths. Near the lath boundaries, the pile-up of dislocations from out-of-lath-plane slip systems contrasts with the ongoing movement of those in-lath-plane, which are mainly responsible for plastic deformation.

Further, this study successfully captures the boundary sliding phenomenon and clarifies the critical resolved shear stress (CRSS) required for this process to become the dominant form of plastic deformation following work hardening. The swift movement of the dislocation network close to the boundaries is particularly emphasized, as it plays an important role in mediating boundary sliding.

In summary, the correlation between the dislocation structure evolution observed through in-situ tensile ECCI and the evaluation made by CMWP fitting elucidate the intricate mechanism of plastic deformation in low-carbon steel lath martensite, with profound implications for enhancing the ductility of the material for industrial applications.

5:00 PM CH04.09.09
Disentangling Thermal from Electronic Contributions in The Spectral Response of Photo-Excited Perovskite Materials Li Jie Wang1,2, Razan O. Nughays1, Omar F Mohammed1 and Majed Chergui2; KAUST, Saudi Arabia; EPFL, Switzerland

Disentangling electronic and thermal effects in photo-excited perovskite materials is crucial for photovoltaic and optoelectronic applications, but remains a challenge due to their intertwined nature in both the time and energy domains. In this study, we employed temperature-dependent variable-angle spectroscopic ellipsometry, density functional theory calculations, and broadband transient absorption spectroscopy spanning from the visible to mid-to-deep-Ultraviolet (UV) ranges on MAPbBr3 thin films. The use of deep-UV detection opens a new spectral window that enables the exploration of high-energy excitations at various symmetry points within the Brillouin zone, facilitating the understanding of the ultrafast responses of the UV bands and the underlying mechanisms governing them. Our investigation reveals that the photo-induced spectral features remarkably resemble those generated by pure lattice heating, and we disentangle the relative thermal and electronic contributions and their evolutions at different delay times using combinations of decay-associated spectra and temperature-induced differential absorption. The results demonstrate that the photo-induced transients possess a significant thermal origin and cannot be attributed solely to electronic effects. Following photo-excitation, as carriers (electrons and holes) transfer their energy to lattice, the thermal contribution increases from ~15% at 1 ps to ~55% at 300 ps, and subsequently decreases to ~35-50% at 1 ns. These findings elucidate the intricate energy exchange between charge carriers and lattice in photo-excited perovskite materials, and provide insights into the limited utilization efficiency of photo-generated charge carriers.

5:00 PM CH04.09.11
Water-in-salt electrolytes have attracted considerable interest in the past decade for advanced lithium-ion batteries, possessing important advantages over the non-aqueous electrolytes currently in use. A battery with a LiTFSI–water electrolyte was demonstrated in which an operating window of 3 V is made possible by a solid–electrolyte interface. Viscoelasticity is an important property for such electrolytes, because high viscosity is normally associated with low ionic conductivity. Here, we investigate shear and longitudinal viscosities using shear stress and compressional longitudinal stress measurements as functions of frequency and temperature. We find that both viscosities are frequency-dependent and exhibit almost identical frequency and concentration dependences in the high-concentration region. A comparison to quasielectric neutron scattering experiments suggests that both are governed by structural relaxation of the TFSI–network. Thus, LiTFSI–water electrolytes appear to be an unusual case of a non-Newtonian fluid, where shear and longitudinal viscosities are determined by the same relaxation mechanism.

5:00 PM CH04.09.12
Evaluation of Anti-Icing/De-Icing Performance of PU Topcoat with CNT Addition in Aircraft Applications
Lee Donghyeon, Yang Seong Baek and Kwon Dong-Jun; Gyeongsang National University, Korea (the Republic of)

Icing on aircraft can lead to increased weight, reduced lift, and pose a risk of accidents. Methods for removing aircraft icing include the use of deicing solutions like glycol or employing techniques such as heating and vibration. However, these methods have limitations in terms of applicable areas, energy consumption, duration constraints, and low efficiency. To prevent ice formation on the aircraft itself, anti-icing methods are employed. Anti-icing methods involve surface etching on metal surfaces or the application of hydrophobic polymer coatings. Commonly used polymers for this purpose are polytetrafluoroethylene (PTFE) and polyurethane due to their ability to cure at room temperature and compatibility with base materials like epoxy. To enhance hydrophobic effects, research is exploring the addition of hydrophobic nanoparticles to create nanostructured surfaces. Nanoparticles, acting as binders, form the topcoat in the coating layer. However, nano surfaces face challenges related to durability and water resistance.

In this study, a nanostructured surface was achieved by incorporating hydrophobic nanoparticles, specifically carbon nanotubes (CNT), into the polymeric topcoat. Polyurethane was utilized as the topcoat, and CNT dispersed in a solvent such as xylene was sprayed after coating. To address durability issues associated with previously researched nano surfaces, CNT was dispersed in the binder to enhance the strength of the topcoat and increase the adhesion between the binder and the exposed CNT on the surface. Additionally, the conductivity of CNT dispersed in the topcoat contributed to coating CNT on the crystal growth directions in the path. To expose hydrophobic CNT on the surface, some hardening of the coating surface was induced before coating with xylene. This allowed for the manifestation of the hydrophobic effect from the carbon surface of CNT and also contributed to surface morphology effects induced by CNT. The addition of CNT increased the contact angle with water from 74.3 degrees to 121.2 degrees, resulting in a significant delay in icing effects, approximately a 260% increase. Moreover, a decrease in adhesion strength and the strength of ice on the surface was observed. When a current of 3V was applied, a temperature increase of about 34 degrees was noted, effectively causing the ice to melt and slide off.

Ongoing research involves investigating the impact of surface roughness changes on aircraft wings or similar structures when applied as an actual model. The study aims to understand the influence of surface variations on aircraft wings and related components. This work was partly supported by Korea carbon industry Promotion Agency grant funded by the Ministry of Trade, Industry and Energy (RS-2023-0026563). This research was supported by the National Research Foundation of Korea(NRF) funded by the Ministry of Science and ICT (RS-2023-002194). This work was supported by Policy R&D program funded by Korea Ceramic Engineering & Technology, Republic of Korea(No. KPP23006-01-0).

5:00 PM CH04.09.13
Advanced Characterization Approaches for Anisotropic Metal Patchy Particles
Julia S. Seifert1, Andreas Voelkl1, Dominik Drobek2, Nabi E. Traoré1, Paola Cardenas Lopez1, Mingjian Wu2, Benjamin Apelo-Zubiri3, Johannes Walter4 and Robin N. Klupp Taylor5; 1Institute of Particle Technology, Germany; 2Institute of Micro- and Nanostructure Research & Center for Nananalysis and Electron Microscopy, Germany

Plasmon resonant nanoparticles have garnered significant interest in recent decades due to their potential as sensing or marker particles in various applications. Particularly, anisotropic plasmonic particles offer the advantage of highly tunable optical properties within a particle system. However, the increased number of shape parameters compared to isotropic particles, challenges for thorough characterization. Precise descriptions of particle shape and product yield are, nevertheless, indispensable for product optimization, which requires, for example, particle growth models. Therefore, in this contribution we present a variety of characterization methods used to extract information from our anisotropic particle system, obtaining the desired parameters on different levels.

We have developed several continuous flow processes for synthesizing gold and silver patchy particles whereby dielectric core particles are coated with thin islands of metal. The size, shape and morphology of the patches determine the optical resonance position which can be tuned over the visible and near-infrared spectral range. The synthesis is performed in a seed-mediated two-step process. Understanding the influence of seed particles on the growth of patches with different dimensions and morphologies is crucial. To this end, we will show how newly developed 4D-STEM analysis was utilized to resolve individual crystallite grains’ orientations and probe the influence of seed particles on the growth of the patches.

On the whole patch scale, coating dimensions and morphology must be thoroughly characterized to obtain quantitative size parameters. These are essential for optical simulations and the development of patch growth models. STEM analysis and electron tomography are indispensable for revealing the patch structures where SEM imaging fails due to resolution limitations. Here we will show how these techniques can be applied to quenched samples, in which the growth has been “frozen” during patch formation, thus providing insight into the growth process. Additionally, patch shape degradation after synthesis and changes in the optical spectra, can only be resolved through TEM imaging. Here, 3D data obtained from electron tomography can further be used as direct input for optical simulations to obtain the obtained results with experimental spectra.

At the overall particle level, it is important to note that not every particle is coated with a patch. Determining the so-called patch yield is crucial for optimizing process efficiency. In this regard, we demonstrate the use of different methods to identify the patch yield of the product. Firstly, single particle scattering and extinction, a novel technique derived from flow cytometry, can distinguish between bare and gold-coated polystyrene particles due to their different optical responses. Secondly, analytical ultraconcentration, as an ensemble measurement, is used to determine patch yield based on differences in particle density and sedimentation velocity.

The diverse characterization methods we demonstrate for patchy particles enhance our understanding of their complex properties and synthesis. These methodologies, adaptable to other anisotropic systems, are expected to be pivotal for future advancements in plasmonic nanoparticle applications.

5:00 PM CH04.09.14
Self-Healing Polymer Composites with Enhanced Strength for Use in Protective Textiles
Evan A. Griffiths, Blaine M. Barrington, Jessica M. Andriolo, Scott Coguill, Brahmananda Pramanik, Richard LaDouceur and Jack L. Skinner; Montana Technological University, United States

Self-healing materials have the potential to increase the lifetime of products exponentially through both non-reversible healing and reversible healing processes. For instance, non-reversible healing has been demonstrated with the use of micro-spheres filled with healing-compounds used to mitigate micro-crack propagation in materials like concrete or asphalt. Upon use, however, micro-sphere rupture is irreversible. Self-repairing traditionally takes the form of polymeric or rubber materials designed to exhibit both cohesive and ionic bonds within the same material.

Reversible self-healing materials not only repair other products but can have extended lifetimes themselves. However, reversible self-healing materials are often mechanically weak compared to non-reversible self-healing materials, thereby, limiting applications. In this work we report mechanical results of aramid nanofiber (ANF) reinforcement of polycaprolactone (PCL). These results and future testing will then be applied to self-healing polymer materials to observe the mechanical reinforcement factors.

To fabricate the aramid nanofibers, macroscale fibers were broken down through hydrolysis in a dimethyl sulfoxide and potassium hydroxide solution. Fibers were then reformed through the addition of water and filtered to remove larger fibers. Following filtration, the remaining fibers were suspended in PCL that had been pre-dissolved in trifluoroethanol. The ANF/PCL mixture was then sonicated for dispersion of the nanofibers within the polymer matrix. For this study, the samples examined were: 1) PCL melted and impregnated with ANFs before solidifying, 2) PCL that was solvent-dissolved before ANFs were blended into the liquid polymer and then let dry to evaporate solvent, and 3) solvent-dissolved PCL/ANF composites (1 and 2 wt% ANFs) were embedded with ANFs before solvent was evaporated from the samples. Mechanical testing for this study included compressive, tensile and split-Hopkinson pressure bar (SHPB). Results of this testing demonstrated an increase of compressive yield strength by 22 %, an increase in tensile Young’s modulus by 28 %, and a decrease in ultimate strength by 32 %. SHPB testing also revealed an increase in dynamic resistance when absorbing impacts at speeds ranging from 10 to 22 m/s where impact duration lasted as much as 23 % longer. Further testing will be performed to characterize shear performance of the samples as well as the Charpy impact energy absorption. Transmission electron microscopy and energy dispersive spectroscopy will be used to
Hydrogen Exchange and Diffusion Kinetics at Elevated Temperatures in Proton-Conducting Solid Oxide Materials

Mudasir A. Yatoo1, Sakuda Yuichi2, Kataro Fujii2, Masatomo Yoshima1 and Stephen Skinner1; 1Imperial College London, United Kingdom; 2Tokyo Institute of Technology, Japan

Storage of purified hydrogen is one of the central challenges in addressing climate change and reducing our reliance on fossil fuels for energy conversion and storage, and therefore there is a global surge in research and development concerning hydrogen purification and storage. In this regard, we are studying proton conduction in solid oxide materials at elevated temperatures for applications in hydrogen separation and compression membranes. Hydrogen compression is the most recommended method to store hydrogen for automotive applications as it allows an increase in the hydrogen volumetric energy density.

Traditionally the protonic conductivity in these materials is measured by indirect methods. For example, conductivity measurements in mixed gas atmospheres, comparing for example dry N2 with humidified N2, thereby allowing the contribution of protons to be evaluated. In our study, we first report the time evolution of protonic conductivity in BaZr1-xCe0.7Y0.2–xYbxO3–δ, BaZr0.95Ce0.05Y2O3, Ba0.85Sr0.15O2–δ, Ba0.85Sr0.15O2–δ, and Ba0.95Mg0.05O2–δ through direct measurements afforded by the Isotope Exchange Depth Profiling technique with deuterium labelling. We also report the kinetics of HD transport through the bulk materials and across metal-ceramic interfaces with a particular interest in the behaviour of the interface between the key Pd/Pd alloy catalyst component and the hydrogen-transporting oxide ceramic material. The transport and interface behaviour information will be of significance in designing hydrogen separation and compression membranes.

Novel Electrical Tree Type Observed using Gigahertz Frame Rate Camera to Image Dielectric Breakdown in Space-Charged Polymer

Kathryn Sturgis1, Noah Hoppis1, Ariana Bussio1, Jonathan E. Barney2, Brian L. Beaudoin1, Cameron Brown2, Bruce Carlson2, Carolyn Chun1, Nicholas Dallmann1, Jack Fitzgibbon1, Ashley E. Hammel1, Samuel Henderson2, Miriam Hieber1, James Krutzler1, Joseph P. Lichthardt2, Mark Marr-Lyon2, Nathan Moody2, Alexander H. Mueller1, Patrick O'Shea1, Karl Smith2, Bryce Tappan2, Clayton Tiemann2, David Walter2 and Timothy W. Koehl1; 1University of Maryland, College Park, United States; 2Los Alamos National Laboratory, United States

We have successfully imaged dielectric breakdown occurring in electron irradiated space-charged polymethyl methacrylate (PMMA) blocks at a nanosecond time resolution. These images, which are the first of their kind, reveal two distinct dielectric breakdown treing effects, one of which is absent from the present literature on dielectric breakdown. This new mode of electrical tree formed during dielectric breakdown of a space-charged polymer demonstrates unique behavior from its better-documented and widely known “branch-type” channels, including structural and formation dynamics differences. Due to its threadlike, smooth appearance, this new type of electrical tree has been coined “vine-type,” in contrast to its “branch-type” counterpart. Both vine-type and branch-type electrical trees were imaged as they formed in the electron irradiated samples, allowing for close study of the channel formation dynamics. The speeds at which the channels form for both types were directly measured from these images and found to exceed 107 m/s and 106 m/s for vine-type and branch-type, respectively—speeds approaching 4% the speed of light in the material. These speeds are faster than previously predicted by models and imply the channel growth is the fastest physical phenomenon in a solid material. Further, the propagation of the electrical tree formation was imaged and three regimes of breakdown channel formation were identified and characterized for the two modes of electrical trees, solving a decades-long mystery on the plasma channel formation process in space-charge dielectric breakdown.
Unraveling The Catalytic Effect of Hydrogen Adsorption on Pt Nanoparticle Shape-Change

Cameron J. Owen 1, Nicholas Marcella 2, Xu Ye 1, Jonathan Vandenmaeke 1, Anatoly Frenkel 1, Ralph Nuzzo 3 and Boris Kozinsky 1,2

1 Harvard University, United States; 2 University of Illinois at Urbana-Champaign, United States; 3 Stony Brook University, The State University of New York, United States; 4 Brookhaven National Laboratory, United States; 5 Robert Bosch LLC, United States

The activity of metal catalysts depends sensitively on dynamic structural changes that occur during operating conditions. The mechanistic understanding underlying such transformations in small Pt nanoparticles (NPs) of ~1–5 nm in diameter, commonly used in hydrogenation reactions, is currently far from complete. In this study, we investigate the structural evolution of Pt NPs in the presence of hydrogen using long time-scale reactive molecular dynamics (MD) simulations paired with experimental X-ray absorption spectroscopy. From these comparisons, we obtain atomic-level mechanistic insights into 'order-disorder' structural transformations exhibited by highly dispersed Pt NP catalysts upon exposure to hydrogen. We report the emergence of previously unknown candidate structure in the 1 nm Pt NP size range, where exposure to hydrogen leads to the appearance of a 'quasi-icosahedral' intermediate symmetry, followed by the formation of 'rosettes' on the NP surface. Hydrogen adsorption is found to catalyze these shape transitions by lowering their temperatures and increasing the apparent rates at which these structural transformations occur.
Micromechanical resonators host localized vibrations which make them useful tools for sensing and exploring the physics of small-scale systems. Devices such as silicon nitride cantilevers or suspended carbon nanotubes can be used as sensing devices through measurements of how their resonant frequencies change due to local perturbations. The small size of these resonators enables extremely precise resolution of masses and forces. While reducing the size of mechanical resonators conceptually improves sensitivity, when a resonator is shrunk down to the molecular scale, a much more complex regime emerges. Polymers, for instance, are known to be highly entropic: coupling to their environment causes large thermal fluctuations among their many flexural modes. The dynamics of such systems are well understood in highly damped environments such as biopolymers inside a living cell. However, in underdamped environments the dynamics are largely unexplored.

In this study, single molecules of DNA are suspended between SU-8 nanopillars with superhydrophobic surfaces that clamp the DNA nanostrings to both ends. The vibrations are measured by using a scannable photonic crystal cavity coupled to a tapered optical fiber. When the cavity is positioned close to the DNA, the near field coupling between the cavity and resonator allows for real-time measurement of the flexural dynamics of the nanostring via optical readout. These measurements are conducted at room temperature and can be used to further study the complex behavior of the nanostring's flexural modes such as thermalization, nonlinear coupling, and chaotic behavior. Looking forward, resonators made from DNA can be programmed to have arbitrary structures to tune their phononic character for added functionality and to probe the physics of nanostrings.

**SYMPOSIUM EL01**

Surfaces and Interfaces in Electronics and Photonics
April 23 - May 7, 2024

Symposium Organizers
Silvia Armini, IMEC
Santanu Bag, AsterTech
Mandakini Kanungo, Corning Incorporated
Gilad Zorn, General Electric Aerospace

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**EL01.01.01**

Controlling Interfaces toward Area Selective Atomic Layer Deposition

Session Chairs: Silvia Armini, Santanu Bag, Stacey Bent, Mandakini Kanungo and Gilad Zorn
Tuesday Morning, April 23, 2024
Room 348, Level 3, Summit

With the growing demands on nanostructure fabrication for advanced electronics, atomic layer deposition (ALD) continues to gain attention as an important method to achieve pattern features at the sub-10 nm length scale. Based on sequential, self-limiting vapor-surface reactions, ALD offers exceptional conformity, thickness control at the Angstrom level, and tunable film composition. Due to the chemical specificity of ALD reactions, several molecular-level parameter systems can strongly impact the ALD nucleation and growth rate, including the specific substrate interface as well as the type of ALD precursor. As a result, the substrate interface and precursor selection can be tuned to intentionally control nucleation rates in ALD, which in turn provides a means to achieve selectivity on spatially patterned substrates. The resulting process of area selective atomic layer deposition (AS-ALD) has attracted significant attention in recent years. In this talk, we will provide examples of tuning surface chemistry to achieve AS-ALD. The development of inhibitory layers such as self-assembled monolayers (SAMs) and small molecule inhibitors (SMIs) to alter the native surface reactivity will be described. Some new SMIs include aryl or alkyl thiol, amine, nitro, and sulfonic acid compounds. The inhibition strategies demonstrate good selectivity in the deposition of thin films on a variety of substrate materials, and selectivity in AS-ALD can be further enhanced by choice of ALD precursor. Finally, we will describe the development of carbon-free inhibitor layers for AS-ALD.

**EL01.01.02**

Investigation of The Optical Constants of Absorbing Atomic Layer Deposition (ALD)-Grown TiO2 Thin Films

Nirmala Chowdhury and Theodosia Gougousi; UMBC, United States

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With the growing demands on nanostructure fabrication for advanced electronics, atomic layer deposition (ALD) continues to gain attention as an important method to achieve pattern features at the sub-10 nm length scale. Based on sequential, self-limiting vapor-surface reactions, ALD offers exceptional conformity, thickness control at the Angstrom level, and tunable film composition. Due to the chemical specificity of ALD reactions, several molecular-level parameter systems can strongly impact the ALD nucleation and growth rate, including the specific substrate interface as well as the type of ALD precursor. As a result, the substrate interface and precursor selection can be tuned to intentionally control nucleation rates in ALD, which in turn provides a means to achieve selectivity on spatially patterned substrates. The resulting process of area selective atomic layer deposition (AS-ALD) has attracted significant attention in recent years. In this talk, we will provide examples of tuning surface chemistry to achieve AS-ALD. The development of inhibitory layers such as self-assembled monolayers (SAMs) and small molecule inhibitors (SMIs) to alter the native surface reactivity will be described. Some new SMIs include aryl or alkyl thiol, amine, nitro, and sulfonic acid compounds. The inhibition strategies demonstrate good selectivity in the deposition of thin films on a variety of substrate materials, and selectivity in AS-ALD can be further enhanced by choice of ALD precursor. Finally, we will describe the development of carbon-free inhibitor layers for AS-ALD.
Titanium dioxide, TiO₂, has been investigated extensively due to its unique and tailorable optical properties, including high refractive index, high dielectric constant, and high photocatalytic activity. The optical properties of thin films can be affected by the deposition process, composition, thickness, conductivity, and density. While TiO₂ is typically regarded as a wide-bandgap semiconductor, with applications limited to the UV light range, TiO₂-based modified materials show promising results for applications with harvesting renewable solar energy. Applications of these sorts, however, require TiO₂-based materials to exhibit absorption in the visible light range. This can be achieved with band gap and optical property engineering.

For Atomic layer deposition (ALD), the process temperature is known to affect the film composition and, consequently, optical properties. We have used ALD to deposit 20-130 nm TiO₂ thin films from tetraakis(dimethyl amino) titanium (TDMA), Ti[N(CH₃)₂]₄, and deionized (DI) H₂O at process temperatures ranging from 200 to 350°C. For films of the same thickness, the actual coloration is dependent on the deposition conditions. Control TiO₂ samples have been produced by a physical vapor deposition method (PVD) at room temperature from a TiO₂ target. X-ray photoelectron spectroscopy (XPS) analysis shows that ALD-grown TiO₂ films incorporate Ti-N/Ti-O-N metallic bonds while the PVD-produced films are purer, as expected. As the ALD process temperature increases, so is the measured at. % of Ti-N/Ti-O-N metallic bonding ranging from ~1 at. % at 250°C to ~4.5 at. % at 350°C.

Ultraviolet-visible spectroscopy (UV-VIS) confirms that the ALD-grown thin films are partially absorbing in the visible range with their absorbance dependent on the process temperature. Similar measurements have shown that PVD-grown films are transparent, as expected. The optical properties of the films have been investigated using spectroscopic ellipsometry (SE) at 380-900 nm. For these partially absorbing ALD films, conventional single-angle SE approaches fail to provide the requisite number of linearly independent equations to allow for the determination of the optical constants, n and k, and film thickness d. We have developed a modified ALD approach that produces samples on quartz substrates that are suitable to be used with a combination of single-angle ellipsometry (SE) data and intensity-based transmission (T) measurements to determine these parameters (n, k) and their spectral dependence simultaneously.

When compared to pure PVD TiO₂ films, the partially absorbing ALD TiO₂ films exhibit a reduced n (ε₁) and increased k (ε₂), [TΓS] which is consistent with the presence of TiO₂N₆ bonding in the film. At 633 nm, n and k for PVD TiO₂ films are ~2.4 and 0, respectively, which is consistent with the literature. For the ALD films, the optical constants are found to depend on the ALD process temperature; values for n range from ~1.7 - 2.3, and k ranges from ~0.2 - 1.2 at 633 nm.

When the as-deposited ALD-grown TiO₂ thin films are annealed at 900°C in an argon environment, the thin film coloration changes, indicating a structural and compositional change. XPS analysis shows that the metallic bonding detectable in the as-deposited films has been removed and the films are fully oxidized TiO₂. We demonstrate that the ALD process temperature, as well as post-deposition thermal treatment for the films, are both avenues for controlling the band gap and tailoring the optical constants of TiO₂ films for a wide variety of applications.

11:15 AM *EL01.01.03
A Public-Private-Academic Partnership: The Microelectronics Commons
Alison Smith and Bryan Smith; NSWC Crane, United States
Public-private-academic partnerships have the potential to drive innovation by leveraging the collective expertise and resources of government agencies, industry, and academic institutions to solve complex challenges. The Microelectronics Commons (Commons) is a national initiative that is executed with oversight from the Office of the Under Secretary of Defense for Research and Engineering’s (OUSD(R&E))’s Principal Director for Microelectronics. This effort benefits both the Department of Defense (DoD) and the United States in spurring development of a domestic microelectronics manufacturing industry by forging critical partnerships with commercial industry, academic, and government partners. The Commons supports laboratory to fabrication (lab-to-fab) testing and prototyping hubs to create a network focused on maturing emerging microelectronics technologies, strengthening microelectronics education and training, and developing a pipeline of talent to bolster local semiconductor economies and contribute to the growth of a domestic semiconductor workforce. In particular, the Commons will address the need for processes, materials, devices, and architectures to be developed and transitioned from research labs to small-volume prototyping in a fab or foundry.

11:45 AM EL01.01.04
CHIPS and Science Act: Opportunities for Materials Science Community
Santanu Bag: Huntington Ingalls Industries, United States
With the passage of the CHIPS and Science Act of 2022, a flurry of activity is expected to kick-off in the semiconducting research, development, and manufacturing field. Numerous programs and funding opportunities have been announced to tackle different challenges in the semiconducting value chain. The CHIPS funding will benefit not only U.S. chip manufacturers, but also tool vendors, U.S. universities, defense contractors, community colleges, K-12 STEM educational programs, and regional hubs. Materials science community plays an important part in the semiconducting industry and could be benefited from this opportunity as well. In this talk, an overview of all these opportunities will be discussed.

1:30 PM *EL01.02.05
Scaling and Scale Up Effects during Area Selective Deposition using Self-Assembled Monolayers and Small Molecule Inhibitors
Angel Yanguas-Gil; Argonne National Laboratory, United States
Area selective deposition (ASD) is a promising bottom-up patterning approach that has attracted significant interest in microelectronics. Area selective deposition methods can be roughly divided into two classes: intrinsically selective processes, which take advantage of preferential reactivity of precursors, and processes based on surface passivation. While growth selectivity is often used as a benchmark to quantify the performance of an ASD process, the scalability of ASD both in terms of pattern size (scaling) and substrate size (in terms of area and aspect ratio) is comparatively less understood.

In this presentation, I will focus on two case studies that explore the scalability of different area selective deposition approaches: the first example explores the impact of pattern size on the stability and density of defects of self-assembled monolayers (SAMs). SAMs exhibit a range of dynamic behaviors that can greatly affect their effectiveness blocking precursors: these include order/disorder transitions, non-negligible surface mobility, or the presence of so-called gauche defects. Using simple dynamic models, we have explored how pattern size affect the stability of SAMs, and how, depending on chain-chain and surface interactions, size effects can lead to substantial changes on the areal density and distributions of defects in SAMs.

In the second example, I focus on how heterogeneous processes during small molecule area selective deposition can affect the scale up of area selective deposition to large scale (i.e. wafer size) and high surface area (i.e. high aspect ratio) substrates. A key aspect of area selective deposition processes using small molecule inhibitors is the need of effectively remove them from the substrate after each ALD cycle. Through a combination of in-situ characterization techniques, kinetic models, and transport models both within features and at the reactor scale, we have explored the impact that surface kinetics has on the elimination of inhibitor molecules. Our results show that reversibility in the inhibition process can greatly increase the purge times required to effectively remove inhibitors from large area substrates, creating inhomogeneities in film thickness even when processes are fully self-limited.

These two examples exemplify the tight coupling between the fundamental aspects of area selective deposition processes and their behavior under conditions relevant for semiconductor manufacturing.

2:00 PM EL01.02.06
Synthesis and Guided Self-Assembly of Mixed-Metal Oxide Arrays from Undercooled Liquid Metal
Julia J. Chang; Andrew Martin, Alana Pauls, Dhanush Jamadagni and Martin M. Thuo; North Carolina State University, United States
In the Information Age, inexorable progression of big data demands rapid upgradation of modern electronics. Internet of Things (IoT), for example, requires numerous “communicable” electronics and powerful central processing units to build a “smart” world, where every physical object is digitally connected. With vast amount of high-performance electronics in need, advancement of nanofabrication technologies become pivotal. Contradiction between better performance and lower cost, however, has long been unreconciled for electronic fabrication, and Moore’s law is an exemplary case of facing such challenge. While Moore’s law has inspired disparate advances in Complementary Metal Oxide Semiconductor (CMOS) devices (~20 doubling in transistors per chip every year), the scaling approach that drives these advances is predicted to stall after ~27 doubling events. This scaling approach faces a triple challenge in: i) continued
miniatuarization with concomitant need for more tools, characterization, metrology, among others, transitioning Moore’s law into ‘more’ law. ii) a looming fabrication challenge as we approach the sub nanometer-length (atomic) scale per component, and iii) global demand for more computation presents an energy and supply challenge unless new, rapid, energy efficient fabrication methods are realized. New paradigm(s) in multiscale manufacturing of microelectronics is therefore needed, among which interface-based (43 more doublings) and/or self-assembled organic (>100 doublings) post-CMOS devices pertains great potential. This calls for a significant shift in microelectronic fabrication with an emphasis to the introduction of new chemistries, composition and functionality while maintaining energy efficiency and low-cost through a device lifecycle. Liquid metal particles bear great potential to reduce energy and capital cost in functional array fabrication since they can act as a controlled reservoir for metal ions. Exploiting partial miscibility of organometallic adducts in aqueous media, steady-state kinetics ad-infinitum living polymerization was demonstrated using liquid metal particles as an infinitely large metal ion reservoir – the so-called HetMet reaction. This reaction led to synthesis of high aspect ratio self-assembled beams that were then translated to graphite-carbon coated metal oxides with tunable band gaps. Herein, we extend this work by coupling the HetMet reaction with confinement from nanograting templates to separate the metal particles from the self-assembling adducts. Using mass transport mechanisms with desired dimensions and periodicity enables deposition of desired arrays, and exploiting fluidic dynamics of this process allows us to control both the nucleation point and the rate of ion transport to the growing seed. Driven by capillary action and solution evaporation, large-area, high-quality organometallic nanowire arrays were fabricated by D-Met, of which an in-air heat-treatment conveniently transformed the organic wires into mixed-metal oxide without compromising wire continuity or array periodicity. Besides planar patterns, fabrication of multi-layer nanostuctures such as 2-layer arrays were also achieved, which is promising for design and fabrication of 3D electronics. With the high structural precision of D-Met fabricated wire arrays, we demonstrate unique electrical and optical properties including diode behavior and wave front resonance. 2:15 PM EL01.02.03 Delfasite-Coated Cotton Fabrics and Their Potential Applications in The Textile Industry for Photocatalytic Self-Cleaning, UV-Blocking and Antimicrobial Activity Shahria Ahmed, Sachin Chopra, Swati Mohan and Jasim Uddin; The University of Texas Rio Grande Valley, United States Delfasite fabrics demonstrate multifunctional applications due to their excellent catalytic properties, which vary depending on their morphology, particle size, and synthetic method. Herein, a few novel applications of the delfasites are reported, which can be implemented in commercial, medical, and domestic settings. In present work we are presenting two different delfasite CuGaO2 and CuFeO2 nanoparticles and its composite with cotton fiber. Multifunctional cotton fabric is prepared by depositing a uniform coating layer of CuGaO2 and CuFeO2, exhibits excellent photocatalytic self-cleaning, UV blocking, and antimicrobial activity. CuGaO2 and CuFeO2 nanoparticles concentration of 1mM and 2mM were deposited over cotton fabric using citric acid as a binder by a simple sonication method. Surface analysis, bindings, stability, stain resistance, and UV blocking characteristics of the functionalized cotton fabric are performed by SEM, EDX, XRD, FTIR, and UV-vis spectroscopy. Both CuGaO2-cotton and CuFeO2-cotton exhibit excellent photocatalytic activity, which is evident from the UV-Vis spectroscopic analysis after mixing with methylene blue dye and subsequent exposure to simulated solar light. 2 mM CuGaO2-cotton fabric has the highest rate of stain extinction compared to others. In addition, CuGaO2-cotton and CuFeO2-cotton block most of the harmful UV radiation, 95–97.5% (approx.) in the case of CuGaO2 and 90% (approx.) in the case of CuFeO2. The modified cotton fabrics present good antimicrobial activity against gram-positive and gram-negative bacteria, which is confirmed by antimicrobial tests with Staphylococcus aureus and E. coli bacteria. The newly fabricated cotton-delfasite composite, with all its promising applications, can be viewed as a valuable, sustainable contribution of materials science to humanity. 2:30 PM BREAK 3:00 PM EL01.02.04 Impact of The Wafer-Scale Fabrication on The Performance of Graphene-Based Flexible Microelectronics and New Strategies for Improvement Elena del Corro1, Marta Delga-Fernandez2, Aina Galarca2, Anton Guimerar, Xavi Illas3 and Jose A. Garrido3, 1ICN2, Spain; 2IMB-CNMM, Spain; 3ICREA, Spain Graphene possesses unique mechanical and electronic properties that make it a crucial material in the biomedical field. Specifically, graphene-based electronic devices have been developed and are in continuous improvement for biomedical recording, stimulating and sensing purposes. Despite the demonstrated capabilities of graphene-based solution-gated field-effect transistors (SGFETs) in this field, their wafer-scale fabrication process introduces uncontrollable residual charges on the graphene surface, which has an impact on the final functionality of the devices in the form of undesired doping and thus a deterioration of the general electrical performance. In this work, we present a detailed study of the effect of residues presence at each step of photolithography in the wafer-scale fabrication process of graphene microtechnology. By means of Raman spectroscopy and spectro-electrochemistry we monitor the doping state of graphene during fabrication processes. As function of pH and the ionic strength of the electrolyte in contact with graphene, we register the frequency of the graphene’s G phonon that can be directly related with the Fermi energy and doping state of graphene. Our study reveals that certain steps in the fabrication process leave a major amount of residues on the graphene surface that leads to inhomogeneities at cm scale in terms of device performance. With this information in hand, we propose a new fabrication strategy including the deposition of a sacrificial copper layer on graphene to protect it against induced contamination during the whole photolithography process. We analyze the impact of this additional layer on the quality of graphene material, after deposition and final etching procedures. Finalized graphene devices and electrically characterized and compared with standard technology. REFERENCES 1. Masvidal-Codina, E., Illa, X., Dasilva, M., et al (2019) High-resolution mapping of infra-slow cortical brain activity enabled by graphene microtransistors, Nature Mater 2. Bonaccini Calia, A., Masvidal-Codina, E., Smith, at al (2022). Full-bandwidth electrophysiology of seizures and epileptiform activity enabled by flexible graphene microtransistor depth neural probes. Nature nanotechnology. 3. J. Yan et al., (2007) Electric Field Effect Tuning of Electron-Phonon Coupling in Graphene, Phys. Rev. Lett 3:15 PM *EL01.02.01 Reinforced Interfaces to Realize Multifunctional Supercapacitors Theo Nees Ng; University of California, San Diego, United States Today’s electrochemical storage devices are restricted in capacity, a key challenge that limits the operational time of wireless devices. To increase the energy storage capacity, multifunctional structures such as structural supercapacitors combine load-bearing and energy-storage functions into the same device, resulting in weight savings and safety improvements. To achieve an efficient structural supercapacitor, we developed strategies based on interfacial engineering to improve both the electrodes and electrolytes. The structural electrodes were reinforced by coating carbon-fiber weaves with a uniquely stable conjugated redox polymer and reduced graphene oxide that raised pseudocapacitive capacitance and tensile strength. The solid polymer electrolyte was tuned to gradient configuration, where it facilitated high ionic conductivity at the electrode-electrolyte interfaces and transitioned to a composition with high mechanical strength in the bulk for load support. The gradient design enabled the multilayer structural supercapacitors to reach state-of-the-art performance matching the level of monofunctional supercapacitors (Science Advances 2023 9, eabd4069) Lastly, as a feasibility study, we fabricated a structural supercapacitor to serve as the weight-bearing hull of a model boat. The boat was integrated with a solar panel for charging up the supercapacitor hull, which in turn powered up the boat motor to cruise across a pool. This demonstration showed the potential of structural supercapacitors to facilitate mass savings and increase the capacity for energy harvesting and storage in future electric systems. 3:45 PM EL01.02.06 Enhancing The Hole Conductivity of An Undoped Silicon Channel by Defect Engineering of Surrounding SiO2 Dielectric Soundarya Nagarajan1, Daniel Hiller2, Ingmar Ratschinski2, Dirk König3, Thomas Mikolajek4,5 and Jens Trommer6; 1NaMLab gGmbH, Germany; 2TU Bergakademie Freiberg, Germany; 3Australian National University, Australia; 4TU Dresden, Germany The road to miniaturization in semiconductor microelectronic technology has led to an ongoing demand for identification of suitable approaches for device performance enhancements and raised requirements of new materials and device structures [1]. Here, we report the electronic device performance improvement opportunity of silicon nanostructures without direct channel doping by adding Al acceptor states into a thin SiO2 layer surrounding the silicon [2]. This novel concept is analogous to modulation doping in III-V semiconductors. The manifestation of the dielectric by incorporation of trivalent Al impurities gives the possibility for electrons from silicon to tunnel to the acceptor states in SiO2 yielding silicon with holes as majority carriers. Our method removes the disadvantages of impurity doping,
Understanding the Degradation Mechanism of Spiro-OMeTAD during the Long-Term Operation of Perovskite Solar Cells and Mitigating it via ALD.

5:00 PM

A single segment of the fabricated TLM structure can also perform equivalently as a transistor with the body contact operated as a back gate. The performance of the transistor is improved by an enhanced hole carrier transport with an ION/IOFF ratio of up to 10^6 at a drain voltage of -1V. The NiSi source/drain contacts placed directly within the SOI region also undergoes a transition from Schottky to low-resistance contact as an effect of the barrier height reduction [8]. The drawbacks of conventional impurity doped devices such as dopant scattering, fluctuating device performance due to dopant diffusion, and even components of lightly or heavily doped source/drain regions can be circumvented by the new method. The aforesaid impurity free doping of the channel would be ideal for a high performance, high mobility device and enables new advancements encompassing areas of low-temperature physics and quantum technology.


5:00 PM EL01.02.07

Multiplexing Reactor for the High-Throughput Screening of Molecular Layer Deposition Processes

David S. Bergesman, Yuri Choe and Duncan Reece; University of Washington, United States

Continued progress in information and communication technologies requires sustained innovations in memory and storage devices' architecture and production processes. For example, scaling technology to sub-10nm using extreme ultraviolet (EUV) sources necessitates new processes for making hybrid organic-inorganic thin film photore sist materials that are highly absorbing of EUV. One potential approach for making these films is through molecular layer deposition (MLD), the organic analog of atomic layer deposition. However, the discovery of desirable MLD materials is slowed by the large number of combinations of inorganic and organic reactants available.

Here, we present an approach for rapidly screening new materials deposited by MLD using a custom-built, high-throughput, multiplexing MLD-style reactor. In such a system, multiple reaction chambers are connected to shared reactors and pumping lines, allowing for the elimination of redundant reaction components and reducing capital costs compared to an equivalent number of independent systems. By carefully controlling pressure gradients in the system and valve operation, different MLD processes can be performed simultaneously in separate reaction chambers, allowing for many materials to be produced at the same time. These materials can then be screened for their properties of interest. To demonstrate this approach, a multiplexing reactor of this design was constructed with six independent reactor systems, two shared reactant manifold lines, and one shared pumping line. Using the well-studied trimethylaluminum (TMA) and water reaction into alumina, depositions in this system are shown to be reproducible, comparable to depositions shown in the literature, and without cross-contamination between chambers. In demonstration of the capabilities of this system, a TMA/water growth curve is developed using a combination of depositions in all systems, along with a measurement of the ALD temperature window using simultaneous depositions in all six chambers at different temperatures. Finally, the ability to simultaneously deposit multiple films is demonstrated using diethylzinc and one of six different organic diols. Using such a system can enable the faster screening of processes for potential materials, like photoresists, which will be needed for many electronic and photonic materials.

5:00 PM EL01.03.01

Understanding the Degradation Mechanism of Spiro-OMeTAD during the Long-Term Operation of Perovskite Solar Cells and Mitigating it via ALD

Mavank Kedil1,2, Chittaranjan Das1,2 and Michael Saliba1,2; 1University of Stuttgart, Germany; 2Forschungszentrum Jülich GmbH, Germany

Metal halide perovskites (MHPs) have emerged as promising photovoltaic (PV) materials with a power conversion efficiency (PCE) of 26% on the laboratory scale. Despite achieving high performance in less than a decade, device degradation under operating conditions is outcompeted in the PV market by silicon and CdTe technologies. To overcome this challenge, interface passivation with organic molecules and composition engineering are commonly explored to improve the device stability. While most studies have focused on the intrinsic stability of the perovskite active layer, there is a lack of understanding of the degradation of other charge-extraction layers and the electrodes, and its effect on the final device performance upon aging. In this work, triple-cation-based PSCs with a planar n-i-p architecture and a champion PCE of 20.1% were aged under maximum power point tracking (MPPT) for 1000 min under 1 sun illumination without any encapsulation in an ambient atmosphere. After aging, we performed soft Ar atom cluster sputtering XPS depth profiling to study the ionic motion/interactions between the perovskite active layer and the overlying charge extraction layer. In addition to iodine migration from the perovskite to the Spiro-OMeTAD electrode interface, we observed a shift in the binding energies (BE) of the constituent species present in Spiro-OMeTAD with p-dopants lithium bis(trifluoromethane)sulfonimide (LiTFSI) and 4-tert-butylpyridine (BTP).

When looking specifically at the core level spectra of S 2p centered at 169.3 eV are present uniformly from the Spiro/electrode interface to the Spiro/perovskite interface in the fresh PSC. Upon aging, the S 2s exhibit a lower binding energy 168.3 eV attributing to the reduction of sulfur present in the Spiro layer. Notably, the F 1s spectrum also showed an extra peak at 685.5 eV for the aged sample from 689.0 eV for the fresh sample. Additionally, the F/S ratio changed after MPPT aging, leading to a final change in the charge extraction properties of the Spiro-OMeTAD layer, leading to the final device degradation. We observed that this chemical redistribution created pinholes in the films, leading to easier penetration of H2O and O2, and perovskite instability.

Applying near-ambient pressure XPS (NAP-XPS) on the perovskite film with and without the spiro-OMeTAD layer at 1 mbar of H2O at 50 °C, 100 °C, and 150 °C showed the formation of metallic lead (Pb0) and iodine due to the degradation of Spiro-OMeTAD, accelerating the decomposition of the perovskite. Interestingly, our XRD results confirm that the interaction between the degraded Spiro-OMeTAD and perovskite leads to the amorphization of perovskite, which is different from what is commonly observed for PbI2. The cross-sectional SEM image of the aged PSCs highlights the spiro/perovskite interface as the breaking point under constant illumination. Finally, to mitigate the instability caused by the degradation of Spiro-OMeTAD, robust passivation of ALD-deposited AIOx of <1 nm has proven to be an effective strategy for the long-term stability of PSCs. By examining the conformity of this sub-nanometer layer via HRTEM and observed the complete coverage of a rough perovskite layer (RMS ± 20 nm) by AlOx, which is a difficult task to obtain due to the chemical deposition of organic materials. In-situ electron diffraction also showed that the grown ALD layer was amorphous and acted not only as a surface passivation layer due to dopant diffusion, and even more important to prevent the degradation of perovskite as a result of the decomposition of Spiro-OMeTAD. Overall, our work provides chemical and mechanical insights into the degradation of the overlying layer on perovskite by combining macroscopic, microscopic, and spectroscopic studies. We also decoupled the role of ALD as a passivation layer for perovskite intrinsic stability and as a nanoencapsulant layer for mitigating the phase transition to amorphous phases upon Spiro-OMeTAD degradation.
In this study, we used a low-pressure thermal annealing (LPTA) treatment to improve the switching characteristics and bias stability of zincoxide (ZTO) thin film transistors (TFTs). For this, we first fabricated the TFT and then applied LPTA treatment at temperatures of 80°C and 140°C. The LPTA treatment reduced the number of defects in the bulk and interface of the ZTO TFTs. In addition, the changes in the water contact angle on the ZTO TFT surface indicated that the LPTA treatment reduced the surface defects. Hydrophobicity suppressed the off-current and instability under negative bias stress because of the limited absorption of moisture on the oxide surface. Moreover, the ratio of metal–oxygen bonds increased, while the ratio of oxygen–hydrogen bonds decreased. The reduced action of hydrogen as a shallow donor induced improvements in the on/off ratio (from 5.5 × 10^9 to 1.1 × 10^7) and subthreshold swing (8.63 to 2 V dec⁻¹ and 0.73 V dec⁻¹), producing ZTO TFTs with excellent switching characteristics. In addition, device-to-device uniformity was significantly improved because of the reduced defects in the LPTA-treated ZTO TFTs.

5:00 PM EL01.03.05
Tunable Dielectric Properties of CVD-Processed Polymer via Click Chemistry Seongchool Jang¹, Gunoh Lee², Kyung Jin Lee² and Hynn-Suk Kim¹; ¹Dongguk University, Korea (the Republic of); ²Chungnam National University, Korea (the Republic of)

Recently, the increasing demand for high-end displays has led to the development of flexible displays using non-traditional flexible substrates rather than traditional rigid substrates. Currently, thin-film transistors (TFTs) for flexible devices mainly use inorganic dielectrics such as SiO₂ and Al₂O₃. These inorganic gate dielectrics have critical issues to apply in flexible devices because of their high temperature process, high-cost production, and limited flexibility. Therefore, the mass production yield inevitably decreases, leading to increase in price of devices. From this point of view, polymer dielectrics have attracted considerable attention as a gate insulator for flexible transistors because of their mechanical nature. Even if polymer gate dielectrics are suitable for future flexible electronics, properties such as dielectric constant, and leakage current, are not suitable for cutting-edge devices. Also, fabrication processes for polymers is usually consist of solution process, which has poor step coverage, side effect like coffee-ring effect and pinholes. Poly(p-xylylene) (PPx, commercialized name is parylene) is well known passivation materials for various electronics, which can be fabricated by chemical vapor deposition system that can give pinhole-free conformal film. Conventional parylene family, such as parylene-C, -D, -N, and -AF4 shows low dielectric constant of ~3, which is does not meet requirements for future advanced electronic. However, physical, dielectric, and electrical properties of parylene family can be tuned by adjusting functional groups. We reported custom synthesized parylene-ethenyl that shows higher dielectric constant, smoother surface and similar leakage current compared to conventional parylene. This approach is quite intricate as it necessitates design from the monomer.

In this work, click chemistry was employed to further tuning the properties of custom-synthesized parylene-ethenyl for dielectric layer for TFTs. IGZO oxide semiconductors were used as the active layer to demonstrate high-performance hybrid TFTs. Unlike most polymers fabricated through solution processes, parylene's fabrication method relies on the Gorham method CVD method. This system provides a thin, conformal, and pinhole-free film, resulting in a compatible interface with oxide materials. Additionally, the deposition temperature is around room temperature, and the additional high-temperature annealing is required, making it suitable for plastic substrates with low-temperature transition temperatures, ideal for flexible or stretchable applications. Four types of click reactions were conducted on parylene-ethenyl, and it was confirmed that all of them exhibited click reactions. After click reaction, parylene-ethenyl demonstrated an improved dielectric constant exceeding 4 without compromising film quality. Successful fabrication of IGZO TFTs combined with parylene-ethenyl showcased reliable switching properties, indicating that the combination of parylene-ethenyl with click reaction and IGZO posed no issues at interfaces. The click reaction is anticipated to facilitate easy advancements to the characteristics of the polymer gate dielectric. Moreover, it opens up the possibility of manufacturing a functional device utilizing the clicked part.

5:00 PM EL01.03.07
Antireflective Properties of Plasma-Polymerized Biomimetic Surfaces Luigi P. Verdoni; Edmund Optics Research and Development, United States

Biomimetic surfaces inspired by Moth’s eyes are characterized by the subwavelength structures that cover the eye’s surface. These nanostructures, possessing tapered geometries of variable height and shape, present as a gradient refractive index and offer antireflective (AR) properties over a high angle of incidence (AOI). A facile technique utilizing inductively coupled reactive ion etching (ICP-RIE) was devised to endow the optical surface with randomly patterned subwavelength nanostructures. In this two step nanostructuring process, an etch mask and recipe were implemented to deliver AR behavior at desired wavelengths, followed by a plasma polymer deposition of a thin fluorocarbon film with a low surface energy. The resultant subwavelength antireflective surface can be tuned from the ultraviolet to infrared wavelengths and has been shown to possess utility in both antiwetting and high laser damage threshold applications.

5:00 PM EL01.03.08
Exploring Dopant Dynamics in Crystalline Germanium through Microwave Annealing (MWA) and High-Pressure Annealing (HPA): A Study on Diffusion, Activation and Recrystallization TaiChen Kang¹ and WenHsi Lee²; ¹Chung Yuan Christian University, Taiwan; ²National Cheng Kung University, Taiwan

This study delves into the nuanced activation behavior of phosphorus and boron dopants in crystalline germanium substrates through meticulous investigation of high-pressure annealing (HPA) and microwave annealing (MWA) techniques. Phosphorus implantation at 10 kV, with a dose of 5 × 10²⁲ atoms/cm², showed intriguing profiles revealing a concentration peak exceeding the maximum equilibrium solubility in germanium. The subsequent HPA at 500 °C for 60 s resulted in a stable profile with a junction depth of 44.1 nm, contrasting the diffusion broadening observed at higher HPA temperatures. MWA at 3P to 5P demonstrated diffusion patterns akin to HPA at 500 °C. Sheet resistance comparisons between HPA and MWA unveiled the superior stability of diffusion profiles at MWA conditions, due to the high-pressure annealing procedure. Hall measurements after HPA at 500 °C revealed a decrease in sheet resistance to 0.63 Ω/square and an increase in N-carrier concentration to 5.76 × 10¹⁹ P/cm², despite subsequent decreases in carrier concentration and mobility after 500 °C, possibly attributed to deactivation induced by high-temperature annealing. The study also explores the activation of boron, demonstrating significant enhancement through solid-phase epitaxial regrowth (SPER) with minimal diffusion, particularly notable despite the low solid solubility. The investigation involves dopant diffusion analysis using SIMS, highlighting the importance of a high dopant concentration at the surface for low contact resistivity. Sheet resistances measured by a four-point probe post-HPA and MWA underscore the effectiveness of higher temperatures in HPA for achieving high B activation through SPER. Comparative analyses and TEM images further elucidate the recovery of amorphous layers in both phosphorus and boron doping scenarios, emphasizing the advantageous SPER behavior facilitated by high-pressure annealing. In summary, this study provides comprehensive insights into the activation dynamics of phosphorus and boron in germanium substrates, emphasizing the nuanced interplay between annealing techniques and dopant behavior for advanced semiconductor device fabrication.

5:00 PM EL01.03.09
Controlled Bipolar Doping of One-Dimensional Van der Waals Nb,Pd,Sb Se Nanomaterials Bom Lee and Jae-Young Choi; Sungkyunkwan University, Korea (the Republic of)

2D layered materials such as graphene, transition metal dichalcogenides (TMDCs), h-BN, and black phosphorus have been extensively studied in a wide range of applications due to their fascinating structural, physical, and chemical properties. However, as the width of the 2D semi-infinite plane becomes narrow to meet the stringent dimensional requirements of the transistor, the dangling bond density at the edge of 2D vdW increases, resulting in degradation of electronic performance. To solve such scale-down problems, research has been conducted in recent years on one-dimensional (1D) vdW materials with a further reduced dimension from a 2D structure. 1D vdW materials, where single molecular chains with strong covalent bonds are assembled by a weak vdW force, are free of broken or dangling bonds on the chain surface, even when separated by a diameter of less than 1 nm. On the basis of these structural features, various 1D vdW materials-based devices have been demonstrated, such as molecular connectors, transistors, and sensors. In recent years, there is a 1D transition metal chalcogenides containing a noble metal such as Pd or Pt have gained attention as promising semiconducting materials for electronic and optoelectronic devices. For example, Nb,Pd,Sb Se, successfully synthesized by Keszler et al. Nevertheless, research into the stable tuning of electrical properties, which is a prerequisite for basic electronic materials, is still in its infancy stage for 1D vdW materials.

In this study, we introduce a new ternary transition metal chalcogenide, Nb,Pd,Sb Se, which was successfully synthesized via chemical vapor transport (CVT) method using iodine as a transport agent. Furthermore, we first demonstrated the chemical doping of Nb,Pd,Sb Se, which is a representative n-type 1D vdW material, through chemically doping AuCl₄⁻ and β-nicotinamide adenine dinucleotide (NADH) as p-type and n-type dopants, respectively. The concentration of holes and electrons controlled by varying the immersion time in the doping solution were effectively confirmed by spectroscopic and transport studies. We also demonstrated an axial p–n junction on NbPdSe6 that exhibits near-perfect rectifying behavior using a selective doping method. We believe that this work can promote research based on 1D vdW semiconductors for future electronic applications.

5:00 PM EL01.03.11
Direct Characterization of Single-Molecule Reaction via Tip Enhanced Raman Spectrum Ruihao Li; Arizona State University, United States

Characterizing chemical reactions at a single-molecule level enables a deep understanding of the mechanism of complex chemical reactions and thus establishes new material science frameworks. Previous works explore the real-time current changes of reactants and its products to figure out the steps of the reaction process. However, it is hard to identify the paths of some reactions accurately because the current signal does not have significant fingerprint of the reactants. Tip-enhanced Raman spectroscopy (TERS) can accurately characterize chemical reactions due to its ability to characterize chemical bond fingerprint information at single-molecule scale precision. By combining Raman spectroscopy with single-molecule detection techniques, we can control single-molecule reactions through electric fields and simultaneously observe the Raman shifts of its corresponding chemical bonds.
Ensuring chemical safety and safeguarding human health require real-time monitoring and discrimination of trace gases using appropriate gas sensors. Typically, this task involves expensive, bulky, and power-intensive devices such as optical and electrochemical gas sensors. Achieving this objective with a single, miniature, low-power semiconductor gas sensor is challenging due to selectivity issues.

In this study, we demonstrated a novel gas sensor called micro-heater integrated nanotube array gas sensor (MINA sensor), which can operate in dual modes. The sensor can detect multiple gases at parts-per-trillion (ppt) level under the continuous heating (CH) mode and distinguish multiple gases under the pulse heating (PH) mode. We constructed the MINA sensor on the nanorough porous anodic aluminum oxide (AAO) templates with a top-bottom electrode structure, which significantly increases the sensor’s surface area for molecular access. To create the sensing material layer, we used atomic layer deposition to deposit a ultrathin and conformal SnO₂ thin film and decorated it with Pd nanoparticles. When operating under the CH mode, the MINA sensor could detect hydrogen, acetone, toluene and formaldehyde with measured LODs as low as 100 ppt, 100 ppt, 100 ppt, and 4 ppb, with the corresponding theoretical LODs as 6.96 ppt, 11.88 ppt, 16.52 ppt, 70.06 ppt. Under PH mode, the MINA sensor provided varying transient responses to different gases due to the variations of gas diffusion and surface reaction activation energy of the gases. By analyzing the conductance amplitude and slope features of a single, different concentrations of hydrogen, acetone, toluene, and formaldehyde can be distinguished. Furthermore, the PH mode saved 66.7% energy compared to the traditional CH mode. The remarkable capabilities of the MINA sensor make it highly appealing for various applications, including distributed-low-power sensor networks and battery-powered mobile sensing systems for chemical safety, environmental monitoring, and healthcare.

Radio frequency (RF) electromagnetic radiation has revolutionized communication networks. As we become more reliant on electronic devices and systems, there is a pressing need for the development of effective EMI shielding materials. These shielding materials protect electronic components from radiation damage and block undesirable signals. Metal networks, such as metal meshes and metal nanowires, have been the subject of much research for transparent conducting electrodes with high transparency and low sheet resistance. In this context, we propose a novel approach in the field of crack lithography focusing on the creation of flexible embedded metal meshes. Our novel method involves the use of a self-forming crack template as a mask. Instead of relying on traditional lithography methods that require complex and expensive equipment to create masks for etching, this approach simplifies the mask creation step through the natural formation of cracks. Our facile fabrication method involves transferring the crack patterns to a PET substrate using RIE. The process also eliminates the need of the sputtering process, traditionally employed in crack lithography for producing conductive meshes. After removing the crack template, we fill the embedded cracks with a highly conductive Ag ink and cure the ink. Our flexible embedded Ag meshes achieve 91.3% visible transmission and a sheet resistance ($R_s$) of 0.54, which corresponds to a figure of merit of 7500. For transparent EMI shielding, the samples exhibit an SE of 42 dB with 91.3% visible transmission.

Another surface modification technique is atomic layer deposition (ALD). ALD, a branch of chemical vapour deposition (CVD), is a technique used to deposit atomic layers of complex and layered thin films. By operating at such a scale, thickness control, conformity of the films, low temperature depositions and even the ability to scale-up are possible. This novel route could be used to produce 'easy-to-clean' coatings for slip-resistant flooring as well as coatings on solar cells.

References

5:00 PM EL01.03.14
Flexible Embedded Metal Meshes by Sputter-Free Crack Lithography for Transparent Electrodes and Electromagnetic Interference Shielding Mohammad Mehdi Zarei, Mingxuan Li and Paul Lee; University of Pittsburgh, United States

Radio frequency (RF) electromagnetic radiation has revolutionized communication networks. As we become more reliant on electronic devices and systems, there is a pressing need for the development of effective EMI shielding materials. These shielding materials protect electronic components from radiation damage and block undesirable signals. Metal networks, such as metal meshes and metal nanowires, have been the subject of much research for transparent conducting electrodes with high transparency and low sheet resistance. In this context, we propose a novel approach in the field of crack lithography focusing on the creation of flexible embedded metal meshes. Our novel method involves the use of a self-forming crack template as a mask. Instead of relying on traditional lithography methods that require complex and expensive equipment to create masks for etching, this approach simplifies the mask creation step through the natural formation of cracks. Our facile fabrication method involves transferring the crack patterns to a PET substrate using RIE. The process also eliminates the need of the sputtering process, traditionally employed in crack lithography for producing conductive meshes. After removing the crack template, we fill the embedded cracks with a highly conductive Ag ink and cure the ink. Our flexible embedded Ag meshes achieve 91.3% visible transmission and a sheet resistance ($R_s$) of 0.54, which corresponds to a figure of merit of 7500. For transparent EMI shielding, the samples exhibit an SE of 42 dB with 91.3% visible transmission.

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suggest a novel device configuration featuring controlled carrier lifetime modulation of Si-based THz modulators via voltage application across a transparent gate electrode.

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Flexible and wearable sensors have gained tremendous interest due to increasing demands in diverse applications such as prosthetics, personal healthcare, and e-skin. However, they are mostly based on electronic signals, restricting their potential in visualized mechanical measuring. Herein, inspired by the structural colors of natural species, we developed a novel mechnochromatic sensor with a wide working range and angle compensators. Employing the colloidal lithography technique, multiple nanostructures were fabricated on a single stretchable substrate. Thus, broadening the detection range to 150% without sacrificing high sensitivity. We also introduced a novel approach using angle compensators to circumvent the issue of angle-dependent colors. By comparing the colors of rigid and stretchable photonic crystals, the users can facilely estimate the strain regardless of the incident and viewing angles. The fabrication principle in this study is based on a reusable mold, which is cost-effective for large-scale production. Thus, we believe this study will have a broad impact on the development of smart mechnochromatic devices for visually measuring the deformation of materials.

5:00 PM EL01.03.19
Towards a Universal Biosensing Platform based on Graphene/Pyrene Surfaces for Neurotransmitters

Marta Delgo-Fernandez1, Aina Galceran1, Jose Caicedo-Roque1, Xavi Illa1, Jose A. Garrido1,2 and Elena del Corro1,2
Catalan Institute of Nanoscience and Nanotechnology, Spain; 1IMB-CNM, Spain; 2ICREA, Spain

The development of new therapeutic treatments and diagnosis of neural-related illnesses is linked to research in the electronic devices field. Devices as neural implants allow the recording of electrical signals to better understand the central and peripheral nervous systems1,2 and, therefore, advance in the diagnosis and treatment of these diseases. One of the main issues of current implants, mostly based on silicon technology (and thus, rigid), is that they are invasive. The use of graphene-based transistors may overcome this drawback, taking advantage of graphene's mechanical and electronic properties, and also opening the peripheral nervous systems. Here, we develop a versatile graphene/pyrenebutyric acid (PyBA) platform for the detection of neurotransmitters, or other analytes of interest, while recording electrical neural activity.

To build this platform, we perform physical evaporation of PyBA, a molecule capable to interact with the p system of graphene thanks to its aromatic nature, and to covalently interact, due to its carboxylic group, with an aptamer of interest through the formation of a peptide bond. We optimize the PyBA evaporation conditions, which are those leading to the formation of a PyBA monolayer on the surface of graphene. This optimization and further detailed characterization of the pyrenebutyric layer is key for ensuring an understanding of the future sensor functionality. The viability of the system is studied with electrical characterizations of the transistors fabricated including the PyBA layer on graphene. Then, the binding of an aptamer that recognizes a specific neurotransmitter – thrombin in our particular case – is explored and used as a prove of the utility of the platform presented. Thrombin is detected by electrical characterization of the functionalized graphene transistors, while morphological characterization of the samples is performed by Atomic force microscopy (AFM) and Raman spectroscopy. The thrombin biosensing results reveal changes in the electrical properties of the graphene corresponding to each concentration tested, and the detection range achieved is correspondent to the one achieved by reported approaches based on in-universal functionalization – more difficult to control -. This demonstrates the ability of the system to recognize the aptame of interest through binding to its specific aptamer. This graphene/PyBA universal biosensing platform is in the pipeline for the development of a new generation of multifunctional graphene-based neural implants.

REFERENCES

5:00 PM EL01.03.20
Cation Bonding on Functional Groups for Greatly Enhanced Dipole Moments and Excellent SERS Sensing as a Universal Approach

Ruey-Chi Wang1 and Hsiu-Cheng Chen2
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2, National University of Kaohsiung, Taiwan

The recently developed dipole-based surface-enhanced Raman scattering (SERS) technique has ushered in a new era of opportunities for crafting cutting-edge sensing platforms, boasting a host of advantages, including the ability to identify molecules, reduced costs, and heightened sensitivity. While significant efforts have been dedicated to augmenting the molecular dipole density on the surface to enhance sensitivity, the constrained dipole moments have limited further advancement and application possibilities. In the work, we present a universal method known as cation bonding to enhance the dipole moments of oxygen-containing functional groups (OFGs) with the goal of achieving high-sensitivity trace sensing through Surface-Enhanced Raman Scattering (SERS).

Utilizing Cu2+ as a representative model, we have demonstrated substantial enhancements in dipole moments through density functional theory-based calculations, which have been further validated through SERS measurements. These enhancements have been compared with typical OFGs and SERS platforms based on graphene oxide (GO). The analysis results from Transmission Electron Microscopy (TEM) show no formation of copper particles, while Energy Dispersive X-ray Spectroscopy (EDS) clearly indicates the presence of copper signals, which indicates the formation of copper ions on the surface and rule out common electromagnetic mechanisms. A comprehensive analysis of the electronic structures of analytes and SERS substrates has been conducted to exclude conventional chemical mechanisms. The results obtained from Infrared Spectroscopy (IR), X-ray Photoelectron Spectroscopy (XPS), and Electrostatic Force Microscopy (EFM) confirm the formation of Cu-C-O bonds and the reversal of dipole moments through copper bonding. The Cu-OFG SERS platforms thus prepared not only exhibit remarkable sensitivity in detecting Rhodamine6G (at concentrations as low as 10^-10 M) but also prove their utility in detecting trace amounts of nitrate (10^-10 M), a harmful contaminant in drinking water, and thiabendazole (0.01 ppm), a parasiticide used in fruit preservation. This cation bonding strategy is highly versatile, applicable to various cations, and opens the door to creating exceptional SERS platforms for a wide array of sensing applications.

5:00 PM EL01.03.23
Electrically Tuneable Silicon-Based Photomodulator for THz Applications

Xavier Romaní1, Peter R. Wilshaw2, Rayko I. Stantchev3,1, Tina Miao1, Tim Niewelt1, Shona McNab2, Sophie L. Pain1, Nicholas Grant1, Ruy S. Bonilla2, Emma Pickwell-MacPherson1 and John D. Murphy1,1 University of Warwick, United Kingdom; 2University of Oxford, United Kingdom; 3National Sun Yat-sen University, Taiwan

Silicon is a well-established semiconductor which is extensively used in a variety of applications. It is a basic component for photovoltaic solar cells and is a widespread substrate in many photonic devices. More recently, silicon has found new use in the ever-growing research area of terahertz (THz) waves. For example, silicon can serve as a THz photomodulator i.e., when the silicon is illuminated by an above bandgap optical source which renders the silicon opaque to the THz radiation. The opacity level (modulation depth) and the switching speed between the transparent and opaque states of silicon (modulation speed) are determined by the lifetime of the photoexcited charge carriers in the silicon wafer. For some applications (such as in THz single-pixel imaging) the effective lifetime of silicon is a critical parameter, which must be carefully considered to reach the best trade-off possible between the modulation depth and the modulation speed. However, neither bare silicon (too low) nor routinely surface passivated silicon (too high) yields effective lifetimes that are best suited for such THz applications. Hence we suggest a novel device architecture featuring controlled lifetime modulation of Si-based THz modulators via voltage application across a transparent gate electrode.

In this work, we report the fabrication, characterisation, and implementation in a THz imaging setup of such a photomodulator. We deposited hafnium oxide via atomic layer deposition as the passivation layer on both side of a high-resistivity silicon substrate. The hafnium oxide provides a sufficient electrical insulation and an adequate surface passivation layer yielding lifetimes in the hundreds of microseconds. We then coated the hafnium oxide layers with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as the conductive layer for the electrical
gating. The choice of PEDOT:PSS is particularly relevant for THz photomodulation as it is transparent to both the THz and the visible light. We performed an injection-dependent lifetime characterisation of the photomodulator using standard photoconductance decay (PCD) measurements while a bias voltage in a -10V to +10V range was applied between the PEDOT:PSS top layer and the silicon layer. We observed results for the effective lifetime as a function of the applied bias voltage that are consistent with similar devices previously reported in literature. We also confirmed the applied voltage homogeneity across the whole photomodulator surface by repeating a similar experiment using a photoluminescence imaging technique.

We implemented the electrically tuneable photomodulator in a THz time domain spectroscopy setup (THz-TDS) capable of single-pixel imaging. Similar to the PCD measurements, we first characterised the photomodulator effective lifetime by monitoring the THz radiation decay for a range of photoexcitation intensities and applied bias voltages. The lifetime curves extracted from this THz-TDS photomodulation configuration showed comparable trends with the lifetime curves produced by PCD. To demonstrate the potential of this electrically tuneable THz photomodulator, we performed single-pixel imaging where the photoexcitation source is now spatially structured so that the photomodulator acts as a THz spatial light modulator. We showed that tuning only the bias voltage, which controls the photomodulator effective lifetime, can massively impact the THz imaging. With such silicon-based THz photomodulator, the effective lifetime is not a constraining fixed factor but rather an additional degree of freedom for THz photomodulation.

5:00 PM EL01.03.24
Toward Solution-Processed UV Photodetectors via Atomically Thin Fluorine-Functionalized Graphene with Consecutive Carbon Quantum Dots Po-Hsuan Hsiao, Kuan-Han Lin, Tsung-Yen Wu and Chia-Yun Chen; National Cheng Kung University, Taiwan

Heterostructures stand for the artificial structures composed of two or more different solid-state materials. When the dimensionality of materials scales down to nanoscale, the interfaces associated with constitute materials play the dominant role on their materials chemistry, materials physics and even being decisive for the correlated device performances. In this presentation, the physicochemical dynamics of fluorine-functionalized graphene (FF-Gra) coupled with carbon quantum dot film (CQDF) is manifested. By probing the involved electronic structures and optical transitions, bound-carrier population and dynamic phenomena is revealed, which exhibit as main features of for the modulation of photophysical origin. All these features implicate the outstanding UV-responsive flexible photodetectors with sound optical transparency, attesting external quantum efficiency (EQE) of 1.68x10%7%, photoresponsivity of 4.6x107 A/W and detectivity of 2.92x1018 Jones based on such nonintuitive quantum-confined hybrid materials. The present photodetector design, along with the mechanism validation was anticipated to be potential for the development of next-generation optoelectronic devices with desired properties.

5:00 PM EL01.03.25
Revealing Gas Sensing Mechanism of PtO2 Originated from The Structural Equivalence with SnO2 Seongsu Cho1, Yeon Sik Jung1 and Hyuk Jin Han2; 1Korea Advanced Institute of Science and Technology, Korea (the Republic of), 2Sunghin Women's University, Korea (the Republic of)

Conventional gas sensing with Pt relies on the spillover effect, where Pt nanoparticles split gases and disperse onto n-type semiconductors such as ZnO, WO3 and SnO2. In the presence of PO2, the p-type semiconductor nature of PtO creates an electron depletion region at the heterojunction with n-type semiconductors, which in turn affects the gas sensor resistance and thus provides information about the surrounding gas composition. The gas sensing mechanism of another oxidation state, PtO2, has conventionally been considered a p-type semiconductor, similar to PtO until now. However, this traditional interpretation does not explain the increased selectivity and sensitivity observed with PtO2 compared to both PtO and Pt. There is also a lack of research comparing the gas sensing properties based on the different oxidation states of Pt.

In this study, we suggest a novel gas sensing mechanism of PtO2 when combined with SnO2, originating from the structural equivalency between PtO2 and SnO2. Previous reports have demonstrated that elevated temperatures and high partial pressure conditions, Pt in PtO2 can replace Sn in SnO2 lattice due to their identical rutile structure and oxidation state (4+) as well as their similar ionic radii. Additionally, PtO2, known for its strong oxidizing properties, creates oxygen vacancies in a reducing gas atmosphere. These vacancies then become active sites for the adsorption of target gases, significantly enhancing gas sensor performance. To verify the sole influence of the oxidation state of Pt, we designed 3D-aligned Pt decorated SnO2 nanowires using Thermally-assisted nanotransfer printing (T-nTP). This method improved mass transport, ensured consistent network connections, and increased the surface area, enabling specific focus on the differences originating from the oxidation state of Pt. Via annealing in an air furnace, the oxidation states of Pt were selectively altered while keeping the other conditions, such as the structure of the gas sensor and the state of the supporting material, SnO2. Specifically, annealing the gas sensor at 900°C results in approximately 99% conversion of PtO into PtO2. We observed that PtO2 decoration on SnO2 exhibited superior selectivity and sensitivity for hydrogen sulfide (H2S) compared to Pt decoration. PtO2 showed approximately 60 times greater sensitivity compared to the sample annealed at a lower temperature, achieving response ratios (Rs / R0) exceeding 50 at a concentration of 1 ppm. Overall, this study presents a newly discovered gas sensing mechanism with PtO2 and demonstrates significantly improved sensitivity and selectivity, particularly in detecting H2S. Moreover, the gas sensors synthesized via T-nTP offer the potential for comparative analysis of gas sensing properties across different oxidation states of other noble metals.

5:00 PM EL01.03.26
Nanoscale Morphology, Defect Identification and Electronic Spectroscopy of Thin Molybdenum Carbide (m-MoC) Crystals under Ambient Conditions Gokay Adabas1, Saima A. Sumarya1, Iker Demirgözlü1, Elif Okaya1, Omer R. Caylana1, Goknur Cambaz Buke1, Cem Seviki2 and Mehmet Z. Baykara1; 1University of California, Merced, United States; 2Eskişehir Technical University, Turkey; 3İÜBB University of Economics and Technology, Turkey; 4University of Antwerp, Belgium

The emerging materials family of thin transition metal carbides (TMCs) have garnered significant recent attention due to their distinctive features such as high thermal and chemical resistance, good electrical and thermal conductivity, high hardness, and potential for energy storage as well as electromagnetic shielding. The application potential of thin TMCs will strongly depend on atomically-scale structural and chemical-physical properties. On the other hand, the necessity of high vacuum and low temperatures for atomic-resolution experiments has led to a debate regarding the relevance of such characterization approaches for real-life applications.

Here, we present a nanometer- and atomic-scale characterization study of thin crystals of molybdenum carbide (m-MoC) grown through chemical vapor deposition (CVD). The experiments are performed via conductive atomic force microscopy (C-AFM), under ambient conditions. It is found that the crystal surfaces are partially covered by graphene. Moreover, atomic-resolution imaging, combined with density functional theory (DFT), allows the identification of various defects found on the crystal surfaces. Finally, current vs. voltage spectroscopy performed on the defects provides information about their local influence on surface electronics.

5:00 PM EL01.03.28
 Mimicking Positive Aging using Atomic Layer Deposition of Alumina in Quantum Dot Light-Emitting Diodes Haoyue Wan 5:00 PM

5:00 PM EL01.03.29
Curvature-Induced Instability in Crystallization of Chiral Liquid Crystals Sepideh Norouzi1, Jeremy R. Money1, Jose A. Martinez-Gonzalez2 and Manirosadat Sadath1; 1The University of South Carolina, United States; 2Universidad Autonoma de San Luis Potosi, Mexico

Crystallization in curved entities such as viral capsids, Radiolaria, and ice-freezing is ubiquitous in nature, wherein the spatial coordination of constituent materials adjusts to adequately accommodate within curvature, resulting in exotic collective properties. Herein, we investigated the nucleation and growth of blue phase (BP) soft crystals within curved topological confinement. BP's represent 3D periodic cubic crystals while they have fluidity. They have the potential to assemble into two crystalline symmetries: BPI with a body-centered cubic structure and BPIII with a simple cubic structure. These cubic crystal lattices are a few hundred nanometers and show selective Bragg's reflection with rapid sub-millisecond response times, which makes them attractive for sensing and photonic applications. They, however, exist in a very narrow temperature range and generate polycrystalline structures when confined in flat films, preventing their widespread use in most practical applications. Moreover, the growing interest in the integration of these ordered materials into miniaturized, flexible devices brings about the need to...
understand the effect of geometrical confinement and curved boundaries on the structure of BPs and their stability and photonic responses. To understand how the interplay of curvature, confinement, and surface anchoring impacts the structural stability and optical response of BPs, we have confined BPs within core-shell and microdroplets with precise size and shell thicknesses. Our observations in shells indicate that increased curvature and strong spatial confinement destabilize BPI promoting its transition into configuration and optical characteristics resembling BPII. Although BPs in shells appeared polycrystalline, the inherent 3D symmetrical curvature in microdroplets facilitated the formation of monodomain crystals, eliminating the need for any specific surface treatments. Moreover, using photo-polymerization technique to stabilize defects in droplets led to an expanded thermal stability range for BPs. Yet, the phase transition temperature in these microdroplets was found to be strongly size-dependent. We have delved into the underlying principles of these molecular arrangements through both experimental and theoretical simulations. These findings can pave the way for designing optically active microstructures, addressing BP-related challenges, offering potential for cutting-edge photonic and sensing applications especially in flexible and wearable devices.

5:00 PM EL01.03.30
Local Defect-Engineering in Monolayer MoS2 through Sulfur Vacancies Controlling with Dip-Pen Nanolithography

Jinho Lee, Jeong-Sik S. Jo, Do Wan K. Kim and Jae-Won Jang

Dongguk University, Korea (the Republic of)

Molybdenum disulfide (MoS2) is a promising layered semiconductor material that can overcome the limitations of conventional silicon-based devices. MoS2 has a unique characteristic in which the band gap changes depending on the thickness; Monolayer MoS2 has a direct band gap of about 1.8 eV, while multilayer MoS2 has an indirect band gap of about 1.3 eV. Therefore, MoS2 has potential applications in various fields such as optoelectronics, sensors, and catalysis. However, the electrical and optical properties of monolayer MoS2 are sensitive to defects on its surface. Sulfur vacancies are the most prevalent defects in MoS2 and they work as electron donors and trap sites. Thus, they create mid-gap states influencing the band structure and the Fermi level of monolayer MoS2. The charge state and the local environment of the sulfur vacancies can either improve or deteriorate the electrical conductivity, the photoluminescence intensity, and the catalytic activity of monolayer MoS2. Thus, it is crucial to control the sulfur vacancies in monolayer MoS2 to optimize its electrical characteristics and device performance. In this study, we propose a method for local defect engineering in monolayer MoS2. The proposed method controls sulfur vacancies through dip-pen nanolithography (DPN), a tip-based lithography technique that enables direct deposition of molecules or ions onto specific regions of the substrate surface.

5:00 PM EL01.03.31
Understanding Surfaces and Interfaces in Nanocomposites of Silicone and Barium Titanate through Experiments and Modeling

Avery Pritchard1, Vanessa Bartling1, Heather Fuentes1, Katrina Nelson1, Jessica Santosa1, Albert Dato1, Todd Monson2 and Renee Van Ginthoven2; 1Harvey Madd College, United States; 2Sandia National Laboratories, United States; 3Air Force Research Laboratory, United States

Computational and experimental studies into particle surfaces and particle-matrix interfaces in nanocomposites of silicone and barium titanate (BTO) nanoparticles will be the focus of this presentation. BTO is a ferroelectric perovskite that is used in electronic devices and energy storage systems because of its high dielectric constant (up to 7,000). Research has shown that the dielectric constant of BTO drastically increases to 15,000 at a BTO particle diameter of 70 nm, which is an intriguing but highly contested result. DIELECTRIC constants of BTO nanoparticles have been determined by fabricating, characterizing, and modeling surface-functionalized BTO powders incorporated into polymer matrices. These studies have indicated that BTO particle size does impact the dielectric constant of the perovskite. However, more sophisticated modeling and advanced characterization techniques are needed to better understand the nature and complexity of interfaces formed between polymers and BTO, as well as investigate the relationships between interfacial properties, nanocomposite properties, and nanoparticle properties.

Here we present experimental and theoretical research into the preparation, transmission electron microscope (TEM) characterization, and simulation of elastomer-matrix nanocomposites containing BTO nanoparticles with diameters ranging from 50 nm to 500 nm. Methods of functionalizing the surfaces of BTO nanoparticles, preparing nanocomposites of BTO and silicone, and determining the dielectric properties of BTO-silicone nanocomposites will be shown. TEM images of BTO nanoparticles in silicone will provide insight into interface formation and be related to (1) nanocomposite properties, (2) COMSOL models of the nanocomposites, and (3) density functional theory simulations of the interactions of water with BTO surfaces. The results from this project will advance our understanding of surfaces and interfaces in BTO-polymer nanocomposites, elucidate the particle size dependence of the BTO dielectric constant, and demonstrate an avenue toward manufacturing flexible elastomer-perovskite nanocomposites for wearable electronic devices and energy storage applications.

SNL is managed and operated by NTIUS under DOE NNSA contract DE-NA0003525. This study was also supported by the National Science Foundation under Grant No. 1945399.

UNDERSTANDING SURFACES AND INTERFACES IN NANO COMPOSITES OF SILICONE AND BARIUM TITANATE THROUGH EXPERIMENTS AND MODELING

SESSION EL01.03: Area Selective Deposition and Etching II

Room 348, Level 3, Summit

Wednesday Morning, April 24, 2024

3:00 PM AM EL01.04.01
Plasma Processes for Isotropic and Anisotropic Atomic Layer Etching

Adrie Mackus; Eindhoven University of Technology, Netherlands

The development of nanoelectronics towards increasingly complex 3D nanostructured devices requires novel combinations of anisotropic and isotropic etching. Atomic layer etching (ALE) will play an important role in the fabrication of such nanodevices because of its Ångstrom-level control and ability to uniformly etch on complex structures. Previously reported ALE processes can be classified in two main categories: plasma processes for anisotropic etching and thermal chemistries for isotropic etching. In this contribution, results for both isotropic and anisotropic ALE will be discussed, focusing on the unique opportunities provided by plasmas. The relatively unexplored category of using plasmas for isotropic ALE allows for processing at lower temperatures and higher etch rates, as will be demonstrated for processes involving fluorination with a SF₆ plasma. Recent work also focuses on isotropic ALE based on etching by di-ketone dosing (e.g., hexafluoroacetylatedone) and plasma cleaning steps. Infrared spectroscopy and simulation studies revealed that the mechanism of etching with diketones involves a competition between etching and inhibition reactions.

9:00 AM EL01.04.02
Atomic Layer Deposition of WOₓ-Doped InOₓ for High-Performance BEOL-Compatible Transistors

Chanyoung Yoo1,2; Balreen Saini2, Jonathan Hartanto2; Cristian Ruano Arens2, John D. Baniecki1, Wilman Tsaï2, Baylor B. Triplett2 and Paul C. McIntyre1,2, 1SLAC National Accelerator Laboratory, United States; 2Stanford University, United States

Metal oxide semiconductors incorporating InOₓ have received significant attention as they possess high electron mobility, can be synthesized at back-end-of-line (BEOL) compatible temperatures, and exhibit excellent transistor characteristics at nanoscale dimensions. Doping InOₓ with several mole % tungsten oxide to form “IW0” has been reported to improve the threshold voltage stability of these semiconductor channel materials. However, currently reported film deposition for IWO is limited to sputtering, which does not allow the growth of conformal films with precise thickness and stoichiometry control on topographically complex BEOL surfaces. This limitation becomes critical when utilizing these films as channel materials in gate-all-around structures. A shift toward deposition methods that support 3D structures is necessary to address the increasing demand for high on-current.

Consequently, we use the 3D-compatible atomic layer deposition (ALD) method to deposit IWO by adjusting the cycle ratios for In and W precursors and the oxidant co-reactant, enabling precise control over the doped film composition. In addition to facilitating highly conformal film growth, ALD-grown IWO may exhibit different point defect contributions and a broader process window for amorphous structure because of the lack of bombardment by energetic species that are present during sputtering. We demonstrate deposition of IWO (1-4 mol% WOₓ) films using ALD and fabricate both bottom- and top-gated thin film transistors with a 3-nm thick IWO channel in a BEOL-compatible process with a maximum temperature of less than 250°C. A transistor with 2 mol% WOₓ-doped IWO exhibits exceptional performance characteristics, including a subthreshold slope of 65 mV/decade, a high Ion off of 70 (W/L = 32, L = 1.5 μm) at VDS = 1.0 V and VG = -2.0 V, and remarkable stability under bias stress. The transistor showed negligible hysteresis and maintained a stable threshold voltage (Vth) under negative and positive bias stress conditions (AVth = -0.06 V and +0.1 V, respectively, at an electric field of 4.2 MV/cm for 1000 s). This Vth stability under bias stress highlights the reliability of ALD-grown IWO for ferroelectric field-effect transistors and its potential to enable high-performance monolithic 3D integrated devices.

Furthermore, we explored the evolution of long-range order within the IWO films through synchrotron X-ray diffraction. We found that doping InOₓ with several mole % of tungsten oxide has a strong anti-correlation with both the ordering and the presence of oxygen vacancies, which are themselves strongly correlated with Vth. This work offers an understanding of the impact of W doping and provides insight into the reliability of InOₓ-based oxide transistors.
Understanding The Formation and Evolution of Surface Oxidation Layers in Nb Thin Films

Jeffrey Dhas, Zihua Zhu, Peter V. Susko, Mingzhao Liu, Eka Bhattacharaya, Jakub Nalaskowski, Sandra Schuiman, Corbet Johnson, Tom Murray, Satyavolu Papa Rao, and Ying-Mei Du

Pacific Northwest National Laboratory, United States; Oregon State University, United States; Brookhaven National Laboratory, United States; NY Creates, United States

Surface oxides formed on metal films have a significant impact on the decoherence and stability of superconducting qubits. Niobium (Nb) exhibits a complex native oxide layer, approximately 10 nm thick, believed to harbor structural and chemical defects contributing to coherence loss in Nb-based devices. In this study, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used to assess the influence of different treatments on the surface oxidation layers of Nb thin films. We employed ToF-SIMS for high-resolution chemical mapping and depth profiling, combined with ex situ O2 annealing experiments. This allowed us to characterize and evaluate the surface oxidation layers of Nb thin films resulting from chemical mechanical polishing (CMP) and accelerated neutral atom beam (ANAB) treatments, comparing them to native oxides formed through air exposure. By combining ToF-SIMS results with XPS and TEM studies, we revealed the differences in oxidation layer thickness and composition, including Nb2O5, Nb2O3, and NbO, on the surface. Moreover, we demonstrated that ANAB-generated oxidation layers exhibit enhanced resistance to further oxidation when compared to native oxides. This finding suggests a promising strategy for mitigating surface oxidation and improving the performance of devices based on superconducting metals.

9:30 AM BREAK

Passivation of Si, Ge and SiGe Surfaces by ALD Nanolayers

Erwin Kessels
Eindhoven University of Technology, Netherlands

For many (opto)electronic devices, it is vital to reduce the recombination of charge carriers at the semiconductor surfaces and interfaces. This is becoming more and more challenging due to the ongoing diversification in semiconductor materials to be used in the devices but also due to the increasing surface-to-volume ratio of the (nano)structures employed in electronics and photonics. Surface passivation can be achieved by employing ultrathin films of semiconductor or dielectric materials which often serve other functionalities in the devices too. The underlying mechanism of the surface passivation can be the reduction of surface defect states (i.e., so-called chemical passivation) and/or band bending due to so-called field-effect passivation effect (e.g., due to fixed charges in the film).

In this contribution, the surface passivation by some innovative nanolayer approaches prepared by atomic layer deposition (ALD) will be presented. The focus will be on Si and Ge surfaces and also include hexagonal SiGe alloy nanowires which are of interest for nanolayers due to their direct-bandgap [1]. The nanolayers include materials such as Al2O3, POx, and (doped) ZrOx as well as stacks thereof [2,3,4,5]. Special attention will be given to the underlying mechanism of the surface passivation achieved as well as its relation to the properties of the nanolayers employed.


Substrate Characteristics and Their Impact on Ruthenium Metal Growth via Atomic Layer Deposition (ALD)

Amnon Rothman and Stacey F. Bent
Stanford University, United States

Noble metal thin films have attracted significant interest owing to their distinctive properties and structures, which make them ideal for applications in microelectronics, catalysis, energy, and photovoltaics. While several parameters influence the properties of these metals for such applications, the deposition process remains a critical factor. Atomic Layer Deposition (ALD) stands out as a prevalent deposition technique due to its surface-sensitive nature. The ALD process is characterized by its self-limiting surface reactions, providing a predictable layer-by-layer growth mechanism and allowing for precise control over film thickness and conformality. However, challenges arise in achieving continuous, pinhole-free noble metal ALD layers on oxide surfaces, often required for photovoltaics. While several parameters influence the properties of these metals for such applications, the deposition process remains a critical factor. Atomic Layer Deposition (ALD) stands out as a prevalent deposition technique due to its surface-sensitive nature. The ALD process is characterized by its self-limiting surface reactions, providing a predictable layer-by-layer growth mechanism and allowing for precise control over film thickness and conformality. However, challenges arise in achieving continuous, pinhole-free noble metal ALD layers on oxide surfaces, often required for photovoltaics.

As stacks thereof [2,3,4,5]. Special attention will be given to the underlying mechanism of the surface passivation achieved as well as its relation to the properties of the nanolayers employed.

Energy Enhanced Atomic Layer Deposition (EEALD)

John F. Conley
Oregon State University, United States

Atomic layer deposition (ALD) is based on alternating purge-separated self-limiting surface chemical reactions in which films are deposited in a layer-by-layer fashion. Inherent advantages of ALD include atomic scale controlled growth of high quality highly conformal thin films at relatively low temperatures. A low thermal budget is often critical for BEOL processing, 3D integration, avoiding unwanted diffusion, and maintaining stable effective work functions and threshold voltages in metal/insulator/metal (MIM) and metal/oxide/semiconductor (MOS) devices and as well as for deposition on glass or flexible substrates for large area electronics. While advantageous for some applications, the low deposition temperatures common in ALD can lead to incorporation of excess -OH groups or other residual impurities from unreacted ligands and result in poor stoichiometry, which may in turn lead to sub-optimal physical, optical, and electrical properties.

A number of approaches have been used to reduce impurities, increase density, improve stoichiometry and morphology, and achieve the desired properties of ALD films. One obvious approach is to increase deposition temperature. However this may move a process into the CVD regime, negating many of the benefits of ALD. The most common approach to improving film quality is to increase deposition temperature. However this may move a process into the CVD regime, negating many of the benefits of ALD. The most common approach to improving film quality is to increase deposition temperature. However this may move a process into the CVD regime, negating many of the benefits of ALD. The most common approach to improving film quality is to increase deposition temperature. However this may move a process into the CVD regime, negating many of the benefits of ALD. The most common approach to improving film quality is to increase deposition temperature. However this may move a process into the CVD regime, negating many of the benefits of ALD. The most common approach to improving film quality is to increase deposition temperature.

To maintain low thermal budget while maximizing film properties, performing annealing during, rather than after, ALD can be beneficial. An alternate approach to help drive reactions and reduce impurity / ligand incorporation is to add extra energy as part of each (or every few) ALD cycles or supercycles. Methods to date include in-situ rapid thermal (MTA, DADA, etc.) annealing, flash lamp annealing, plasma exposure, UV exposure, etc. I collectively refer to all of these as energy enhanced ALD (EE-ALD) [1-16]. (Note that these are distinct from plasma enhanced ALD (PEALD), see [17] for excellent review.) Documented benefits of the various forms of EE-ALD include higher GPC, denser films, lower temperature, improved dielectric constant and refractive index, lower leakage, lower residual impurities. A potential downside of energy enhancement is the additional time these steps add to the ALD super-cycle, particularly the cool down time when in-situ annealing is incorporated.

In this invited talk, I will describe, compare, and contrast the various EE-ALD techniques, focusing on mechanisms (thermal vs. chemical), placement in ALD supercycle, benefits, and drawbacks. I will also discuss the challenges to be addressed in finding the ideal EE-ALD technique. Finally, I will introduce an entirely new method of EE-ALD, microwave enhanced ALD (ME-ALD).


In this work, we systematically investigate the frontier molecular orbital energies of organic semiconductors and their molecularly mixed blends, as well as the impact of different solvents and development of state-of-the-art donor and non-fullerene acceptor materials has led to contradictory claims about the role of energetic offsets at the acceptor (A) - donor (D) interface and key device parameters is missing. This is primarily because of a lack of criteria for choosing the most suitable method to determine the ionization energy (IE) and electron affinity (EA) of organic semiconductors that could precisely predict the energy level alignment at the D/A interfaces. Consequently, the development of state-of-the-art donor and non-fullerene acceptor materials has led to contradictory claims about the role of energetic offsets at the D-A interface. This makes it difficult to establish design rules for the development of future materials. In this work, we systematically investigate the frontier molecular orbital energies of organic semiconductors and their molecularly mixed blends, as well as the impact of different solvents and molecular orientation on the resultant energies, via different probing techniques; in particular, low-energy inverse photoelectron spectroscopy (LE-IPES), which is a relatively novel and non-destructive technique that enables the direct determination of EA of organic semiconductors with high precision. By characterizing and fabricating thin films and devices based on over a dozen different D/A blends, we demonstrate the significant differences that have been an ongoing debate in the field for energetic losses and device performances.

11:15 AM EL01.04.07
High Precision Capillary Printing of Polymer Patterns for The Area-Selective ALD of Transparent Conducting Oxide Vincent Jousseaume1, Marc Pascal1,2, Achille Guittton1, Tony Jullien1, Luana Golanski1 and Chloe Guerin1; 1CEA, LETI, France; 2Humminck, France

Thin films of transparent conducting oxides (TCO) are used as electrodes for optoelectronic devices and microdisplays. However, these oxides are often difficult to pattern with standard lithography and etching processes especially in the case of ZnO, which is very sensitive to water. This problem becomes very limiting when it is necessary to redress the characteristic dimensions of the devices (typically for structures below 5 mm). An alternative approach is the area selective deposition (ASD) of these oxides. More precisely, one way consists in using polymeric film that can act as ALD inhibiting layer and prevent deposition in certain areas. In this work, polymeric thin films were printed by an innovative direct nanoprinting technique [1]. This high precision capillary printing (HPCAP) method is directly derived from AFM technologies, replacing scanning probes by nano capillaries. These "nanopenes" are filled with a solution containing the material to deposit and can draw complex geometries at the surface of the substrate with resolution between 50 nm and tens of µm and positioning precision as low as 20 nm.

Different patterns with poly(methyl methacrylate), poly(vinyl pyrrolidone) or an epoxy-based resist (SU-8) were printed on a silicon substrate. Then, TCO films were deposited on the patterned polymers by low-temperature ALD. The thin film growth and material structure were analyzed using several characterization techniques including ellipsometry, atomic force microscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy.

Our results show that it is possible to produce regular micrometeric polymer patterns using this HPCAP printing technique. Furthermore, this approach combines with ALD can effectively allow to localize the growth of an oxide such as ZnO. An exclusion zone around the polymer in which ZnO is not deposited is also observed depending of the polymer used. Finally, in the favorable configurations, the polymer can be selectively removed without impacting the ZnO layer. Thus, an array of pixels with 10 nm of width has been successfully produced. In conclusion, a solution combining the direct nanoprinting of a polymer pattern followed by the ALD of a transparent conducting oxide appears to be a promising path toward the realization of a matrix of pixels sub-10 nm.


11:30 AM *EL01.04.08
Atomic Layer Etching of Metals for Microelectronics Robert L. Opila and Omar Melton; University of Delaware, United States

As microelectronics evolves more and more metals are being used. Deposition techniques like atomic layer deposition (ALD) are not always available. As a result, precise, selective etching methods are becoming more and more important. For example, magnetoresistive random-access memory (MRAM) is a leading option for non-volatile digital data storage and depends upon precise stacking of a variety of magnetic metals. Atomic layer etching (ALE), as a time reversed ALD method, has potential for accurately etching nearly all materials, particularly those that cannot be deposited with precision. Herein, we demonstrate the etching of some transition metals used in MRAM applications, Co, Fe, and CoFeB where the tunneling barrier (MgO) acts as an etch stop. The etch is conducted using a thermal approach (versus plasma), where the film is etched by sequential dosing with to two different chemical moieties, chlorine and acetylaceton (acac). Thus, optimizing kinetic factors to overcome thermodynamic limitations, thereby developing a controlled etch driving towards one atomic layer at a time. Similar techniques demonstrate that Cu is etched under comparatively mild conditions, whereas Pt requires more aggressive temperatures and pressures to facilitate the etch. Etching of candidates for lowest level metalizations will also be discussed.

SESSION EL01.05: Surfaces and Interfaces II
Session Chairs: Santanu Bag, Mandakini Kanungo and Gilad Zorn
Wednesday Afternoon, April 24, 2024
Room 348, Level 3, Summit

1:30 PM *EL01.05.01
Advancing Measurement Science for Microelectronics: CHIPS R&D Metrology Program Maria Dowell; National Institute of Standards and Technology, United States

The CHIPS and Science Act of 2022 called for NIST to “carry out a microelectronics research program to enable advances and breakthroughs…that will accelerate the underlying R&D for metrology of next-generation microelectronics and ensure the competitiveness and leadership of the United States….”, NIST is leveraging its measurement science expertise, standards development contributions, and stakeholder engagement practices to address the highest priority metrology challenges identified across industry, academia, and government agencies. The program expands upon NIST’s strong track record of supporting the semiconductor technology and manufacturing ecosystem by developing, advancing, and deploying measurement technologies that are accurate, precise, and fit-for-purpose.

Under the CHIPS and Science Act of 2022, NIST is expanding its support of the microelectronics technology and manufacturing ecosystem by developing, advancing, and deploying measurement technologies that are accurate, precise, and fit-for-purpose.

2:00 PM EL01.05.02
Probing the Interfacial Energies in Organic Semiconductor Blends Anirudh Sharrar; Jules Bertrandie, Jianhua Han, Julien F. Gorenflot, Frédéric Laquai and Derya Baran; King Abdullah University of Science & Technology, Saudi Arabia

In the realm of shrinking new-generation electronic and photonic devices, the role of functional thin-film interfaces is pivotal for optimizing device design. For example, the energetics of materials play a critical role in charge transfer at the interface between functional materials with dissimilar properties, as in the case of organic photovoltaics (OPVs). Yet, a clear correlation is needed in order to optimize device performance. Consequently, the development of state-of-the-art donor and non-fullerene acceptor materials has led to contradictory claims about the role of energetic offsets at the D-A interface. This makes it difficult to establish design rules for the development of future materials.

In this work, we systematically investigate the frontier molecular orbital energies of organic semiconductors and their molecularly mixed blends, as well as the impact of different solvents and molecular orientation on the resultant energies, via different probing techniques; in particular, low-energy inverse photoelectron spectroscopy (LE-IPES), which is a relatively novel and non-destructive technique that enables the direct determination of EA of organic semiconductors with high precision. By characterizing and fabricating thin films and devices based on over a dozen different D/A blends, we demonstrate the significant differences that have been an ongoing debate in the field for energetic losses and device performances.

We show that the IE and EA values measured using ultraviolet photoelectron spectroscopy (UPS) and LE-IPES are the most relevant in understanding the charge generation mechanism in
OPVs. We further demonstrate how the energy levels of organic semiconductors evolve when blended with energetically dissimilar materials,\cite{1} and the impact of morphology and phase segregation on the resultant energetics. Probing a range of small molecule - small molecule and polymer: small molecule D/A blends, we show that the photovoltaic gap \(E_{\text{CV}}(E_{\text{LUMO-VA}})\) measured from neat materials can be insufficient in some cases, for establishing material-property relationships in solar cells. By controlling the D/A ratio in molecular blend films, we probe the changes induced in \(E_{\text{CV}}\) of D/A blends as a result of intermixing, intramolecular, and electrostatic interactions between the D/A materials. We rationalize these findings to the resultant photovoltaic parameters and voltage losses in OPVs.

Lastly, from OPVs based on six different D-A blends having systematically varying IE-offsets \(\Delta IE\), we convincingly demonstrate that \(\Delta IE\) plays a crucial role in charge generation. In contrast to earlier works, we show that a vanishing \(\Delta IE\) is detrimental to device performance. Overall, these findings establish a solid base for reliably evaluating material energetics and interfacing properties toward interpreting property-performance relationships in solution-processed OPVs.

\[\alpha \rightarrow \beta\] The alpha-phase formamidinium lead triiodide (FAPbI\(_3\))

**References**


**2:15 PM EL01.05.03**

Interfacial Engineering with Aromatic Diammonium Acetates for Amplifying Hole Extraction in Tin Perovskite Solar Cells

Donghoon Song, Yuean Xu and Qiuming Yu; Cornell University, United States

Perovskite solar cells have emerged as one of the most promising photovoltaic technologies because of their high efficiency, solution processability, and mechanical flexibility, which enables ubiquitous energy harvesting. From device perspective, interfaces play critical roles in charge transport and collection, which turns to be particularly important for tin-based perovskite solar cells. Tin perovskite solar cells (TPSCs) stand at the forefront as toxicity-lean technology, featuring compelling properties such as the large light absorption coefficient, small exciton binding energy, ideal bandgap, slow hot carrier cooling, and high charge carrier mobility. Especially, tin perovskites are adjustable to a bandgap of ~1.34 eV being optimal for single-junction solar cells according to the Shockley-Queisser limit. Beyond merely a toxicity issue, such superb properties drive TPSCs to an efficiency of power conversion (PCE) close to 15%. To close a gap with that (~20%) of lead counterparts, more attentions have been bestowed on tin perovskites to mitigate fast crystallization and Sn(II) oxidation, and to modify their interfaces to attain efficient and stable charge collection. Currently, the inverted p-i-n planar architecture is adopted widely for TPSCs because charge transport is more efficient due to the nature of p-type tin perovskites. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) has been used as hole transport layer (HTL) due to the high-performance and reproducibility in an inverted planar architecture. PEDOT:PSS benefits from the demanding properties for TPSCs including a suitable work function (WF: ~5.0–5.2 eV), decrement conductivity, and dopant-free merits. However, ambient annealed PEDOT:PSS thin films are terminated with a thin layer of PSS, which has acidity and is unfavorable for hole collection. We tackle this challenge via interface engineering. Specifically, we treated the surface of PEDOT:PSS using aromatic diammonium acetate salts dissolved in a highly volatile but interactive solvent, which not only modifies PEDOT:PSS itself but also its interface with tin perovskite. The salts are embedded into PEDOT:PSS to bridge and ameliorate its interface with tin perovskite and hence to amplify its hole extraction characteristics. Consequently, we attain a high device efficiency as ~12.1% and impressive stability without encapsulation for ~2800 h. The materials and methodologies of our development are extendable to other perovskites- and PEDOT:PSS-based bio, energy, and electronic applications. Moreover, they can expand on surface and interface engineering to gain broader scopes, thereby lying a critical bridging stone on paths to diverse applications.

**2:30 PM BREAK**

**3:00 PM EL01.05.04**

Evaluation of Bulk and Rear Interface Passivation of Thin Film Photovoltaics by Surface Photovoltage Spectroscopy

Nathan D. Rock 1, Michael Scarpulla 2, Adam Phillips 3, Ebin Bastola 2, Ed Sartor 3, Andrea Mathew 3 and Matthew Reese 3; 1University of Utah, United States; 2The University of Toledo, United States; 3National Renewable Energy Laboratory, United States

Thin film photovoltaics have the potential to dramatically reduce cost and carbon footprint of photovoltaic manufacture. However, current solutions like GaAs are cost prohibitive except for special applications, while more affordable CdTe, SbSe and perovskite devices lag behind silicon in efficiency. To identify and resolve these deficiencies, a fuller understanding of the role of interface and bulk passivation, diffusion length, surface recombination velocity, and band structure is necessary.

We present surface photovoltage (SPV) spectroscopy data on multiple CdTe and SbSe photovoltaic devices, comparing the effects of bulk and surface passivation strategies. The effects of doping, wet etchants, CdCl\(_2\) annealing, and surface reconstruction are presented and the results interpreted by advanced modeling which fully describes the device under test.

**3:30 PM EL01.05.05**

Non-Equivalent Atomic Vibrations at Interfaces in a Nitride Superlattice

Eric R. Hoglund 1, 2, Harrison Walker 2, Kamal Hussain 3, De Liang Bao 2, Haoyang Ni 3, Jefferey Baxter 3, Asif I. Khan 3, Sokrates Pantelides 4, Patrick E. Hopkins 2 and Joshua A. Hachtel 2; 1Oak Ridge National Laboratory, United States; 2University of Virginia, United States; 3Vanderbilt University, United States; 4University of South Carolina, United States; 5University of Illinois at Urbana-Champaign, United States

The structural and chemical discontinuities at interfaces in III-V material heterostructures are what lead to their emergent electronic properties. However, the spectrum of vibrations in the materials often have large mismatch and large interface thermal resistances can limit device performances. The unique structure and chemistry at interfaces in these materials do not only lead to unique electronic properties, but also unique atomic vibrations. In the case of heterostructures made from AlN-Al\(_{0.65}\)Ga\(_{0.35}\)N-AlN, the nonequivalence of the two interfaces has long been recognized in that they host different two-dimensional carrier gasses.\cite{1} The nonequivalence of the corresponding atomic vibrations, however, has not been investigated so far due to a lack of experimental techniques with both high spatial and high spectral resolution. Herein we experimentally demonstrate the nonequivalence of AlN-Al\(_{0.65}\)Ga\(_{0.35}\)N-AlN interface vibrations using monochromated electron energy-loss spectroscopy in the scanning transmission electron microscope (STEM-EELS)\cite{2} and density-functional-theory (DFT). We demonstrate that angle-resolved STEM-EELS possess mixed real- and reciprocal-space selectivity of the vibrational response, which enables direct mapping of the nonequivalent interface vibrations using monochromated electron energy-loss spectroscopy in the scanning transmission electron microscope (STEM-EELS)\cite{2} and density-functional-theory (DFT). We demonstrate that angle-resolved STEM-EELS possess mixed real- and reciprocal-space selectivity of the vibrational response, which enables direct mapping of the nonequivalent interface vibrations using monochromated electron energy-loss spectroscopy in the scanning transmission electron microscope (STEM-EELS)\cite{2} and density-functional-theory (DFT).

References


4:00 PM EL01.05.06

Improved Photovoltaic Performance through Ionically Regulated Space Charge Zones in n-FAPbI\(_x\) Perovskite Solar Cells

Jhyun Kim 1, Ji-Sang Park 2, Gye Yeong Kim 3 and William Jo 1, 3; 1Ewha Womans University, Korea (the Republic of), 2 Sungkyunkwan University, Korea (the Republic of), 3 Korea Institute of Science and Technology, Korea (the Republic of)

The alpha-phase formamidinium lead triiodide (n-FAPbI\(_x\)) is considered the most promising photoactive layer material due to its narrow bandgap and superior thermal stability for perovskite
layers. The current study introduces an innovative 3D plasmonic structure comprising silver nanoparticles (AgNPs) and HMM (4 periods of Au/TiO2) to enable highly sensitive and reliable studies on bromide- and chloride-based perovskite quantum dots should be performed. Herein, we demonstrate that surface ligand exchange studies of green-emitting CsPbBr3 perovskite high catalytic activity, collectively contributing to hysteresis and instability in perovskite solar cells. Therefore, to improve the electron transporting properties of TiO2, various surface modifications and doping strategies have been tried. Among various approaches, the alkali metal doping of TiO2 has proven to be beneficial to achieving overall improvement of the PSCs' performance. Our research explores how adding lithium (Li), sodium (Na), and potassium (K) to mesoporous TiO2 affects its electronic properties. We also investigate the chemical interaction between the perovskite layer and TiO2, as well as the doped TiO2 with alkali metals. We use soft (XPS) and hard X-ray photoelectron spectroscopy (HAXPES), along with resonance photoemission spectroscopy and X-ray absorption spectroscopy (XAS). Ultimately, we evaluate how alkali metal doping influences the efficiency and stability of the device. XPS and HAXPES analyses reveal that upon introducing Li, Na, and K to TiO2, surface Ti4+ undergoes reduction to Ti3+, while bulk Ti4+ states remain unchanged. The reduction is more pronounced with Li, decreasing from Na to K. This implies Li acts as a dopant, whereas Na and K modify the TiO2 surface. XAS studies support this conclusion, showing changes in the TiO2 layers. Resonance photoemission spectroscopy indicates that Li induces more defect states that result from Ti4+ reduction. Upon perovskite deposition, these defect states diminish, indicating electron transfer from perovskite to TiO2, oxidizing it. The reduction of defect states is highest in Li-doped TiO2. Additionally, Ti2p peak shifts to lower binding energy, indicating upward band bending at the TiO2/perovskite interface. This band bending is consistent across all TiO2 types and their perovskite interfaces studied here. Notably, the TiO2/perovskite interface with Na and modifications exhibits a higher presence of Pb0 states, suggesting a defective interface. The Li doped TiO2 based PSCs have higher power conversion efficiency compared to the others. The enhanced power conversion efficiency observed in Li-doped TiO2-based PSCs can be attributed to the improved conductivity resulting from lithium incorporation. This augmentation facilitates the efficient transportation of photo-generated electrons. However, for sustained and stable PSC performance, Na and K-modified TiO2 devices exhibit superior characteristics. The spectroscopic investigation, in conjunction with device performance, shows that there is a favorable upward band bending from TiO2 to the perovskite, and the defects of TiO2 are passivated by the perovskite itself. Among used alkali modifiers, the Li dopes the TiO2 to increase the electron conductivity and with fewer interface defects, amounting to superior power conversion efficiency. On the other hand, Na and K act as modifiers for the TiO2 layer, contributing to a more stable device performance. This stability can be attributed to their relatively larger ionic radii compared to Li.

5:00 PM EL01.06.05
Surface Engineering Studies on CsPbBr3 Perovskites Quantum Dots for Optoelectronic Applications Sinyoung Cho1, Jigeon Kim1, Soon Moon Jeong1, Min Jae Ko2, younghoon kim3 and Jong-Soo Lee1; 1Daeugu Gyeongbuk Institute of Science and Technology, Korea (the Republic of); 2Hanyang University, Korea (the Republic of); 3Kookmin University, Korea (the Republic of) Lead halide perovskite quantum dots have been considered as the most promising materials for next-generation optoelectronics because of their high light absorption, narrow emission, and excellent photophysical and optoelectronic properties. Organic ligands with long hydrocarbon chains used as ligands in quantum dot synthesis should be exchanged to short organic/inorganic ligands for improving the charge transporting in optoelectronic device applications. However, previous research related to surface ligand exchange for solar cell application have been largely focused on iodide-based CsPbI3 perovskite quantum dots so far. For various solar cell applications such as tandem solar cell and Building-integrated photovoltaics (BIPVs), ligand exchange studies on bromide- and chloride-based perovskite quantum dots should be performed. Herein, we demonstrate that surface ligand exchange studies of green-emitting CsPbBr3 perovskite quantum dots, utilizing several materials such as NaOAc. Improved charge transporting property within CsPbBr3 perovskite quantum dots thin films contribute to the electroluminescent solar cell applications with high open-circuit voltage of 1.6 V and power conversion efficiency of 3.9%. Also, quantum dot light-emitting diodes with synthesized CsPbBr3 perovskite quantum dots...
was fabricated via interfacial engineering, showing 6.5% of EQE and 22.5 cd/A of current efficiency.

5:00 PM EL01.06.06
Towards Improved Device Performance: A Study on Defects and Interfaces in MHP Devices using Electron Spin Resonance Spectroscopy
Jose A. Delgado1,2, Ross Kerner2, Joseph Luther2 and Joseph Berry1,2; 1The University of Colorado Boulder, United States; 2National Renewable Energy Laboratory, United States
Electron spin resonance (ESR) spectroscopy has been identified as a powerful method for nondestructively probing intrinsic defects and interfaces in metal halide perovskite (MHP) devices. Key challenges in MHP devices stem from defects originating from synthesis, interface reactions, lattice strain, energy level mismatches, and other interfacial issues. Furthermore, intrinsic perovskite defects, which tend to propagate post-device deployment [1-3], have substantial implications on device stability. Traditional approaches, like photoemission, often fall short in accurately characterizing these defects due to their constraints at near-surface regions. To circumvent these limitations, nondestructive methods with an acceptable probing depth and sensitivity are needed. In our study, UV and visible light sources were applied to MHP samples to analyze degradation dynamics. We acquired both ex situ and in situ EPR spectra from MHP single crystals, precursor powders, and perovskites interfaced with transport materials. The results provide valuable insights into defect origins and degradation pathways, further emphasizing the importance of a comprehensive understanding to improve MHP-based device longevity and performance.

5:00 PM EL01.06.08
Interfacing Durable Materials to Enable Structural Electronics
Georgi Kaufmann1, Mychal Taylor1, David Boose1, Emily Huntley1, Samuel Leguizamon1, Michael Gallegos1, Leah Appelhans1, Randy Schunk1 and Bryan Kaehl1,2; 1Sandia National Laboratories, United States; 2Center for Integrated Nanotechnologies, United States
In-mold structural electronics (IMSE) is a manufacturing approach to integrate devices into any architectural form factor, providing design freedom and device simplification while delivering advantageous size, weight and power. IMSE typically links integrated circuits and discrete components formed using screen-printing nanoparticle-based inks onto flat, thermoplastic substrates that are molded into 3D forms—material/electrode/processes with wide variable interfaces that are woefully suited for demanding environmental applications. Our project seeks to demonstrate the application of more robust and reliable materials, compatible in extreme environments, such as metal foils for circuit patterning and moldable thermosets. We have explored patterning of copper foils onto b-staged dual cure epoxies and dual cure epoxies that are subsequently formed into test coupons to study interface delamination, encapsulation and environmental stability. Additionally, we have adapted the chemistry of frontal ring-opening metathesis polymerization (FROMP) of dicyclopentadiene (DCPD), a rugged thermoset material, to be compatible with IMSE. Foil patterned pre-forms are vacuum molded into devices such as 3D RF circuits, battery interconnects, and capacitive touch panels that are subsequently locked into shape at ambient temperature using FROMP. This represents a breakthrough for IMSE technologies, enabling 3D device integration into challenging environmental architectures.

5:00 PM EL01.06.09
Thermal Stability of Metastable GeSn Nanowires
Anis Attiaoui1,2, John Lentz1, Jarod Meyer1, Kunal Mukherjee1 and Paul C. McIntyre1,2; 1Stanford University, United States; 2SLAC National Accelerator Laboratory, United States
The (Si)GeSn semiconductor material system is highly desired as a potential candidate for optical interconnects and monolithic photonic integration on Si. The demonstrated fundamental direct band gap of this complex metal-oxide-semiconductor (CMOS) compatible semiconductor has sparked great interest due to its unique properties. Unfortunately, the low solubility of gray-Sn (ε-Sn) in Ge (1 at.%) and the large lattice mismatch between ε-Sn and Ge of approximately 14%, make it difficult to maintain its thermal stability. In fact, rapid thermal annealing (RTA) at temperatures above 400 °C leads to Sn segregation and island formation for Ge0.9Sn0.1 [1]. Moreover, the low temperature growth of GeSn (~350 °C) can promote the formation of many point defects (mostly divacancies) and act as poorly understood impurities [2]. An often-observed background p-type doping of ~1016-1017 cm−3 leads to strong electric field leakage in devices due to charge carrier trapping. Consequently, it is highly desirable to enhance the thermal stability of this material. Herein, we present a method to counteract annealing-induced surface segregation of Ge core/GeSn shell nanowires grown by previously reported methods [3]. Surface passivation significantly improves the thermal stability of GeSn alloys through the atomic layer deposition (ALD) of a very thin Al2O3 oxide layer (~5 nm). Next, annealing the ALD-coated NWs at different temperatures (300°C, 350°C, 400°C, 450°C, and 520°C), above the growth condition of the NWs (~275°C) was systematically investigated. First, structural characterization (X-ray diffraction and scanning electron microscopy (SEM)) demonstrated the unaltered strain state and morphology after annealing (9±1 at. % Sn composition). Second, low-temperature (80K) infrared photoluminescence spectroscopy was undertaken on the annealed NWs to better quantify the recombination mechanisms after annealing. Interestingly, two key findings were observed: an average of 5-fold increase in the PL integrated intensity after annealing, and a blueshift of the band-to-band optical transition. This blueshift suggests that deep level traps are not a potential mechanism for such bandgap shift, as a bandgap contraction would be expected in that case. Understanding the mechanism behind such a blueshift is still an ongoing work. However, a plausible hypothesis can be linked to the nature of the short-range orderings in these materials, as it has been shown theoretically to be the case [4]. Third, single NW devices were fabricated to measure the resistivity variation before and after annealing. The resistivity increases from 0.28±0.02 Ω-cm for an as-grown NW to 0.42 ± 0.08 Ω-cm, when annealed at 450°C. The resistivity increase suggests a modest decrease in the p-type carrier density of the NW. The effect of annealing on the structural and optoelectronic properties of the GeSn NW is explored in this work. Further results on the optical bandgap and resistivity changes will be reported.

References:

5:00 PM EL01.06.11
Magnetic Assembly of Vertical Nanogaps for Highly Sensitive Electrical Biosensors.
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1University of Science & Technology, Korea (the Republic of); 2Korea Institute of Machinery & Materials, Korea (the Republic of)
Nanogap biosensors have emerged as potential tools for the detection and analysis of minute quantities of biomolecules, offering unparalleled sensitivity, a low limit of detection (LOD), and enhanced output signals. However, their potential is often limited by the intricate and labor-intensive processes required to precisely engineer the the tiny gap between electrodes. In this work, we present an innovative fabrication method to obtain vertical nanogap platforms for electrical biosensing. Leveraging magnetic attraction, we freely construct 40 nm gaps by assembling antibody-tagged nanowires onto a nanodisk positioned between a pair of microelectrodes. An electrically conductive bridge is established when gold nanoparticles, conjugated with targeted antigen, are captured within the gaps. This results in a substantial amplification in the output current across the electrodes. Our platforms demonstrate an LOD of 18 pM with a linear detection range up to 150 pM. This approach offers a versatile biosensing platform with potential integration into a myriad of applications, from lab-on-chip systems to biomedicine and point-of-care diagnostics.

5:00 PM EL01.06.12
Adsorption Kinetic Approach of a Mixed Alkylamido-Cyclopentadienyl Hafnium Precursor in H2O2 Atomic Layer Deposition
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In this study, the growth kinetics of HfO2 via the atomic layer deposition (ALD) using a mixed alkylamido-cyclopentadienyl hafnium precursor are proposed based on experimental data. The hydroxyl concentration on the targeted surface, which is sensitive to the surface condition prior to the ALD, governs the saturated growth per cycle (GPC) values. Moreover, we found that the bulkiness of remaining ligands on adsorbed species hinders the adsorption of CpHf(N(CH3)2) (Cp-Hf) molecules.
Considering this phenomena, we proposed a kinetic model by calculating the energetic terms to quantify the steric hindrance effect of the first elementary surface reaction of precursor Cp-Hf. The targeted Si substrate at several levels to evaluate the relaxation of saturated GPC and steric hindrance effect on the nature of the surface. According to the experimental ALD process, the film growth was found to be influenced by the steric hindrance factor, especially at the temperature range from 150 °C to 250 °C, but the hindrance effect decreases with increasing temperature and disappears at 300 °C. The effective activation energy of the adsorption of Cp-Hf molecules on Si substrates was estimated to be 0.2 eV. Although our present model is limited to the ALD of HfO2, we foresee that the kinetic model could potentially assist the study of metal oxide ALD which utilizes a wide range of precursors.

5:00 PM EL01.06.14
Thermal Transport and Mechanical Stress Mapping of a Compression Bonded GaN/Diamond Interface for Vertical Power Devices
William Delmas, Aman Jarzembski, Matthew Bahr, Anthony McDonald, Wyatt Hodges, Ping Lu, Julia Deitz, Zachary T. Piontkowski and Luke Yates; Sandia National Lab, United States
In this work, we have developed a technique to map the thermal transport and mechanical stress at the GaN/diamond interface using a novel compression bonding method. The technique involves applying a pressure of 3-5 GPa to the GaN/diamond interface, which causes the GaN to deform and the diamond to remain rigid. This produces a compressive stress in the GaN, which can be used to measure the thermal conductivity of the GaN. Additionally, the technique allows us to map the mechanical stress distribution at the interface, which can be used to assess the reliability of the GaN/diamond interface. This work represents a significant step forward in the development of high-performance GaN power devices.
In the last 20 years Gallium Nitrde (GaN) electronics have outstripped conventional silicon devices in both efficiency and breakdown voltages. This enhanced performance of GaN devices comes at the cost of increased operating temperatures, kindling a need to develop more robust thermal management schema for such technologies. One such design proposes taking advantage of passive heat dissipation by bonding the GaN device to a high thermally conductive substrate, such as diamond. This would allow the heat generated in the GaN to flow into the diamond, reducing operating temperatures. To test this design, GaN and diamond die were bonded under 2 kN of force via an Ar activated intermetallic bonding layer of Ti/Au. The total bonding area of GaN/diamond stacks was quantified using confocal scanning acoustic microscopy (C-SAM), revealing both bonded and unbonded areas. These areas were confirmed to be bonded/unbonded using a combination of Focused Ion Beam milling and Transmission Electron Microscopy, with the unbonded regions being identified as a delamination at the Ti/diamond layer. Raman microscopy revealed a uniform compressive stress of ~80 MPa in the well bonded areas in addition to, stress oscillations where the sample transitions from being bonded to unbonded, corresponding to a net stress differential of up to ~150 MPa. The thermal properties of the GaN/diamond stack were measured through spatially resolved frequency-domain thermoreflectance (FDTR), with the bonded area boasting a thermal boundary conductance (TBC) of ~100 MW/m²K. FDTR also revealed the presence of micron-scale unbonded regions that showed up as fully bonded under C-SAM. Furthermore, Co-Local Raman/FDTR mapping was demonstrated for the first time with the mapping of a micron-scale unbonded region, showing that stress differentials border the low TBC region. Overall, our work demonstrates a new method for thermal management in vertical type GaN devices that maintains low intrinsic stresses while boosting thermal boundary conductance.

Acknowledgements: Sandia National Laboratories is a multi-mission laboratory managed and operated by the National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract No. DE-NA0003525. SAND2023-1173A

5:00 PM EL01.06.15
Spectroscopic Analysis of Polymer and Transition Metal Dichalcogenide Interface for Photodetection Applications

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Two-dimensional transition-metal dichalcogenides (2D TMDs) have been extensively studied for photodetection applications due to their strong optoelectronic behavior in the visible range and tunable band gap. [1] However, the optoelectronic properties of 2D TMDs can deteriorate due to surface defects and exposure to air and water. [2] Researchers have used a variety of materials to combat this degradation and passivate the surface, but polymers are ideal for passivating 2D TMDs for photodetection applications as many are transparent in the visible range. [3] Researchers have used polymers to perform significant modulation of the optoelectronic properties of hybrid devices via doping, passivation, dielectric screening, and capacitive effects. [4] These schemes illustrate that polymers can contribute multiple mechanisms to the polymer/2D TMD interface. In this work, the 2D TMD and polymer interface is assessed spectroscopically for three common polymers to evaluate the efficacy of each polymer in passivating the MoS2 surface for photodetection applications. Evaluating this interface with spectroscopic methods, especially with ultrafast and dynamic pump probe measurements, mimics the physics occurring during photodetection operation and thus provides a clearer understanding of the fundamental physics at play.

For this study, a representative group of three commonly available polymers were chosen to understand the relative passivation effects: parylene N (Pa-N), polymethyl methacrylate (PMMA), and polyvinylidene difluoride-trifluoroethylene (PVDF-TrFE). Pa-N is an extremely inert polymer used frequently in organic electronics as a dielectric and biomedical devices as a chemical barrier. [5] PMMA is an electron beam photore sist frequently used to encapsulate 2D TMD devices for passivation. [6] PVDF-TrFE is an electroactive polymer that has been shown to be piezoelectric, pyroelectric, and ferroelectric, and as a result, is widely applied for flexible sensors. [7] PMMA and PVDF-TrFE have functional groups containing oxygen and fluorine that would be expected to better fix sulfur vacancies or provide doping than Pa-N.

Spectroscopic measurements including Raman spectroscopy, photoluminescence spectroscopy, and time-resolved terahertz spectroscopy (TRTS) were performed on these samples to observe the effect of polymer passivation on a MoS2 monolayer. The photoluminescence measurements were done with a hyperspectral microscope to facilitate greater averaging of the photoluminescence response across the sample surface. The results of the Raman and photoluminescence spectroscopy show an n-doping effect on the MoS2 spectra after coating with Pa-N and PMMA through a downshift in the Raman peaks and a redshift in the photoluminescence peak. In the TRTS measurements, the peak of the response was higher for all polymer samples, which suggests more charge is generated in polymer passivated samples upon excitation either due to doping or successful passivation. For PVDF-TrFE, the lifetime of the carriers was longer than any other sample. These results indicate that polyole PVDF-TrFE best passivates the surface of the MoS2 of the polymer tested. Further work is being done to understand the exact mechanism by which it passivates the surface, but it is suspected that the fluorine present in the PVDF-TrFE contributes electrons that help to fill the sulfur vacancies. This effect could be used successfully in photodetection to help improve the detectivity.


5:00 PM EL01.06.16
Improving Hazardous Gas Detection Behavior with Palladium Decorated SnO2 Nanobelts Networks

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Transparent Conductive Oxides (TCOs) have been widely used as sensors for various hazardous gases. Among the most studied TCOs is SnO2, due to tin being an abundant material in nature, and therefore being accessible for moldable-like nanobelts [1]. Sensors based on SnO2 nanobelts are generally quantified according to the interaction of the atmosphere with its surface, changing its conductance [2]. The present study reports on the fabrication of a nanobelt-based SnO2 gas sensor, in which electrical contacts to nanobelts are self-assembled, and thus the sensors do not require any expensive and complicated fabrication processes. The nanobelts were grown using the vapor–solid–liquid (VSL) growth mechanism with gold as the catalytic site [3]. The electrical contacts were defined using testing probes; thus, the device is considered ready after the growth process. The sensorial characteristics of the devices were tested for the detection of CO and CO2 gases at temperatures from 25 to 75 °C, with and without palladium nanoparticle deposition in a wide concentration range of 40–1360 ppm. The results showed an improvement in the relative response, response time, and recovery, both with increasing temperature and with surface decoration using Pd nanoparticles. These features make this class of sensors important candidates for CO and CO2 detection for human health.

Acknowledgements: This research was funded by FAPESP, grant number 2019/18963-6, CNPq 305655/2018-0 and 30490/2022-0. The authors are grateful for institutional support from the Department of Bi-oystems Engineering at São Paulo State University (UNESP), the Department of Physics at the Federal University of São Carlos (UFSCar), and the postgraduate program in Electrical Engineering (PGGEE/UNESP).

Reference:

5:00 PM EL01.06.17
Tunable Ordering of 2D Tin on Silicon

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The optical and electronic properties of binary alloys can depend on atomic scale, site-to-site correlations. This is clearly illustrated in group IV alloys of tin, silicon, and germanium, where a direct bandgap is theoretically predicted in the random alloy, but an indirect bandgap is experimentally observed and thought to result from short range order (SRO). The balance between the deposition rates, temperature, and templating by the substrate influences the atomic-scale organization within thin films in interwinded ways, which is doubly challenging due to the atomic-scale characterization required for visualization. Here, we combine the ability to deposit materials with sub-monolayer coverage, apply heat in a separate controlled step, and in situ atomic-scale imaging of each discrete step with scanning tunneling microscopy (STM), to visualize the growth of Sn:Si.

The fundamental goal of our work is to systematically characterize SRO, to better understand its impact of electronic properties of a material. Existing STM work on Sn monolayers deposited on Si and Ge, in both 100 and 111 orientations, has shown the nucleation of different long-range surface reconstructions. How this influences growth is an open question, as Sn also surface
segregates at moderate growth temperatures. By analyzing growth in discrete steps, comprised of Sn deposition, annealing, followed by Si deposition, and further annealing, using STM in situ, the dynamic nature of the thin film growth at the substrate interface can be better understood. This talk will focus on analyzing the STM data of different growth and heating combinations to reveal the forces driving ordering and surface segregation. This step-by-step mode of growth enables the creation of metastable configurations that manipulate the degree of order itself, which, in the future, can help in better understanding the relationship of order to optical and electronic properties.

To develop the perovskite formation process, it becomes necessary to explore the fabricating principles underlying the photosensitive layers. To this end, various aromatic solvents with different functional groups (such as methylenebenzene and chlorobenzene (CB)) are selected and analyzed during perovskite crystallization [1]. This demonstrates the excellent detectivity and fast response speed of the perovskite photodetector treated with CB, owing to its enhanced interfacial affinity with ETI and improved charge dynamic behavior. Thus, this showcases the optimization of morphological affinity and the realization of a fast and highly sensitive photodetector via selective use of anti-solvents. Meanwhile, the strategy of a highly sensitive photodetector fabrication is introduced via the relaxation effect of perovskite intermolecular exchange [2]. Chloronaphthalene (CN) is utilized to fabricate high-quality photosensitive layers in a perovskite nucleation environment due to the unique properties of CN, such as its high boiling point and bulky napthalene ring. Steric hindrance is thereby induced in the perovskite adduct, delaying intermolecular interactions and creating a stable perovskite nucleation environment which promotes grain growth. Accordingly, higher crystallinity and larger grains are found in CN treated thin films. Based on this, photodetector performance is greatly improved due to the development of long grain boundary lengths as grain size increases. This is because the increase in surface mobility and ohmic shunt within the device are suppressed, leading to improved charge transfer and recombination properties. This demonstrates improved device stability, with photodetector parameters observed for approximately 1000 hours. An advanced method for controlling the adduct phase of perovskite via 1,8-octanedithiol additive (1,8-ODT) engineering is presented [3]. In this process, 1,8-ODT is utilized as an anti-solvent additive, forming a coordination bond with Pb2+ ions and facilitating rapid perovskite phase conversion. The optimized photodetector exhibits low dark current density, as well as high responsivity and detectivity at 680 nm. Based on this, stability tests reveal that the performance remains at approximately 90% even after approximately 260 hours. The properties of stable and recoverable perovskite photodetectors are introduced via moisture trap engineering [4]. Perovskite decomposition mechanism by moisture and the effect of moisture trap introduction are specifically proposed. The degree of hydration and perovskite photodetector characteristics are compared via solubility changes based on each H2O content. As a result, stable photodetector driving characteristics are reproducibly observed despite moisture content when moisture trap engineering is introduced. Finally, we propose a highly sensitive photodetection strategy via passivation engineering, specifically silica nanocrystal encapsulation [5]. We designed quantum dots (QD@APDEMS) based on silane barriers with hydrophobic ligands. These quantum dots exhibit excellent dispersibility and durability, facilitating an effective film formation. This approach is applicable to bulk perovskite photosensitive layers. As a result, the introduction of QD@APDEMS leads to an improvement in charge dynamics, attributed to perovskite grain expansion and the formation of films with fewer defects. This effect can be attributed to grain boundary passivation via QD@APDEMS. Furthermore, the deep HOMO level of QD@APDEMS effectively suppresses hole charge carrier injection and shunt leakage.


We conclude in our previous findings that bismuth substantially increases the two-dimensional Erlich-Schwöebel (ES) potential barrier of atomic terraces, inducing an upward adatom flux that contributes to surface smoothing. This work examines the effects of such bismuth surfactancy over a wide range of bismuth fluxes from none to some incorporation to understand how bismuth surfactancy can enhance the surface morphology and film structure of low-temperature grown GaSb. Furthermore, this research can potentially improve the growth of other homoepitaxial III-V semiconductor systems under non-ideal conditions and will contribute to the understanding of the bismuth surfactancy effects in dilute GaSbBi alloys.

High-resolution X-ray diffraction (HRXRD) was performed to confirm the bismuth incorporation into the films. All films are grown at the stoichiometric point at ~0.4 monolayer (ML) per second. Bi:V flux as measured by the beam flux monitor (BFM) is varied from 0, no bismuth, to 0.2, where we have found an observable (~1%) Bi incorporation. The effects of bismuth surfactant on the GaSb surface are characterized by atomic force microscopy (AFM). Raman spectroscopy is used to characterize and compare the film quality. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) are used to analyze film surface and surface composition. High-resolution X-ray diffraction (HRXRD) was performed to confirm the bismuth incorporation into the films. We conclude our previous findings that bismuth substantially increases the two-dimensional Erlich-Schwöebel (ES) potential barrier of atomic terraces, inducing an upward adatom flux that contributes to surface smoothing. This work examines the effects of such bismuth surfactancy over a wide range of bismuth fluxes from none to some incorporation to understand how bismuth surfactancy can enhance the surface morphology and film structure of low-temperature grown GaSb. Furthermore, this research can potentially improve the growth of other homoepitaxial III-V semiconductor systems under non-ideal conditions and will contribute to the understanding of the bismuth surfactancy effects in dilute GaSbBi alloys.

Homoepitaxial growth of GaSb is crucial for applications in mid-IR optoelectronics, such as thermal imaging, optical communication, LEDs, and thermophotovoltaic cells. At cold growth temperatures, the surface of GaSb degrades and can result in surface defects and device performance degradation. Yet, lower growth temperatures are favorable for reasons ranging from compatibility with other layers that require low-temperature growth to lowered bulk mobility to prevent defects. Recently, we have demonstrated that bismuth surfactancy can lead to a significant improvement in the surface morphology of GaSb. A series of 200nm thick GaSb is grown via MBE in a Veeco GENxplor system in otherwise identical growth conditions except for the variation of the bismuth surfactancy flux used during growth. All films are grown at the stoichiometric point at ~0.4 monolayer (ML) per second. Bi:V flux as measured by the beam flux monitor (BFM) is varied from 0, no bismuth, to 0.2, where we have found an observable (~1%) Bi incorporation. The effects of bismuth surfactant on the GaSb surface are characterized by atomic force microscopy (AFM). Raman spectroscopy is used to characterize and compare the film quality. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) are used to analyze film surface and surface composition. High-resolution X-ray diffraction (HRXRD) was performed to confirm the bismuth incorporation into the films. We conclude our previous findings that bismuth substantially increases the two-dimensional Erlich-Schwöebel (ES) potential barrier of atomic terraces, inducing an upward adatom flux that contributes to surface smoothing. This work examines the effects of such bismuth surfactancy over a wide range of bismuth fluxes from none to some incorporation to understand how bismuth surfactancy can enhance the surface morphology and film structure of low-temperature grown GaSb. Furthermore, this research can potentially improve the growth of other homoepitaxial III-V semiconductor systems under non-ideal conditions and will contribute to the understanding of the bismuth surfactancy effects in dilute GaSbBi alloys.

Herein, we report the pH neutralization of PEDOT:PSS by adding basic amino acids, which are arginine, lysine, and asparagine. The addition of amino acids can not only modulate the pH of PEDOT:PSS reduce the operational stability and lifetime of perovskite LEDs (PeLEDs).

Halo perovskites are promising materials for light-emitting diodes (LEDs) applications owing to their excellent optoelectronic properties such as long carrier diffusion length, high quantum yield, and facile bandgap tunability. Additionally, polycrystalline (PSS) polyethylene sulfonate (PEDOT:PSS) is commonly used as hole transport layer (HTL) in perovskite electronic devices owing to its high hole mobility, solution processability, and optical transparency. However, PEDOT:PSS can potentially degrade the adjacent layers owing to its acidic nature caused by the moisture absorbed by PSS chains from environment. Therefore, the acidic and hygroscopic properties of PEDOT:PSS reduce the operational stability and lifetime of perovskite LEDs (PeLEDs).

In this work, we report the pH neutralization of PEDOT:PSS by adding basic amino acids, which are arginine, lysine, and asparagine. The addition of amino acids can not only modulate the pH of PEDOT:PSS, but also stabilize the perovskite layer, and passivate the defects at the interface of PEDOT:PSS and perovskite. The addition of amino acids results in enhanced stability and photoluminescence yield of the perovskite nanocrystalline layer. When the amino acid-doped PEDOT:PSS is adopted as HTL layer in PeLEDs, the external quantum efficiency (EQE) of green-emitting PeLEDs (λ=518 nm) is improved from 8.99 to 11.96 %. The addition of amino acids in PEDOT:PSS can improve the operational stability and lifetime of perovskite LEDs (PeLEDs).

We developed an efficient, scalable, and cost-effective NIRD photodetector by depositing a nanostructured Sb$_2$Se$_3$ film onto a p-type micro-pyramidal silicon substrate, fabricated through a wet chemical etching process. Pump-probe spectroscopy was employed to investigate the impact of annealing on Sb$_2$Se$_3$ films, shedding light on their suitability for advanced photodetector applications. We excited both annealed and unannealed samples near the band gap at 650 nm (1.9 eV) with an average power of 1 mW, probing the near-infrared (NIR) region spanning 800-1400 nm. The recorded kinetics at various probe wavelengths which provides crucial insights into the behavior of these materials. The transient absorption kinetics were captured over an extended time window ranging from 0 to 6 nanoseconds. The entire spectrum is blue-shifted, a phenomenon attributed to lattice heating induced by the femtosecond laser—a well-known effect termed the Burstein-Moss shift. A negative band, centered around 850 nm, represents photoluminescence (PL) emission spectra with a longer duration due to defects within the band structure, as evidenced by a time constant (τ) exceeding 5 nanoseconds, accounting for nearly half of the carrier concentration. Notably, a broad photo-induced absorption (PL) region spanning 910-1150 nm is observed, characterized by rapid decay within 1 or 2 picoseconds. The fastest time constant (τ′) of approximately 1 picosecond is attributed to the thermal relaxation of carriers within the conduction band and the associated surface states, while a subsequent time constant (τ2) of around 25 picoseconds further adds depth to our understanding. This study underscores the importance of annealing in optimizing the properties of Sb$_2$Se$_3$ films and contributes valuable insights into the dynamics of carrier relaxation and the role of defects in these materials. These findings are instrumental in advancing the development of high-performance photodetectors and related technologies. Our findings reveal that at the optimized thickness of the Sb$_2$Se$_3$ layer, the micro-pyramidal silicon substrate significantly enhances responsivity, achieving nearly double the performance compared to Sb$_2$Se$_3$ deposited on flat silicon or glass/ Sb$_2$Se$_3$ samples at a wavelength of 1064 nm (power density = 15 mW/cm$^2$). Notably, the micro-pyramidal silicon-based device operates at zero bias voltage, paving the way for self-bias devices.

We report the highest specific detectivity of 2.25×10$^{15}$ Jones at a power density of 15 mW/cm$^2$ and a bias voltage of 0.5 V. This superior performance is attributed to the field enhancement provided by the Kretschmann configuration of the silicon pyramids, creating "hot spots" at the Si/Sb$_2$Se$_3$ junction. With a remarkable responsivity of 47.8 AW$^{-1}$, our design demonstrates its suitability for scalable and cost-effective plasmonic-based NIR photodetectors, addressing the need for high responsiveness in advanced imaging and optical communication applications.

Enhanced NIR Photoresponse in Nanostructured Sb$_2$Se$_3$ Film on Micro-Pyramidal Silicon Substrate

Herein, we introduce non-fullerene acceptors which have opened new avenues with regard to improve the figure of merits of OPDs including wide absorption and fast response. [1] To investigate the effect of electron acceptors on dark current, OPDs are fabricated according to the types of acceptors in photosensitive layers, because anodic charge injection to acceptors has a major role of dark current under an applied reverse bias, which influences the performance of organic photodetectors. [2] The origin of dark current generated in an organic photodetector is observed through the modeling between current and voltage. To elucidate the dominant mechanism, the barrier energies in anodic contact are set from 0.6 to 1.0 eV using photosensitive layers composed of different acceptors. The current density–barrier energy characteristics measured under reverse bias strongly suggests the main source of dark current. The linear relationship observed in the current density–voltage characteristics also confirm tunneling effects rather than thermionic emission. Consequently, the non-fullerene acceptor-based OPDs show a high detectivity and a faster response time, because of the excellent dark current suppression of the carrier injection and the low trap density of non-fullerene acceptor. Eh-IDTBR (ethylhexyl- rhodanine-benzothiazole-zoled indacenodithiophene) has been employed in OPDs and the results have been compared with fullerene derivatives (PC$_71$BM), in combination with electron donor PBDDT-FeT BT- EML. eh-IDTBR based OPDs has shown excellent detectivity in comparison to PC$_71$BM based OPDs due to suppressed injected carriers and trap density. Furthermore, morphological and electrical changes depending on thermal and electrical stress have been investigated in the two different acceptor systems. Carbon nanotubes (CNTs) have attracted huge attention owing to their outstanding flexibility, transparency, and conductivity, so that CNTs can replace an indium-tin oxide (ITO) for efficient and flexible photodetectors. Especially, CNTs-based electrode with high chemical resistance is the excellent candidate for organic photodetectors (OPDs), because the devices have been fabricated through solution process. In addition, The OPDs require dense nanotubes arrays to form top layers suitable to enhance the performance. The CNT electrode with high transmittance reduces dark current better than a conventional ITO electrode, but it is limited to high transmittance through a low p level and exhibits the higher detectivity than that of ITO-based devices owing to its deep work function related with the high electron injection barrier energy. [3] The stable OPDs fabricated utilizing the CNT electrode stably operate after 500-binding tests. By investigating the charge injection mechanism according to barrier energy between transparent anode and photosensitive layer in organic photodetector, This work can help devise an effective strategy to suppress dark current for effective current photodetector device implementation with increase of process yield and reduction of unit prices.

2) Jang et al., Adv. Funct. Mater. 2023, 33, 2206915
3) Jang et al., Nano Today, 2021, 37, 101081

Organic semiconductor-based photodetectors (OPDs) have attracted a variety of attention attraction as a substitute for photodetectors with conventional inorganic materials for image sensors with high sensitivity. The organic semiconductor has tunable optical, electrical and mechanical properties by designing their structure. OPDs are evaluated by both dark current and photocurrent. However, research to investigate the causes of dark currents has been insufficient. Herein, we introduce non-fullerene acceptors which have opened new avenues with regard to improve the field enhancement of OPDs including wide absorption and fast response. [1] To investigate the effect of electron acceptors on dark current, OPDs are fabricated according to the types of acceptors in photosensitive layers, because anodic charge injection to acceptors has a major role of dark current under an applied reverse bias, which influences the performance of organic photodetectors. [2] The origin of dark current generated in an organic photodetector is observed through the modeling between current and voltage. To elucidate the dominant mechanism, the barrier energies in anodic contact are set from 0.6 to 1.0 eV using photosensitive layers composed of different acceptors. The current density–barrier energy characteristics measured under reverse bias strongly suggests the main source of dark current. The linear relationship observed in the current density–voltage characteristics also confirm tunneling effects rather than thermionic emission. Consequently, the non-fullerene acceptor-based OPDs show a high detectivity and a faster response time, because of the excellent dark current suppression of the carrier injection and the low trap density of non-fullerene acceptor. Eh-IDTBR (ethylhexyl-rhodanine-benzothiazole-zoled indacenodithiophene) has been employed in OPDs and the results have been compared with fullerene derivatives (PC$_71$BM), in combination with electron donor PBDDT-FeT BT- EML. eh-IDTBR based OPDs has shown excellent detectivity in comparison to PC$_71$BM based OPDs due to suppressed injected carriers and trap density. Furthermore, morphological and electrical changes depending on thermal and electrical stress have been investigated in the two different acceptor systems. Carbon nanotubes (CNTs) have attracted huge attention owing to their outstanding flexibility, transparency, and conductivity, so that CNTs can replace an indium-tin oxide (ITO) for efficient and flexible photodetectors. Especially, CNTs-based electrode with high chemical resistance is the excellent candidate for organic photodetectors (OPDs), because the devices have been fabricated through solution process. In addition, The OPDs require dense nanotubes arrays to form top layers suitable to enhance the performance. The CNT electrode with high transmittance reduces dark current better than a conventional ITO electrode, but it is limited to high transmittance through a low p level and exhibits the higher detectivity than that of ITO-based devices owing to its deep work function related with the high electron injection barrier energy. [3] The stable OPDs fabricated utilizing the CNT electrode stably operate after 500-binding tests. By investigating the charge injection mechanism according to barrier energy between transparent anode and photosensitive layer in organic photodetector, This work can help devise an effective strategy to suppress dark current for effective current photodetector device implementation with increase of process yield and reduction of unit prices.
Oxygen sensors have a wide range of applications, from monitoring respiration and oceanography to food and pharmaceutical industries. These sensors measure the oxygen concentration in a gas or liquid, typically air or exhaust gases, and play a crucial role in improving efficiency, reducing emissions, and ensuring safety and environmental compliance. Screen printing is a widely adopted method for producing energy storage devices, especially in printed electronics. It creates patterns of conductive materials, such as electrodes and current collectors, on various substrates. In this work, an electrochemical sensor was fabricated using printed technology for O2 detection at room temperature. This design consists of zinc metal as an anode and carbon-based material as a cathode. The oxygen concentration can be observed using optical signals. A complete product development process has been demonstrated, including material screening, hardware design, and sensor tests. The sensor exhibits a fast response ($T_{90} \sim 2.7$ s) and high sensitivity. Furthermore, the sensor fabrication is an environmentally friendly process with minimized consumption of toxic materials, such as Pd, and release of pollutants.

**8:15 AM EL01.07.02**

**Efficiency Enhancement of Bifacial Sb$_2$Se$_3$ Photovoltaic Devices with Cu$_2$O Back Buffer: A Modeling Study**

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Thin-film solar cells based on an Antimonite Selenide (Sb$_2$Se$_3$) absorber layer have been emerging as third-generation photovoltaic devices with promising properties. A Sb$_2$Se$_3$ absorber has 1.1 eV bandgap, a high absorption coefficient at visible light ($>10^4$ cm$^{-1}$), good carrier mobility ($<15$ cm$^2$/Vs), long carrier lifetime ($>67$ ns), and simple binary compound with high vapor pressure and low melting point ($550^\circ$C).

Due to the versatility of Sb$_2$Se$_3$ thin-films, Sb$_2$Se$_3$ has been studied by varying compositions and concentrations of incorporated elements for various applications. In particular, Ge-incorporated Sb$_2$Se$_3$ thin-films (hereafter, Ge-Sb$_2$Se$_3$) have been reported as a good polycrystalline absorber candidate with Ge concentration <15%.

To further improve the efficiency of polycrystalline Sb$_2$Se$_3$ devices, both front and rear-side illumination could be captured by utilizing the bifacial device configuration of Sb$_2$Se$_3$ devices. For our analytical simulation, we used in-house MATLAB modeling suites that have been developed in our group. We have proposed new bifacial devices to improve the overall device performance and optimized developed device models with various parameters. With a Cu$_2$O back buffer layer, the best efficiency of front-side illumination is 19.7%, Voc (744.4 mV), Jsc (40.14 mA/cm$^2$), and FF (66.1%). For the rear-side illumination, the performance is 13.0%, Voc (724.5 mV), Jsc (31.6 mA/cm$^2$), and FF (56.7%). Consequently, the bifacial factor is 66%.

**9:00 AM EL01.03.03**

**Enhanced Sub-Band Gap Photosensitivity by an Asymmetric Source-Drain Electrode Low Operating Voltage Oxide Transistor**

Utkarsh Pandey; Indian Institute of Technology (BHU), Varanasi, India

Electrical characteristics of a thin film transistor (TFT) can be tuned by using an asymmetric work function source-drain (S-D) electrode. However, to realize the effect of this asymmetric S-D electrode, a low operating voltage TFT is required. On the other hand, sub-bandgap photosensitivity of a photodetector required a suitable material interface engineering. In this work, an asymmetric S-D electrode has been used to enhance the photosensitivity of a solution processed low voltage driven metal oxide TFT. An ion-conducting LiInSnO$_4$ thin film has been used as the gate dielectric of this TFT that limits the operating-voltage of this TFT within 2 V whereas ZnO has been used as the channel semiconductor. This asymmetric S-D electrode of TFT allows a selective carrier (electron or hole) injection and collection from the channel. As a consequence, the On/Off ratio and photosensitivity of the device improve significantly. The On/Off ratio of asymmetric TFT is 10$^2$ times greater than symmetric TFT. More interestingly, the subthreshold swing (SS) of this asymmetric S-D electrode TFT (210 mV/decade), was reduced more than 4 times than that of the symmetric electrode (975 mV/decade) device. The LiInSnO$_4$/ZnO interfaces states which has been identified in the UV-Vis absorption of LiInSnO$_4$/ZnO thin film is capable to generate sub-band gap photocurrent in the devices. As a consequence, this ZnO based phototransistor can detect light efficiently ranging from 400 to 800 nm. Overall, photosensitivity of this asymmetric S-D electrode TFT has been enhanced by – 405 and – 377 times under red and blue illumination respectively with respect to the symmetric S-D electrode TFT whereas the detectivity of the device increases by ~10 and ~4 times.
Core/shell heterostructuring of semiconductor quantum dots (QDs) provides a convenient platform for exploring the limits of synthetic control over quantum optical properties. Even “simple” control of component composition and feature size in a nano-heterostructure affords opportunities for band-structure engineering, which leads to altered photoluminescence properties, including emission color, lifetime, photostability, etc. More interestingly, however, colloidal synthesis provides possibilities for nearly-atomically precise manipulation of the core/shell interface. This can include alloying, introduction of defects or dopants, and selective facet growth. Here, I will describe several examples of how advanced colloidal synthesis can be used to finely tune nanoscale heterostructure to realize novel properties: dual-color emission, charged-state versus excitonic emission, and resistance to photobleaching by either dimming or catastrophic failure. First, we show that adventitious or intentional introduction of hole traps at the InP/CdSe QD interface, as well as arm length and arm diameter tuning in CdSe/CdS core/arm tetrapods, can provide conditions for realizing two-color excitonic or multi-excitonic emission, respectively, both potentially characterized by suppressed blinking. Second, we assign for the first time the synthesis-structure-function correlations for non-blinking CdSe/CdS core/shell QDs to define the limits of “on-demand” single-photon production under thermal or high-photon-flux stress. The new insights show, e.g., the relationships between shell defects and charged-state emission and between interfacial alloying and photobleaching resistance, each precisely controlled by synthesis conditions. Taken together, the different nano-heterostructure systems reveal the opportunity for achieving designed quantum optical properties through synthesis, while the remaining limitations expose where alternative strategies might be needed to realize, e.g., transform-limited, ultrafast single-photon emitters.
Magically sized clusters (MSCs) are small sized inorganic nanoparticles which are less than 2 nm in size with a thermodynamically stable structure. Their highly surface-dependent properties facilitate the existence of various types of isomers. Particularly, isomers which exhibit dissymmetric circular dichroism signals, also known as optical isomers, are of great importance. Chiral MSCs with large circular dichroism signals will be discussed as compared to other chiral semiconductor nanocrystals. To investigate the chiroptical origins of our chiral MSCs, characterizations including XRD and Raman were conducted to explore ligand geometry and structural properties. By surface characterizations including FT-IR and TGA, we have found that particular mode of surface ligand binding is critical for the chirality. Low crystal symmetry of MSCs is thought to induce the large transition dipole moment of MSC, which in turn yields high chiroptical activity. In contrast, similar sized QDs showed silent chirality presumably due to the high crystal symmetry and the consequent low transition dipole moment. Propagation of chirality using chiral MSCs as the building block will also be addressed. We believe that unique characteristics of MSCs may open a new avenue in designing and synthesizing unprecedented chiroptical materials.

Attractively Precise Indium Arsenide Magic-Sized Cluster Mahminn Choi, Jinbin Shin, Deoum Shin, Jougoong Kang2 and Sohee Jeong1, 1 Sungkyunkwan University, Korea (the Republic of), 2 DGIST, Korea (the Republic of)

In the domain of atomically precise nanoscale science, clusters serve as intermediate assemblies of atoms or molecules, stabilized with organic ligands. These formations, distinctly larger than a single atom yet considerably smaller than bulk materials, exhibit physicochemical properties divergent from established material systems. The elucidation of their structure is paramount because these clusters provide an ideal platform to clarify the intricate relationship between structure and physicochemical properties. Recently, magic-size clusters (MSCs) were discovered; these are atomically precise semiconductor clusters, and their structures have been unraveled. To clarify the relationship between the structure and physicochemical properties, the synthetic method, isolation, and characterization techniques must be refined. The Indium arsenide (InAs) quantum dot has emerged as a promising material for various infrared applications. During the synthesis of the InAs quantum dot, the presence of InAs MSC, as indicated by distinctive absorption peaks, was investigated. However, the isolation and characterization of InAs MSC have not been reported until now.

Herein, we synthesized and isolated atomically precise InAs MSCs to scrutinize their structure. With the optimal synthetic temperature, the InAs MSC revealed two distinct optical transitions. To gain a theoretical understanding, we modeled the InAs MSC using density functional theory (DFT) calculations, identifying a structure with notable stability. This model displayed two optical transitions, from HOMO to LUMO, consistent with the optical transitions we observed. The X-ray diffraction spectrum also aligned with the simulation results. For a deeper atomic-level understanding, we employed X-ray absorption spectroscopy and characterized the cluster using X-ray absorption fine structure (XAFS) techniques. By comparing with an InAs quantum dot, which is larger than the InAs MSC, we noted increases in the In-As peaks and decreases in the In-O peaks, attributable to size-dependent surface-to-volume ratios. Furthermore, spectral intensity offered insights into coordination numbers. Our fitting analysis of the XAFS spectrum enabled precise estimations of coordination numbers for various bonds. Notably, the coordination number for the In-As bond in the InAs cluster was found to be five, in agreement with computational predictions. Collectively, these results not only validate our theoretical model but also deepen our understanding of the structural and optical properties of InAs MSCs.

Structure and Reactivity of Atomically-Precise III-V Nanoclusters Soren Sandeno, Kyle Schnitzenbaumer, Sebastian Krajewski, Ryan Beck, Dylan Ladd, Kelsey Levine, Damara G. Dayton, Michael Tonev, Werner Kaminsky, Xiaosong Li and Brandi M. Cossairt; 1 University of Washington, United States; 2 Transylvania University, United States; 3 University of Colorado Boulder, United States

Advances in the synthesis of III-V quantum dots, including InP and InAs, have led to their development for current and next-generation solid-state lighting, wide color gamut displays, and infrared optoelectronics. The most widely adopted synthesis of these III-V quantum dots involves indium carboxylates and E(SiMe3)3 (E = P, As) and is understood to proceed through the formation of metastable, atomically-precise intermediates that are often referred to as clusters. In this work, we report that the surface chemistry of In1-PxOyCrz is can be leveraged to modify the core structure and control the reactivity of the clusters. Bulkier surface ligands hinder P(SiMe3)3 diffusion and allow for the stabilization and isolation of In26P13(O2CR)39, which has been characterized by single-crystal X-ray diffraction. When employing As(SiMe3)3 in an identical synthesis, no cluster forms and instead the inclusion of an L-type phosphine ligand is required to isolate an atomically-precise material. The surface and core of the InAs cluster is characterized, revealing important contrasts with InP with implications for understanding the landscape of accessible binary semiconductor clusters.

Exploring The Chemical Paths to Doped II-VI Magic Size Clusters Kevin Kittilstvedt, Hyunggu Kim and Jillian Denhardt; University of Massachusetts Amherst, United States

The introduction of targeted, substitutional chemical dopants in a semiconductor lattice is a useful strategy to impart new functionality and in some instances emergent phenomena when synthesized at the nanometer lengthscale. One major challenge in the quantum dot field has been overcoming the thermodynamic penalty associated with introducing an impurity ion into the critical nucleus, which typically leads to a undoped core and dopants only doped in the shell or surface of the nanocrystal. The role of metastable magic size clusters in the synthesis of various quantum-confined nanostuctures including doped nanostructures have received much attention in the past decade. In this talk, we will explore the common routes to prepare (doped) magic-size nanoclusters and introduce an alternate method that employs (doped) molecular clusters as single-source precursors.

Doped InP Magic-Sized Clusters Sunjinee D. Kim; POSTECH, Korea (the Republic of)

Magic-sized clusters (MSCs) can be isolated as intermediates in quantum dot (QD) synthesis, and they provide pivotal clues in understanding QD growth mechanisms. Two families are introduced that have chlorine or zinc incorporated InP MSCs. In each family line, different MSCs could be either directly synthesized or could be converted from one to another. As the synthesis of the InAs quantum dot, the presence of InAs MSC, as indicated by distinctive absorption peaks, was investigated. However, the isolation and characterization of InAs MSC have not been reported until now.

Doping InP Magic-Sized Clusters Sungjee D. Kim; POSTECH, Korea (the Republic of)

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Doping InP Magic-Sized Clusters Sunghee Jeong; Sungkyunkwan University, Korea (the Republic of)

In the domain of nanocrystal-centric optoelectronic devices, control over the carrier type control is essential, however, integrating foreign atoms into semiconductor nanocrystal lattices remains challenging. A recent standout in this semiconductor lattice domain, Indium Arsneide (InAs) colloidal nanocrystals, has been in great attention due to their promising prospects, especially in near to short-wavelength infrared optoelectronics.

In this presentation, we introduce a novel methodology where doping polarity in InAs nanocrystals is innately steered from the synthesis onset. By harnessing the capabilities of II-V clusters as reaction precursors, we offer a pathway that not only addresses existing challenges but also achieves versatile control over doping polarity with the right parameter adjustments. Our exploration underscores the robust realization of p-type doping in InAs nanocrystals, indicating their integration in state-of-the-art printed electronic architectures.
Cutting-edge applications of quantum dots (QDs) as next generation emitters require a precise understanding of their synthesis and structure, since atom-scale differences between individual nanoparticles can result in particle-to-particle variation in their optoelectronic properties. A strategy to synthesize atomically precise QDs ensembles utilizes magic-sized clusters (MSCs), which are kinetically stable, atomically defined intermediates along the QD reaction potential energy surface. The synthesis of cadmium selenide MSCs is well preceded, and recent work has established two different structural motifs: a cation-rich, “zincblende-like” tetrahedron and a “wurtzite-like,” quasi-spherical cluster with a stoichiometric inorganic core. However, the wide range of protocols used to access these species has made the direct comparison of their structure, surface chemistry, and optoelectronic properties difficult. Additionally, the physical and chemical relationship between these MSC polymorphs has yet to be established. Here, we demonstrate that both cation-rich and stoichiometric CdSe MSCs can be synthesized from identical ranges of protocols used to access these species has made the direct comparison of their structure, surface chemistry, and optoelectronic properties difficult. Additionally, the physical and chemical relationship between these MSC polymorphs has yet to be established. Here, we demonstrate that both cation-rich and stoichiometric CdSe MSCs can be synthesized from identical.

Quantum dots are nanometer-sized crystallites of semiconductor that have a roughly spherical shape. Due to extensive research, quantum dots are now commercially used as a robust fluorescent material in displays and lighting. However, even with our best procedures, state-of-the-art samples still contain particles with a distribution in size and shape. Because this causes variations in their optical properties, their performance for applications is reduced. This leads to a fundamental question: can we achieve a sample of semiconductor nanocrystals in which all the particles are exactly the same? To illustrate this possibility by examining two classes of nanoparticles. First, we will consider thin rectangular nanoparticles known as semiconductor nanoribbons.

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In our contribution we will compare and contrast the results of calculations on ligand-capped cadmium sulfide nanoparticles, perhaps the archetypical atomically precise semiconductor nanoparticles, and their hydrogen terminated silicon counterparts, the e.l. ensembles of computational nanoparticle research. Both ligand-capped binary semiconductor nanoparticles and hydrogen terminated silicon nanocrystals are interesting from an application point of view,3,4 but are also derived from bulk materials that are both structurally similar but electronically different. We will discuss not only how the optical and electronic properties differ between the two classes of particles and how they change with particle size but also how these changes are linked to the particles’ surface chemistry and changes in the dielectric screening and the fundamental electronic structure of the particles with particle size. An example of the latter being the onset of band-like behaviour.

7. 9:30 AM E10.2.03.04

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In recent years, solution-based techniques have garnered significant interest as a cost-effective and easily scalable approach for manufacturing high-performance thermoelectric materials. In this method, a powdered material is first prepared in a solution and then subjected to purification and thermal processing to produce the desired dense polycrystalline material. Unlike traditional methods, solution-based syntheses offer an exceptional level of control over various particle properties, including size, shape, crystal structure, composition, and surface chemistry. This precise control over the properties of the powders creates distinct opportunities for crafting thermoelectric materials with precisely tailored microstructural characteristics.

Throughout our research, we will illustrate various instances where exercising control over distinct nanoparticle characteristics, such as surface attributes or stoichiometry, directly influences specific properties of the dense material, thereby enabling us to fine-tune its performance optimally. Our focus will be particularly directed towards Ag₃Se, a thermoelectric material of great significance, especially in applications near room temperature.

10:45 AM EL02.03.06
HF-Free Synthesis of Colloidal A₂BF₆ Nanocrystals
Eden A. Tzanetopoulou, Julie Schwartz and Daniel R. Gamelin; University of Washington, United States

Fluoride-based lattices are widely studied due to their low toxicity, high photostability, and optical transparency. These properties, along with their generally low phonon energies compared to oxides, make fluoride lattices attractive hosts for luminescent impurities. In particular, A₂BF₆ (A = Na, K, Cs, NH₄; B = Si, Ti, Zr, Ge) compounds doped with Mn⁴⁺ in the B⁴⁺ site are leading candidates for narrow-line red emitters in display and lighting technologies.¹ Solution-processability of these materials would enable widespread manufacturing of next-generation classical and quantum photonic structures or devices, but fluoride lattices containing cationic excitations are essentially entirely unexplored as colloidal nanomaterials, in large part because of the current reliance upon concentrated hydrofluoric acid (HF) in nearly all doped A₂BF₆ syntheses. This talk will describe results from a versatile new synthesis² developed to eliminate the handling of HF entirely. Colloidal nanocrystals of several A₂BF₆ lattices (NH₄)₂ZrF₆, Cs₂ZrF₆, (N(CH₃)₄)₂ZrF₆, K₂SiF₆) have now been prepared for the first time. In-situ A-site cation exchange has also been demonstrated in these materials, allowing the post-synthetic conversion of, e.g., (NH₄)₂ZrF₆ nanocrystals into Cs₂ZrF₆ nanocrystals. Under some conditions, a nanoscale Kirkendall effect occurs that yields hollow A₂BF₆ nanostuctures. Recent results showing nanocrystal size and shape control will also be discussed. These results highlight the versatility of this bottom-up synthesis for preparing a wide variety of previously inaccessible colloidal fluoride nanostructures.

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11:00 AM EL02.03.07
Colloidal Synthesis of P-Type Zn₃As₂ Nanocrystals
Seongchan Kim, Jaeyeong Seo, Namyoung Gwak, Seungki Shin and Nuri Oh; Hanyang University, Korea (the Republic of)

Zinc pnictides (Zn₃Pt₃, where Pt represents P, As, or Sb) are compound II–V semiconductors composed of earth-abundant elements belonging to the II and V groups of the periodic table. These materials exhibit exceptional properties, such as high carrier mobility, low effective mass of charge carriers, anisotropic charge transport characteristics, and narrow band gaps. Notably, Zn₃As₂, which has a band gap of approximately 1.0 eV, has significant potential for optoelectronic applications across a wide range of wavelengths. Given the substantial advantages and opportunities associated with intrinsically p-type nanomaterials, particularly considering the abundance of well-established inorganic n-type nanomaterials, Zn₃As₂ is a highly promising material owing to its inherent p-type characteristics and appropriate bandgap. Colloidal synthesis of nanocrystals (NCs) from compound semiconductors offers precise control over their size, resulting in a wide range of tunable electrical and optical properties. These colloidal NCs, such as Zn₃As₂ NCs, exhibit characteristics that make them highly suitable for low-cost large-area processing, opening up diverse applications in fields such as solar energy harvesting and photodetection spanning the visible to infrared regions. However, despite the outstanding properties of colloidal Zn₃As₂ nanocrystals, research in this area is lacking because of the absence of suitable precursors, the occurrence of surface oxidation, and the intricacy of the crystal structures. Zn precursors such as diethylzinc, or As precursors such as tris(trimethylsilyl)arsane exhibit high reactivity but yield Zn₃As₂ NCs that are too small. Also, previously reported Zn₃As₂ NCs have exhibited low crystallinity, which was primarily attributed to the difficulty in achieving precise stoichiometry during their formation.

In this study, a novel and facile solution-based synthetic approach is presented for obtaining highly crystalline p-type Zn₃As₂ nanocrystals with accurate stoichiometry. By carefully controlling the feed ratio and reaction temperature, colloidal Zn₃As₂ nanocrystals are successfully obtained. Moreover, the mechanism underlying the conversion of As precursors in the initial phases of Zn₃As₂ synthesis is elucidated. Furthermore, these nanocrystals have been employed as active layers in field-effect transistors that exhibit inherent p-type characteristics with native surface ligands. To enhance the charge transport properties, a dual passivation strategy is introduced via phase-transfer ligand exchange, leading to enhanced hole mobilities as high as 0.089 cm² V⁻¹ s⁻¹.¹ This study not only contributes to the advancement of nanocrystal synthesis, but also opens up new possibilities for previously underexplored p-type nanocrystal research.

11:15 AM EL02.03.08
The Chemistry of Tin Halide Perovskite Nanocrystals
Loredana Protesescu; University of Groningen, Netherlands

Metal halides perovskites with nanoscale geometries have revolutionized the field of solution-processed photovoltaics and light-emitting devices due to their strong absorption and exceptional photoluminescence properties combined with a remarkable tolerance to structural defects. However, the further development of these materials to practical commercialization is hindered by their toxic components like lead and their inherent structural lability. Moreover, we still have little understanding of their crystallographic structures, chemical and physical interactions, and surface chemistry at a fundamental level.

The chemical design of metal halide perovskites proved to be the key to addressing those issues. In this work, I will discuss the physical and chemical parameters which can help us to achieve a stable, tunable and monodisperse CsSnX₃ perovskite nanocrystals with defined optical features. Pertaining to the formation energies of nanocrystals, the interplay of the 2D Ruddlesden-Popper (L₁₋₂C₈Sn₉X₁₆) phases with 3D CsSnX₃ nanocrystals is apparent with respect to ligand combinations (ammonium, carboxylate, phosphate), precursor ratios and temperature when SnX₃ salt is used as a precursor. X-ray diffraction and scattering studies combined with optical spectroscopy and electron microscopy helps us in acquiring the useful insights into directing the chemistry of Sn-halide perovskites at nanoscale. This research work showcases the consistent necessity for the development of mechanistic understanding to design efficient synthetic routes to achieve high-quality tin-halide perovskite nanocrystals.

11:45 AM EL02.03.09
Tin Chalcogenide Colloidal Quantum Dots for Infrared Photodetection
Barbara V. Martín, Jianying Ouyang, Neil Graddock, Jianping Lu, Nathan Yee, Tyler Davidson-Hall, Jianfu Ding, Tao Ye and Patrick Malenfant; National Research Council Canada, Canada

Printable, flexible and low-cost photodetectors with sensitivity in the near-infrared (NIR, 700-2500nm) window are in high demand. Much research on infrared active colloidal quantum dots (CQDs) has been conducted based on lead or mercury chalcogenides. However, environment-friendly alternatives with tunable sensitivity in the NIR and high performance should be investigated to better protect our environment. We have developed silver chalcogenide CQDs and demonstrated their application in NIR photodetection, including Ag₃Se and Ag₃Te QDs with detection up to 1.2 μm and 1.4 μm. To further push the sensitivity to longer wavelength, we have been developing tin telluride (SnTe) CQDs. SnTe QDs possess good optical properties in the range of 1.5-2.5 μm. So far, only a few studies were reported; the reaction mechanism is poorly understood, the synthesis is challenging and the products are prone to oxidation.

Our SnTe CQDs were synthesized with tin precursors that are less toxic, less expensive and less susceptible to oxidation than that commonly used (Bis(bis(trimethylsilyl)amino tin(II))₃. The use of Sn₃P₃ as an alternative Sn source was found to be highly efficient in producing SnTe CQDs with superior optical properties. The Sn₃P₃/Sn ratio significantly influences the sensitivity of SnTe CQDs towards the NIR. In-situ FTIR and XPS studies revealed that the Sn₃P₃/Sn ratio has a direct impact on the bandgap of SnTe CQDs. The sensitivity of SnTe CQDs towards the NIR can be tuned by adjusting the Sn₃P₃/Sn ratio. Further, the morphology of SnTe CQDs can be controlled by varying the reaction conditions, leading to the formation of mono-dispersed SnTe CQDs.

We have also investigated the application of SnTe CQDs in photodetection. Their sensitivity towards the NIR is comparable to that of mercury-based CQDs, but with the added advantage of being less toxic and environmentally friendly. The use of SnTe CQDs in photodetection can lead to the development of low-cost, flexible and printable photodetectors with high performance in the NIR. Our SnTe CQDs can offer a low-toxicity route for low-cost solution-processable fabrication of high-performance infrared photodetectors with sensitivity up to 2.5 μm.
Sustainable, Additive, Scalable Nanomanufacturing of Quantum Materials at The Attoscale

John D. MacKenzie 1,2, 1University of Washington, United States; 2Washington Clean Energy Testbeds, United States

Conventional semiconductor processing has made immense progress in the 70 years since its introduction, pushing progress in performance, critical dimension and functionality per unit cost forward at an unparalleled rate. Even though the roadmap to single nanometer devices is still being set, it is highly likely that this field will continue to innovate given the need for increasing information processing, storage and transfer in virtual reality, artificial intelligence and the integration of electronics with virtually every aspect of our lives. At the same time, there are global concerns about climate and sustainability and, here, the future for conventional manufacturing is less certain. Whether applied to optoelectronics, microelectronics or emerging areas such as optical quantum devices, conventional approaches are dominated by cycles of subtractive and high waste lithographic processing and energy intensive and increasingly complex sets of materials that run counter to a goal of sustainable, lower carbon footprint and lower environmental impact. We will show here that advances in solution-processable materials and corresponding additive manufacturing approaches can provide alternative, and even more capable processing routes not feasible with conventional processing.

An overview of additive nanomanufacturing will be presented along with progress towards applying electrohydrodynamic (EHD) printing as a fully additive pathway towards quantum optical devices and integrated photonics. Although nanoscale 3D printing via processes like two photon stereolithography can produce submicron structures, this is largely limited to passive materials that require subsequent subtractive processing to render functional elements. Techniques like pressure driven inkjet printing, such as piezoelectric or thermal evaporation actuated printing common to consumer inkjet systems, can digitally deposit functional materials from nanoparticle and reactive precursor inks. These types of printing have also been scaled industrially in applications such as flat panel displays. The surface energy and decreasing inertia bottlenecks for ink droplets of decreasing size and increasing surface/volume ratio leads to size and positioning accuracy limits of around 10 microns. Unfortunately, this is two or more orders of magnitude too large for applications at the leading edge of micro- and opto-electronics.

Leveraging the flexibility and dynamic range inherent to electric fields, EHD printing has been shown to overcome the droplet size limitations of mechanical jetting to deterministically position functional material inks additively with zero moving part actuation.

It will be shown here that direct printing of functional materials and precursors using EHD can be pushed to deterministic positioning of quantum dots and nanocrystal precursors at the nanoscale. This includes our ability to additively pattern high index dielectrics for optical metasurfaces and shelled luminescence II-V QDs at resolutions <100 nm from attoliter scale droplets. Our work on heterointegration of perovskite nanocrystals and QDs with photonic caviities, including selective deposition of quantum dots on free-standing close-spaced cavity pairs that demonstrate optical cross coupling will also be outlined. This demonstrates an exceptional example of heterointegration on optical structures at ambient pressures and temperatures that cannot be readily achieved by any conventional approach (e.g. semiconductor epitaxy, lithography or stochastic coating demonstrations). We will conclude with results of additive single QD deposition for devices such as single photon emission sources via dilute QD ink deposition, and formation of nanocrystals from in-situ attoliter scale reactions in printed reagent ink droplets. This will show that the resolution of techniques such as electron beam lithography can be surpassed in an additive, wasteless, sustainable scalable nanomanufacturing process.

Nondestructive High-Resolution Direct Optical Lithography of Colloidal Emissive Nanocrystals

Himchan Cho, Korea Advanced Institute of Science and Technology, Korea (the Republic of)

High-resolution precision patterning is a crucial requirement in the fabrication of immersive near-eye displays that incorporate high-color-purity emissive nanocrystals such as colloidal quantum dots and perovskite nanocrystals as color filters or electroluminescence (EL) emission layers in the form of an RGB matrix. 1 Direct optical lithography, which involves a photochemical reaction of photosensitive ligands or additives, offers a new platform for patterning colloidal nanocrystals, providing high pattern uniformity with a simple procedure. 2 However, a significant decrease in photoluminescence (PL) quantum yield during the patterning process has been a major challenge. To address this challenge, we have developed direct, scalable, and nondestructive methods for high-resolution patterning of colloidal emissive nanocrystals without sacrificing their luminescent properties. With photochemically activated reactions, leading to in situ exchange 3-4 or crosslinking 5 of long-chain organic ligands, we have demonstrated uniform PL and EL patterns of red, green, and blue quantum dots and perovskite nanocrystals with feature sizes as small as sub-1 μm, while preserving their structural, electronic, and emissive properties. The underlying patterning mechanisms were identified by investigating the photochemical transformations of surface ligands and additives at each step of the process. Our approach provides a promising solution for patterning of colloidal emissive nanocrystals, which can be implemented in next-generation augmented reality displays and other optoelectronic applications.

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Data-Driven Exploration of Silver Nanoplate Formation in Multidimensional Chemical Design Spaces

Hant Thurt Chiang, Kiran Vaddi and Lilo D. Pozzo; University of Washington, United States

Artificial Intelligence (AI) driven closed systems, which are usually composed of an AI agent to plan experiments, robots to perform experiments, and a high throughput characterization method to evaluate experiments have recently shown to be successful in optimizing structural properties of colloidal nanoparticles. However, a limitation of these kinds of systems is that they have only been demonstrated in constrained design spaces which is where the targeted structure has a high probability of being formed. In addition, while many samples are being synthesized and characterized, minimal amounts of information on the relationship between experimental design parameters and the structure of the nanoparticles is obtained from the experiment. To solve these problems, we introduce a novel AI driven closed system and test it with a model system of silver nanoparticle synthesis with the objective of synthesizing nanoplates. Our method first searches the design space for silver nanoplates based on UV-Vis spectroscopy curves, which are autonomously classified into “plates” or “not plates” using a distance metric. This information is then used to train a gaussian process classifier which then iteratively suggests experimental parameters for a new batch of samples that are likely to be nanoplates. After the chemical design space is constrained to contain mostly nanoplates, we then use small angle x-ray scattering characterization to obtain size/shape parameters. This information is used to train a gaussian process regressor, from which we can extract design rules such as the effect of the composition of the reagents on the obtained size/shape parameters.

2:00 PM EL02.04.02

SESSION EL02.04: Scalability in Synthesis, Characterization and Integration of Colloidal Nanocrystals

Session Chairs: Emily Miura and Nayon Park

Wednesday Afternoon, April 24, 2024

Room 347, Level 3, Summit

2:15 PM EL02.04.05

Nondestructive High-Resolution Direct Optical Lithography of Colloidal Emissive Nanocrystals

Himchan Cho, Korea Advanced Institute of Science and Technology, Korea (the Republic of)

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2:30 PM BREAK

3:30 PM EL02.04.04

Precision Synthesis and Accelerated Optimization of Colloidal Quantum Dots with Self-Driving Fluidic Labs

Milad Abolhasani; North Carolina State University, United States

Despite the intriguing physicochemical properties and widespread applications of colloidal quantum dots (QDs) in energy and chemical technologies, their discovery and synthesis optimization are still based on Edisonian techniques. Existing QD discovery and development strategies using batch reactors with irreproducible and uncontrollable heat/mass transport rates very often fail to comprehensively explore the vast synthesis and processing space of QDs. These limitations necessitate the development and implementation of new strategies to accelerate the pace of QD discovery and development. Recent advances in reaction miniaturization, automated experimentation, and data science provide an exciting opportunity to reshape the discovery, development, and manufacturing of QDs. In this talk, I will present a Self-Driving Fluidic Lab (SDFL) for accelerated discovery, optimization, and manufacturing of colloidal QDs with multi-step chemistries, through the integration of flow chemistry, online characterization, and machine learning (ML). 1-5 I will discuss how modularization of different synthesis and processing stages in tandem with a constantly evolving ML-assisted QD synthesis modeling and decision-making under uncertainty can enable resource-efficient navigation through high dimensional experimental design spaces. Example applications of SDFLs for the autonomous precision synthesis of metal halide perovskite, II-VI, and III-V QDs will be presented to illustrate the potential of
Controlling composition, structure, and thus properties of nanomaterials continues to be of importance to numerous fields, with potential and realized applications for colloidal nanomaterials ranging from quantum dots for displays and bioimaging, to metal nanoparticles for (electro-)catalytic conversions. The vastness of synthesis parameter space, in combination with limited understanding of the nucleation and growth mechanisms for many nanomaterials still hampers progress in identifying nanomaterials with desired properties for existing and newly envisioned purposes. Furthermore, the identification of optimal synthesis recipes for these nanostructures remains a major hurdle. To no surprise, many research efforts have been devoted to these challenges over the past 20+ years.

This presentation will focus on our efforts to develop and apply a number of enabling capabilities achieved through reactor engineering, focusing on the synthesis and characterization of quantum dots. We have demonstrated how the use of automated flow reactors not only helps in run-to-run reproducibility but also in uncovering mechanistic information. Examples include reactors with dedicated nucleation, growth, and shell formation zones, and investigation that revealed mechanistic insight of how water concentration affects QD synthesis outcome. In subsequent work, we employed an autonomous flow reactor architecture to map synthesis- parameter spaces of specific QD systems, a project that relied on fast, fully automated in-situ characterization using UV-vis in combination with multi-step machine learning workflows. The utility of flow reactors, however, is limited when considering chemistries with longer reaction times. Hence, more recently we developed a fully automated batch reactor for parameter space mapping of QD synthesis via hot injection, the most frequently used method in both QD research and in QD production at scale. This batch platform is being augmented with purification capabilities, to address some of the challenges of in-line, in-situ characterization of raw reaction mixtures, and to enable using advanced optical and structural characterization methods to provide insight into the actual structure of the QD materials.

In summary, we developed an integrated approach for the rapid synthesis, purification, and characterization of QDs to determine structural properties, with ongoing work focusing on structural mapping of QD synthesis.

4:30 PM EL02.04.07

Continuous Flow Synthesis of Lead Sulfide Quantum Dots for NIR/SWIR LED Applications Pierre Machu1,2, Anna Karina Antonini1, Céline Rivaux1, Gabriel Mugny2 and Peter Reiss3; 1CEA, France; 2STMicroelectronics, France

The development of new industrial applications in fields such as cell phones and automobiles depend on the ability to produce low-cost LEDs emitting in the NIR/SWIR range. A method for region. However, scaling up this synthesis remains a challenge due to the difficulty of handling and the high toxicity of the H2S gas released during synthesis using this sulfur precursor.

Various sulfur precursors have been utilized to prepare PbS QDs, including elemental sulfur[2] and substituted thioureas[3]. The latter show a great potential as the reaction rate can be adjusted over several orders of magnitude by altering their substituents, which gives access to precisely controlled particle sizes in a wide range. Moreover, there are approximately 10^8 different thioureas that can be synthesized in simple reactions using commercially available chemicals.

To enhance the reproducibility of the syntheses and scale them up to larger quantities, continuous flow synthesis is an appealing alternative to widely used batch synthesis. Among other advantages, the strongly enhanced heat and mass transfer in small tubular reactors combined with controlled pressure can be cited. On the other hand, flow synthesis comes with several restrictions, which require in most cases an adaptation of the synthesis protocol. In particular, both the lead and sulfur precursors should be perfectly soluble at room temperature to avoid clogging, and the injected volumes should be balanced to keep consistent flow rates.

In this study, we developed new synthesis conditions affording monodisperse PbS QDs via flow synthesis exhibiting identical optical properties as with classic batch synthesis, with excitonic peak to valley ratios >3. Moreover, the excitonic peak position could be adjusted with the residence (=reaction) time, in contrast to batch reactions. The flow synthesis of highly luminescent PbS/CdS core/shell QDs was also achieved using ex-situ prepared cadmium oleate via the cation exchange method. Summarizing, the developed flow process gives access to grams of high-quality PbS/CdS core/shell QDs in a couple of hours and in a highly reproducible manner, at wavelengths of particular interest for NIR QLEDs.

Direct Photocatalytic Patterning of Colloidal Perovskite Nanocrystals

Perovskite nanocrystals (PeNCs) are emerging materials with significant potential for various optoelectronic applications, especially in LED technologies. For their integration into AR/VR optoelectronics showed power conversion efficiency (PCE) of 8.1%, detectivity of over 10^11 around 400-930 nm, and response time of 400 ns. Which is the highest PCE and fastest response time among published solution-ink-exchanged AgBiS2 CQD optoelectronics showing promise for lead-free optoelectronics.

References:

Korea Advanced Institute of Science and Technology (KAIST), Korea (the Republic of); 3Korea Institute of Science and Technology, Korea (the Republic of); 4National University of Singapore, Singapore; 5Los Alamos National Laboratory, United States; 6Chungbuk National University, Korea (the Republic of)

Silver bismuth sulfide (AgBiS2) colloidal quantum dots (CQDs) are promising lead-free light absorbing materials for CQD optoelectronics due to their low cost, earth-abundant element, and high absorption coefficients. However, AgBiS2 CQD photovoltaics are hampered by low open-circuit voltage (Voc) due to the complication of passivating charge neutral (100) surface of AgBiS2. Here, we propose a ligand combination for solution ligand exchange to passivate the (100) facet of the AgBiS2 with improved ink stability. We demonstrated that incorporating alkyl solvents can enhance the ink stability of solution ligand exchanged CQD ink and surface ligand coverage ratio. We revealed the synergic passivating mechanism of cation ligands on AgBiS2 CQD surface through density functional theory. This multi-facet passivated AgBiS2 CQD solid possessed low trap density and Urbach tail. Consequently, fabricated multi-facet passivated AgBiS2 CQDs optoelectronics showed power conversion efficiency (PCE) of 8.1%, detectivity of over 10^11 around 400-930 nm, and response time of 400 ns. Which is the highest PCE and fastest response time among published solution ligand-exchanged AgBiS2 CQD optoelectronics showing promise for lead-free optoelectronics.
Lead chalcogenide Quantum Dots (QDs) possess versatile attributes, primarily due to their large exciton Bohr radius and extensive infrared radiation absorption capabilities. Among them, PbS and PbSe QDs have been integrated into various optoelectronic devices, such as solar cells and photodetectors, showcasing superior performance. Notably, their excellent absorption properties in the SWIR region underscore their potential in LiDAR systems. Although PbSe QDs display superior mobility characteristics compared to PbS,[1] they have a lower chemical yield. Furthermore, lead chalcogenide QDs exhibit size-dependent air-stability,[2] with PbSe showing significantly compromised air-stability, especially in the SWIR region. PbSxSe1-x QDs might provide an alternative solution to overcome these critical shortcomings.

Long Hu et al. highlighted enhanced mobility in FETs and better PCE in solar cells through the simple admixture of PbSe with PbS.[3] Wanli Ma et al. described PbSxSe1-x QDs that exhibited improved L<sub>col</sub>, compared to PbS and enhanced V<sub>T</sub>, relative to PbSe.[4] Despite the potential of PbSxSe<sub>1-x</sub> QDs in photovoltaic applications, a deeper investigate into their air-stability and other material properties remains essential. Additionally, studies to date have not conclusively explored properties concerning compositional shifts, primarily because inevitable wavelength alterations occur with changes in the anion ratio.

We successfully synthesized PbSxSe<sub>1-x</sub> QDs active in the SWIR region through a simple synthesis method by injecting a mixture of anion precursors. The QDs, synthesized uniformly, were compositionally engineered to absorb within a consistent wavelength range. Compared to the chemical yield observed in PbSe QDs, there was a marked enhancement for our PbSxSe<sub>1-x</sub> QDs, with the yield being approximately three times greater. Under ambient conditions, the blue shift phenomenon resulting from oxidation is reduced and surface analysis provided evidence that the formation of Se oxide (either SeO<sub>2</sub> or SeO<sub>3</sub>) was notably diminished. The mobility in FETs was improved compared to that of PbS QDs and PbSxSe<sub>1-x</sub> QDs ink was produced for the first time through a ligand exchange from long chain to short. Moreover, PbSxSe<sub>1-x</sub> in the NIR region demonstrated solar cell efficiencies exceeding 10%, the highest on record. These findings emphasize the promising future of PbSxSe<sub>1-x</sub> QDs in infrared optoelectronic applications.

References

5:00 PM EL02.05.09
π-SnS Colloidal Quantum Dots for Field-Effect Transistors
Thanavat Phutthaphongloet<sup>1,2,3</sup>, Ricky Dwi Septianto<sup>1</sup>, Retno Miranti<sup>1</sup>, Nobuhiro Matsushita<sup>1</sup>, Yoshioishi Iwasa<sup>1</sup> and Satria Bisri<sup>1</sup>; 1RIKEN CEMS, Japan; 2Tokyo Institute of Technology, Japan; 3Tokyo University of Agriculture and Technology, Japan

Significant progress in QD optoelectronic devices and energy devices has been made mainly by Pb-bas, Hg-based, and Cd-based binary compounds, or the involvement of rare noble metal alcohols. While some have reached commercial markets, their high degree of toxicity is the primary concern for practical applications. We recently developed a rapid one-pot method to synthesize a novel phase of tin monosulfide quantum dots (QDs), π-SnS<sup>1</sup>. This cubic QD phase exhibits a larger band gap bandgap (1.53-1.69 eV) than the other SnS phase (the orthorhombic α-SnS), and more thermodynamically stable. This method yields QD radii below 10 nm, allowing us to explore the quantum confinement effect, which can be utilized for high-performance photodetector devices. Despite these prospects, obtaining the scalable synthesis of this SnS QD phase with good monodispersity is still challenging. On the other hand, the electronic transport properties of this material have never been investigated, which will directly influence the design of its practical uses for electronic or optoelectronic device applications.

Here we report a controllable synthesis of monodisperse π-SnS QDs and demonstrate the field-effect transistors of colloidal π-SnS QD assemblies. We can synthesize the SnS QDs with diameters ranging from 5 nm to 8 nm and better air stability through synthesis protocol optimizations than the previously reported method. Furthermore, by performing the integration of synthesis and optical absorption measurement, we can fine-tune the synthesis methods so that we can obtain the synthesis condition boundary to obtain either π-SnS QDs or α-SnS. Synthesis temperature is found to become the critical factor that can lead to different end results. The π-SnS phase was generated at a specific injection temperature range. We are able to fabricate field-effect transistors of the π-SnS QD FETs exhibit p-type characteristics with charge carrier mobility comparable to the early development of many other metal chalcogenide QDs. This investigation will provide insights into the factors influencing the formation of different phases of SnS QDs. Furthermore, the first success of demonstrating transistor operation of π-SnS QD assemblies presents new opportunities to investigate their charge carrier transport for developing environmentally friendly QD electronics.

applications in quantum sensing and as single-photon sources, investigations on the optical properties of CrX3, characterized by broad d-d photoluminescence (PL), are severely lacking. The incorporation of carefully designed atomic defects such as lanthanides opens up a pathway to modulate the overall electronic and magneto-optical properties. Here we report preparation, structural characterization, and spectroscopic studies of all three CrX3 compounds doped with the optical impurity Yb3+. 4 K PL measurements show efficient sensitization of Yb3+ luminescence upon photoexcitation into lattice absorption bands for all three compounds, converting their nondescript broadband d-d PL into sharp f-f emission. The PL of CrI3:Yb3+ and CrBr3:Yb3+ occur at energies typical for [YbX6]3− with these halides, with PL decay times of 0.5 – 1.0 ms at 4 K, but CrI3:Yb3+ displays anomalously low-energy Yb3+ emission and an unusually short PL decay time at 4 K. Data analysis and angular overlap model (AOM) calculations show that Yb3+ in CrI3:Yb3+ has a lower spin-orbit splitting energy than reported for any other Yb3+ in any other compound. We attribute these observations to exceptionally high covalency of the Yb3+/f orbitals in CrI3:Yb3+ stemming primarily from the shallow valence-shell ionization potentials of the iodide anions. These results provide rare fundamental insights into the electronic structure and luminescence of the remarkably undereXamined [YbI6]3− motif.

5:00 PM EL02.05.14 Ligand Boosting of CsPbBr3 Nanoplatelets for Highly Stable Efficiency Blue LED Subin Yun, Artvazx Kirakosyan, Min-Gi Jeon, Joonseok Kim and Jihoon Chung; Chungnam National University, Korea (the Republic of) Perovskite light-emitting diodes (PeLEDs) with an external quantum efficiency (EQE) exceeding 20% have been achieved in both green and red emissions. On the other hand, the efficiency of blue perovskite materials has lagged far behind, with EQEs of 12.3% emitting the sky blue (wavelength at 475–490 nm) and 8.8% emitting the blue (wavelength at 460–475 nm). Several strategies have been proposed for the synthesis of blue-emitting perovskite nanocrystals such as (i) mixed halide perovskites and (ii) low-dimensional nanoplatelets (NPLs). Whereas the mixed halide perovskites show a variable energy bandgap, they have critical drawbacks such as a deep trap state in the bandgap owing to the formation of Cl− vacancies and phase segregation arising from ion migration. In CsPbBr3 NPLs, the emission wavelength can be controlled depending on the number of [PbBr6]3− layers. However, the high density of surface defects in 2D perovskite nanocrystals results in a low photoluminescence quantum yield (PLQY), which imposes challenging issues. Here, we demonstrate that the PLQYs of CsPbBr3 NPLs could be significantly enhanced by adopting inorganic ligands, which can effectively passivate the surface defects. To boost the PL and PLQY of NPLs, several organic/inorganic ligands (such as PbBr2, CH3HgBr, and N2H3Hg (HZBr)) are used. The PLQY of CsPbBr3 NPLs is significantly enhanced from 34% to 90% when HZBr is used as the ligand, which can be effectively coordinated at the surface of this NPL for the CsPbBr3 NPLs. In addition, we conducted the cryogenic PL spectroscopic measurement. Interestingly, in the HZBr-treated sample, the activation energy for carrier trapping is increased from ~180 to 290meV indicating that the surface vacancies and the associated defect states are well passivated. Furthermore, the exciton-longitudinal optical (LO) phonon coupling coefficient and LO phonon energy are reduced from ~280 to 100meV and from ~30 to 20meV, respectively. It suggests that the contribution of exciton-LO coupling to the broadening of PL became weaker.

SESSION EL02.06: Surface Chemistry, Electronic and Optical Properties of Semiconducting Nanocrystals I
Session Chairs: Hao Nguyen and Nayon Park
Thursday Morning, April 25, 2024
Room 347, Level 3, Summit
8:30 AM EL02.06.01 Chemical Modification of CdSe Nanomaterials through Carborane Ligand Exchange Eugenia S. Vasilieaidou, Victoria Rubio, Elijah Cook, Tasnim Ahmed, Alexander Spokony and Justin Caram; University of California, Los Angeles, United States Inorganic nanocrystals capped with surfactant-like organic ligands exhibit a broad range of properties that emerge from the combination of the individual inorganic-organic components. By expanding towards functional organic ligands that are bound on the nanocrystal surface, the charge-transport and biocompatibility of nanocrystals are enhanced, thus achieving greater chemical control of nanomaterials for targeted applications. Herein, we functionalize CdSe nanocrystals through binding with electron-donating carborane ligands (C2B10H12). The synthetic preparation for CdSe quantum dots (QDs) and CdSe nanoplatelets is developed where variable concentration ligand exchange of the CdSe nanomaterials with the carborane ligands leads to changes in the photoluminescence (PL) intensity. Post-synthetic ligand exchange of the native oleate capping ligands for carborane results in a red-shift of the optical band gap of the studied CdSe QDs, while their colloidal stability is maintained based on TEM imaging. Fourier-transform infrared (FTIR) analysis demonstrates the successful incorporation of the carborane ligands onto the CdSe surfaces with the characteristic B-H resonances at 2600 cm−1 and 1250-600 cm−1 in the spectrum. Furthermore, we explore tuning the surface dipole of the CdSe core from a non-functional oleate ligand to functional carborane dipole, where the carborane dipole enables long-range ordering and higher control on the electronic properties of the resultant CdSe core/carborane shell. Altogether, this work illustrates the unique aspects of functional surface carborane ligands in controlling the optoelectronic and dipole properties of CdSe nanocrystals, which could advance their potential applications in solid-state device and bioimaging applications.

8:45 AM *EL02.06.02 Structural Transformations of Group III-V and II-VI Magic-Sized Clusters Driven by Atomic-Bond Exchanges Joonho Kang; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of) Multistep nucleation and growth of quantum dots (QDs) utilizes the competition of kinetic persistence, small inorganic clusters, specifically magic-sized clusters (MSCs), as intermediates. Therefore, understanding and control of the reactivity (or stability) of MSCs is essential to such non-classical QD synthesis. In this talk, using ab initio molecular dynamics (AIMD) simulations, we reveal the destabilization process of a carbohydrate-ligated In12P20, induced by a surface ligand network modification beyond a critical limit. At elevated temperatures, the release of three In(O2CR)3 subunits triggers the sudden loss of stability in the remaining In34P20 core, leading to structural transformations through In–P bond breaking and rearrangement. This isomerization manifests as an In–P bond exchange between a pair of In atoms, resulting in a “rupture” on the cluster surface. The structural disruption in the InP cluster causes noticeable changes in the simulated UV–vis absorption spectra and XRD patterns, which agree well with experimental findings on MSC destabilization induced by reactions with primary amines at low temperatures. Our analysis elucidates that the MSC instability is driven by the intricate interactions between the surface ligand network and the inorganic core of the group III-V MSC. Finally, we discuss the fundamental differences in the isomerization of the InP MSC and a related CdS cluster of similar size, highlighting the distinct nature of surface ligand networks in the group III–V and II–VI cluster systems.


9:15 AM *EL02.06.03 The Surface Chemistry of Colloidal Semiconductor Quantum Dots Ivan Infante; BCMaterials - Basque Center of Materials, Spain Despite significant progress in recent years in understanding the chemical reactions occurring on the surfaces of II–VI, III–V, and lead halide perovskite quantum dots (QDs), there are still fundamental questions that remain unanswered regarding the nature of QD surfaces, QD-ligand interactions, and the formation of trap states. Addressing these aspects is crucial for enhancing the optoelectronic efficiency of QDs.

In this study, we present a pioneering multiscale modeling approach that combines Density Functional Theory and Molecular Dynamics simulations. Our approach encompasses QDs ranging from small to real-sized QDs passivated with oleate ligands and immersed in organic solvents. Through this methodology, we gain invaluable insights into the surface characteristics and the binding energies of ligands under different experimental conditions. This methodology not only provides a deeper understanding of the intricate behavior of colloidal semiconductor nanocrystals but also paves the way for future advancements in their diverse applications.
Colloidal InP quantum dots (QDs) have emerged as potential candidates for constructing nontoxic QD-based optoelectronic devices. However, charge transport in InP QD thin-film assemblies has been limitedly studied. Herein, we report the synthesis of 8 nm edge length (6.5 nm in height), tetrahedral InP QDs and study charge transport in thin films using the platform of the field-effect transistor (FET). We design a hybrid ligand-exchange strategy that combines solution-based exchange with S22 and solid-state exchange with N32 to enhance interdot coupling and control the n-doping of InP QD films. Further modifying the QD surface with thin, thermally evaporated Se overlayers yields FETs with an average electron mobility of 0.45 cm2V−1s−1, 10 times that of previously reported devices, and a higher on–off current ratio of 103–104. Analytical measurements suggest lower trap-state densities and longer carrier lifetimes in the Se-modified InP QD films, giving rise to a four-time longer carrier diffusion length.

10:00 AM BREAK

10:30 AM EL02.06.05
Photogenerated Spin states in Quantum Dot – Molecule Conjugates Jacob Olishansky; Amherst College, United States

The inherent spin polarization in photogenerated spin-correlated radical pairs makes them promising candidates for quantum computing and quantum sensing applications. Notably, these states are spin-polarized (non-Boltzmann populated) at moderate temperatures, and can therefore be initialized in well-defined quantum states. This feature allows them to be probed and manipulated using microwave pulses within standard electron paramagnetic resonance spectrometers equipped with pulsed lasers. Quantum dot – molecule conjugates offer a tunable platform for hosting these spin-correlated radical pairs. We have therefore designed a series of quantum dot – molecular systems that can produce photogenerated spin-polarized states. The molecules are chosen for their ability to undergo efficient charge separation, and the nanoparticle materials, ZnO quantum dots, are chosen for their promising spin properties. Transient and steady state optical spectroscopy performed on ZnO quantum dot–molecular conjugates shows that reversible photogenerated charge separation is occurring. Transient and pulsed electron paramagnetic resonance experiments are then performed on the photogenerated radical pair, which demonstrate that (1) the radical pair is polarized at moderate temperatures and well modeled by existing theories, (2) the spin states can be accessed and manipulated with microwave pulses, and (3) the spin system can be tuned with quantum dot size and molecular linker length. This work opens the door to a new class of promising qubit materials that can be photogenerated in polarized states and hosted by highly tailorable inorganic nanoparticles.

11:00 AM EL02.06.06
Erbium Spin Defects in Colloidal Ceria Nanocrystals with Near Microsecond Spin Coherence Jeesoon Wong1,2, Arashdeep Thind1, Iasleen Bindra1, Jiefei Zhang2, Gregory Grahn1,2, Christina Wicker1, Vuxuan Zhang3, Jens Niklas3, Oleg Poluektov2, Robert F. Klie3, E. Joseph P. Heremans2,2,2, David Awschalom1,2,2, and Paul Alivisatos1,1,1; 1The University of Chicago, United States; 2Argonne National Laboratory, United States; 3University of Illinois at Chicago, United States

We experimentally demonstrate spin coherence times approaching a microsecond in erbium doped ceria nanocrystals with an ensemble average level of a single erbium per nanocrystal. To achieve these spin coherence times, ceria was chosen as a host material with a low natural abundance of nuclear spins. As a result, we observe population lifetimes that approach a millisecond, suggesting substantial improvements to the spin coherence should be possible. We postulate that the spin coherence is limited by the nuclear spin bath of hydrogen atoms from the oleic acid ligands on the surface of the nanocrystal. Quantum beats are observed which correspond to the Larmor frequency of hydrogen, which further suggests the erbium ions are sensitive to the nearby hydrogen nuclei. Scanning transmission electron microscopy measurements combined with electron energy loss spectroscopy further show that Ce3+ and O vacancies are prevalent on the surface of the nanocrystal, likely playing a role in the observed spin coherence and lifetime. Nonetheless, the spin coherence already demonstrated suggests that spin defects in nanocrystals are a promising materials platform for quantum information processing.

11:15 AM EL02.06.08
Colloidal Atomic Layer Deposition enables Synthesis of Nano-Heterostructures with Atomic Layer Precision Dmitri V. Talapin; University of Chicago, United States

In contrast to molecular systems, which are defined with atomic precision, nanomaterials generally show some heterogeneity in size, shape, and composition. The sample inhomogeneity translates into a distribution of energy levels, band gaps, work functions, and other characteristics. The lack of atomic control during nanomaterial synthesis also limits our ability to perform “total-synthesis” of sophisticated nano-heterostructures with precisely arranged multiple components and fine-tuned properties. We discuss a general synthetic strategy which largely circumvents these limitations of traditional colloidal synthesis. Colloidal Atomic Layer Deposition (c-ALD) allows significant reduction of inhomogeneity for nanomaterials without compromising their structural perfection. We report a novel realization of c-ALD step sequence which significantly improves synthetic control and quality of synthesized nanomaterials. In traditional gas-phase ALD, the substrate and gaseous reactants act as the stationary and mobile phases, respectively. Such distinction facilitates removal of unreacted precursors by pulsing inert gas after each half-reaction. For c-ALD, we inverted the stationary and mobile phases – reactants form the stationary phase while the substrate is moved in and out of the reactor as the mobile phase. This approach brings c-ALD closer to traditional ALD and is expected to make it a similarly powerful and versatile technique. Our improved c-ALD enables synthesis of epitaxial nanostructures without compromising their structural perfection. Colloidal Atomic Layer Deposition (c-ALD) allows significant reduction of inhomogeneity for nanomaterials without compromising their structural perfection. Colloidal Atomic Layer Deposition (c-ALD) allows significant reduction of inhomogeneity for nanomaterials without compromising their structural perfection. Colloidal Atomic Layer Deposition (c-ALD) allows significant reduction of inhomogeneity for nanomaterials without compromising their structural perfection.

11:45 AM EL02.06.09
Improving the Impact of Solvent and Particle Properties on Optical Manipulation of Colloidal Nanomaterials Brandon Reynolds and Matthew Crane; Colorado School of Mines, United States

The precise control over the placement of colloidal nanomaterials has led to enticing emergent phenomena including transport through superlattices, strong coupling with optical cavities for quantum applications, and hybridization when different colloidal materials are interfaced. These applications and many more require precise spatial placement of nanoparticles as well as precise control over orientation. As an example, defects in wide-band gap nanomaterials or spins in semiconductor nanomaterials offer promising solutions for quantum technologies that are inaccessible to bulk materials, if the colloidal materials can be precisely positioned in an optical cavity. This requires a tool that acts on a single colloid in three dimensions, controls the angle of the colloid, and is applicable to a variety of particles and a variety of solvents. Optical manipulation methods such as optical trapping provide a unique platform that addresses these criteria, by trapping a particle in three dimensions and allowing for orientation control through polarization. However, we have limited understanding of how optical manipulation may change in the environments necessary for colloidal nanomaterials – i.e. organic solvents, ligands, or high refractive index materials. Here, we investigate the impact of particle composition, geometry, and size as well as solvent identity on optical trapping forces using a combination of experiments and multiphysics simulations. We investigate the impact of key variables such as viscosity and refractive index on optical trapping strength. Combining these results, we identify key relationships between solvent and colloidal nanomaterials to manipulate and orient nanomaterials and suggest guidelines to further improve optical manipulation.
Improving strong quantum confinement in lead halide perovskite nanocrystals enhances the electronic interactions between charge carriers and dopants within each nanocrystal and promotes the delocalization of the exciton wavefunction in the closely packed assemblies of these nanocrystals. We investigated: (i) the generation of hot electrons via exciton-to-hot-electron upconversion in strongly quantum-confined cesium lead bromide (CsPbBr3) nanocrystals doped with Mn2+ and (ii) the coherent photon emission from the superlattices of CsPbBr3 quantum dots, where strong quantum confinement plays a significant role. The enhanced exciton-dopant interaction in the more strongly confined CsPbBr3 nanocrystals proved beneficial for hot electron upconversion and allowed for the utilization of the long-lived dark exciton in such processes at low temperatures. The closely-packed QD superlattice of the strongly confined CsPbBr3 quantum dots, which are 4 nm in size, exhibited superfluorescence from excitons delocalized across many quantum dots, rather than from an ensemble of electronically non-coupled quantum dots, especially as the temperature decreased. Positioning the superlattice within the micro-ring resonance cavity further amplified the coherent emission from the interconnected quantum dots.

2:30 PM EL02.07.03
Assessing Photoinduced Carrier and Heat Transfer in Tin-Doped Indium Oxide Nanocrystals

Sara Russo, Lauren Cisneros and Matthew Crane; Colorado School of Mines, United States

Degenerately doped semiconductor nanocrystals exhibit tunable localized surface plasmon resonances with strong optical absorption cross sections and band gaps. Upon excitation, these materials produce non-equilibrium carrier distributions that rapidly relax, presenting a brief window for utilization. These features mark plasmonic nanocrystals as promising candidates for new applications that require efficient light absorption and highly directed energy and carrier utilization, such as photodetectors, photovoltaics, and photocatalysts, if we can understand and engineer efficient transport mechanisms. Here, we investigate hot carrier and heat transfer from prototypical tin-doped indium oxide (ITO) nanocrystals to adsorbates as a model system for harvesting and utilizing light in plasmonic semiconductor nanocrystals. Using transient absorption spectroscopy, we track carrier and energy transfer from ITO nanocrystals to adsorbates and evaluate the impact of aliovalent dopant concentration, wavelength, and energy level alignment. We find that these variables strongly impact carrier transfer to adsorbates. Utilizing local temperature reporters, we simultaneously quantify heat transfer from ITO nanocrystals into the environment. Combining these results, we suggest general design rules to optimize carrier energy transfer from plasmonic semiconductors.

2:45 PM BREAK

3:15 PM EL02.07.05
High Mobility and Low Trap Density in 3D PbS Quantum Dots Superlattices by PbI2 Passivation

Jaccoo Pinna1, Elisa Pili2, Razieh Mehrabi Koshs3, Dnyaneshwar S. Gavhane1, Francesco Carl1, Bur J. Koo4, Giuseppe Portale1 and Maria Antonieta Loi4; 1University of Groningen, Netherlands; 2Diamond Light Source, United Kingdom

Lead chalcogenide colloidal quantum dots (QDs) are one of the most promising materials to revolutionize the field of optoelectronics. This is due to their unique optical properties, namely the bandgap tunability in a wide wavelength range (800 – 3000 nm). Even if the past two decades of research resulted in significant development of this technology, these materials still show moderate mobility and high trap densities, which are a limitation for their applications. Most of the problems stem from the disordered nature of the deposited films and poor control over the ligand exchange (LE). It is predicted that ordered assemblies of QDs, the so-called superlattices (SLs), should display mobilities up to four orders of magnitude higher than the disordered counterparts. Recently, we demonstrated mobilities above 270 cm2/Vs in 3D SL of PbSe QDs[1], when surface traps are filled using an ionic-gel gate. Nevertheless, using PbSe QDs is undesirable for applications due to its tendency to oxidise very easily. On the other hand, PbS shows much higher stability even in air when proper passivation strategies are adopted. While there are several reports in the literature on PbS-based superlattices, the focus has been on structural characterisation and often transport properties are not measured. A recent report on 2D square SL with PbS QDs demonstrated electron mobilities of 15 cm2/Vs with ionic liquid gating.

Here we demonstrate for the first time highly ordered 3D SLs of electronically coupled PbS QDs and an effective trap passivation with iodide-based ligands. To be suitable for photodetection, we grow films up to 220 nm of thickness with outstanding coherent ordering, both in-plane and along the thickness, as proved by electron microscopy and advanced x-ray scattering techniques. Here we grow films up to 220 nm of thickness with outstanding coherent ordering, both in-plane and along the thickness, as proved by electron microscopy and advanced x-ray scattering techniques. To achieve electronic coupling, we perform LE with ethylenediamine which, despite the noticeable thickness, removes the olic acid ligand. We finally test the transport properties with an ionic-gel gated field-effect transistor and observe n-type transport, high conductance, and modulation. The measured electron mobilities achieve a maximum of 220 cm2/Vs, which is one order of magnitude above the state-of-the-art for PbS SLs with comparable gating, proving how the 3D structures outperform the 2D ones thanks to the better ordering. Finally, a passivation treatment with PbI2 is shown to reduce the surface trap density as demonstrated by a significant reduction of the subthreshold swing. The combination of strong absorption in the short-wavelength infrared range and the record charge mobilities make these metamaterials an excellent candidate for fast-response photodetector in a wavelength range where traditional semiconductors perform poorly with the high cost. We also demonstrate how surface trap passivation will be a key element to control in order to implement these 3D SLs in photodetectors.

References:

3:30 PM EL02.07.07
The Role of Colloidal Er-Doped SiO2 Thin-Film Interfaced with Czochralski Silicon on Enhanced Bandgap Emission for Optoelectronic Applications

Sufian Abdurabb1, Anthony T. Fior2 and Nuggehalli M. Ravindra3; 1Khulifa University, United Arab Emirates; 2Integron Solutions LLC, United States; 3New Jersey Institute of Technology, United States

Colloidal silica bulk glass and coatings have been studied extensively for many years. In this work we report a new optoelectronic phenomenon introduced by interfacing Er-doped sol-gel silica on Czochralski silicon (Cz-Si). The discovery is noteworthy on two aspects: (i) strong enhancement of band gap emission, and (ii) modeling the observed luminescence spectra reveals strong dominance of correlated electron-hole (e-h) radiative recombination. Colloidal interfacial reactions with Cz-Si surface are known to introduce random interfacial strain fields that favors the radiative recombination interactions. The modeling of the room-temperature photoluminescence spectra exhibit attenuates a strong attenuation of the shorter tail of the emission spectra; thus, amplifying the excitonic e-h. The presentation will also include a comparative study of the bandgap emission of thermally oxidized Cz-Si with the colloidal prepared spin-coated silica on Cz-Si to highlight the discovery.

3:45 PM EL02.07.06
Optical and Electrical Investigations to Unveil Charge Storage and Transport Mechanisms in ITO Nanocrystals

Anjana P. Muraleedharan1,2, Nicolo Petrini1, Siddharth Kuriyil1, Luca Rebecchi1, Priyadarshi Ranjan1, Mushes Kumar Thakur1, Andrea Rubino1, Nicola Curreli2 and Ilka Kriegel2; 1Italian Institute of Technology, Italy; 2University of Genova, Italy

Transparent conducting oxide (TCO) zero-dimensional (0D) nanocrystals (NCs) such as Indium-Tin-Oxide (ITO) are of special importance for opto- electrical devices because of their unique features of optical transparency in the visible region and controllable electrical conductivity. In order to fully realize the potential of these materials to integrate them into useful devices, greater understanding of the charge transport in nanocrystal thin films along with a deep insight into the charge storage mechanism in solution is necessary. Doped metal oxide nanocrystals (MO NCs) are potential candidates for accumulating multiple electrons or holes in the system induced doping process termed ‘Photodoping’. It has been demonstrated recently that metal oxide (MO) nanocrystals can act as act as photocatalysts when coupled with a suitable system acting as hole or electron acceptor, storing the charges that are generated upon illumination with photon energy above the MO bandgap. ITO NCs with different InOx (IO) shell thicknesses are charged using a UV LED in a controlled and inert atmosphere, simultaneously monitoring the changes in the absorption spectra over time with time resolution of few seconds. In this way we extract information on the dynamics of the light-driven charging process of a set of ITO/InsO3 core/shell (ITO/IO) NCs with “artificial” depletion regions. In addition, we leverage a metal-insulator-metal device configuration to probe the electronic transport in Tin doped Indium Oxide nanocrystals (ITO nanocrystals) to understand the electrical effects of photodoping. The electronic conduction in ITO NC thin film is studied in dark and light (UV) conditions in order to understand light- induced charge generation. ITO, being a wide bandgap material with high native doping levels, manifest electronic conduction that resembles semiconductor behaviour.

References:
Synergistic Passivation of AgBiS2 Ternary Colloidal Quantum Dots: A Strategy for Enhancing Stability and Performance Investigated with First Principles Calculations

AgBiS2, which is a ternary compound, has attracted significant attention owing to its high absorption coefficients, tunable bandgap, and environmental stability. Various strategies have been adopted for the development of AgBiS2 QD solar cells; however, a relatively low power conversion efficiency (PCE) for AgBiS2-based QD solar cells compared to lead-based QD solar cells is a significant drawback. The main drawback of solution-processed AgBiS2 is attributed to the use of long-chain hydrocarbon ligands during the synthesis process, which impedes charge transport in practical applications. Consequently, the exchange of surface ligands emerges as a promising strategy to overcome this limitation. Nevertheless, the theoretical understanding of the surface properties of AgBiS2 QD solids is still lacking, which can potentially influence the exchange kinetics in the synthesis process.

In this presentation, an effective passivation of AgBiS2 QD surface is proposed by designing a synergistic passivation strategy with Ag2I2, AgBr2, and Na+ based on density functional theory (DFT) calculations. Utilizing (111) and (100) facets which are expected to be the primary components of QD solids, single-ligand passivation calculations on each surface demonstrated that individual cations do not effectively adhere to the (111) surface. On the other hand, the simulation revealed that the synergistic ligand approach was shown to be complementary to selective surface passivation. It was found that the initial covering of the metal halide anion reconfigures the surface, leading to subsequent cation passivation. Moreover, it was also demonstrated that the synergistic passivation can be both passive (both (111) and (100)) and active, providing a more straightforward strategy for multiple facets. Furthermore, the experiments have demonstrated the feasibility of the theoretically suggested synergistic passivation and the improvement in performance. In particular, XPS measurements indicated that stable AgBiS2 QD ink was realized through synergistic passivation mechanism as suggested by the simulation. Finally, the solar cell that was fabricated based on our QD ink achieved a power conversion efficiency (PCE) of 8.14%, which is 11% higher than the previous best report.
overcome surface energy barriers to selectively deposit charged droplets and deterministically position functional materials, including QDs, down to nanoscale resolutions.

Quantum yields, in some cases. Here we have used electrohydrodynamic inkjet (EHDIJ) printing as a highly precise and scalable nanomanufacturing method for digital deposition of attoliter-photons. Colloidal quantum dots (QDs) are uniquely suited to complement this range of devices due to their solution-processability, broad tuneability, and near-unity photoluminescence efficiency. Nanophotonic structures are a foundation for the emerging field of light-based quantum networks and devices. These nanoscale structures act through their ability to couple with and manipulate quantum effects. These structures are also referred to as nanomolecules (AuNCs). They have small enough optical band gaps to absorb in the near infrared (near IR) region (700-900 nm) which is beneficial for biological applications. One of the most investigated superatom clusters is Au$_{25}$L$_{18}$, where L = hexanethiol exhibits luminescence efficiencies of 2.5 × 10$^{-4}$ in the near region with cross-sections of 2700 GM at 1290 nm which can be useful for two-photon imaging with IR light. Doping the AuNC metal core with foreign atoms is considered a powerful method for transforming Au$_{25}$L$_{18}$ into stable clusters with different electronic structures resulting in increased luminescence. In addition, this can induce magnetism which is important for magnetic imaging, and computing applications. The electronic states of these clusters can further be manipulated by increasing ligands containing a chromophore or possessing redox capability. While these effects are documented, the mechanisms involved remain controversial and little work has been done with respect to its bi-counterpart. The results of this study will offer more insight to better designed AuNCs with bi-icosahedral geometrical structures that are dopable (Pt, Ag, Cd, Hg) for use as novel nonlinear optical materials (NLO). The electrochemical band gap and brightness factors will also be presented.

Gold nanostructures have been the focus of research over the past two decades because of their potential as excellent two-photon absorbers, which make them good sensors and imaging agents. This is due, in part, to their size-specific properties. Of particular interest is a class of gold nanostructures called superatomics, or magic numbered clusters, that exhibit quantum confinement effects. These structures are also referred to as nanomolecules (AuNCs). They have small enough optical band gaps to absorb in the near infrared (near IR) region (700-900 nm) which is beneficial for biological applications. One of the most investigated superatom clusters is Au$_{25}$L$_{18}$, where L = hexanethiol exhibits luminescence efficiencies of 2.5 × 10$^{-4}$ in the near region with cross-sections of 2700 GM at 1290 nm which can be useful for two-photon imaging with IR light. Doping the AuNC metal core with foreign atoms is considered a powerful method for transforming Au$_{25}$L$_{18}$ into stable clusters with different electronic structures resulting in increased luminescence. In addition, this can induce magnetism which is important for magnetic imaging, and computing applications. The electronic states of these clusters can further be manipulated by increasing ligands containing a chromophore or possessing redox capability. While these effects are documented, the mechanisms involved remain controversial and little work has been done with respect to its bi-counterpart. The results of this study will offer more insight to better designed AuNCs with bi-icosahedral geometrical structures that are dopable (Pt, Ag, Cd, Hg) for use as novel nonlinear optical materials (NLO). The electrochemical band gap and brightness factors will also be presented.

Magic-sized InP Clusters as Platforms for Core-Only Emitters with Narrow Linewidths

Purcell enhancement and the unique ability to direct emission from photon sources into the applications.

Colloidal quantum dots (QDs) excel at converting light or electricity into bright, tunable, color-pure luminescence, a property that promises a bright future for display technology that can reproduce the range of spectral hues discernable to humans. While several materials are disqualified due to hazardous substance restrictions, indium phosphide (InP) is energetically qualified and not RoHS restricted. Imparting synthetic control over the resultant photophysical properties of InP is an outstanding challenge, however. Our efforts have focused on developing the synthesis of atomically precise InP magic-sized clusters that show unique and distinct photophysical behavior from their larger QD counterparts. Importantly, these clusters demonstrate exceptionally narrow emission linewidths and long-term ambient stability, making them a promising platform for emissive materials. This is achieved by exchanging carboxylic acid ligands for phosphonic acid ligands, employing reaction additives, and exploring post-synthetic atomic surface modifications. Despite exhibiting exceptionally narrow ensemble linewidths, the as-synthesized clusters suffer from low photoluminescence quantum yield. Low brightness is remedied by including phosphine oxides in the synthesis, which affords highly monodisperse InP nuclei demonstrating improved photoluminescence intensity and lifetimes. Ongoing and future efforts are focused on exploring the formation, physical structure, and the role of ligands and extraneous additives on modulating the surface chemistry and resultant photophysical behavior of phosphonic acid-capped InP magic-sized clusters.

Scalable Nanomanufacturing of Quantum Dot Heterointegrated Nanophotonic Cavities

We believe these results will motivate the development of future suspended heterointegrated devices that utilize EHDIJ printing as a sustainable, additive, and scalable method for quantum photonics nanomanufacturing.
channel or ambipolar transport with a hole mobility as high as 3.5 cm² V⁻¹ s⁻¹ at 290 K and 6.5 cm² V⁻¹ s⁻¹ at 170–220 K, one order of magnitude larger than that of previous QD solids.

effect transistors (e.g., epi-SL). Finally, I will present systematic measurements of charge transport in individual, highly-ordered PbSe QD epi-SL grains. One technical challenge in making these devices is the limited to large-area, polycrystalline samples in which superlattice grain boundaries and intragrain defects suppress/obscure miniband effects. In this talk, I will first discuss the synthesis of large-grained PbSe QD SLs, including detailed analysis of their chemical and physical structure. Next, I will discuss the mechanism by which a ligand-capped PbSe QD SL is converted into an electron-hole recombination, consequently reducing luminous efficiency. Ideally, if the surface oxides of InP QDs can be effectively removed and the exposed DBs can be passivated with surface complexes of Indium Phosphide Quantum Dots for Shell-Less Light-Emitter

Synthesis and Characterization of Single-Grain Epitaxially-Fused PbSe Quantum Dot Superlattices

Epitaxially-fused superlattices of colloidal quantum dots (QD epi-SLs) may exhibit electronic minibands and high-mobility charge transport, but electrical measurements of epi-SLs have been limited to large-area, polycrystalline samples in which superlattice grain boundaries and intragrain defects suppress/obscure miniband effects. In this talk, I will first discuss the synthesis of large-grained PbSe QD SLs, including detailed analysis of their chemical and physical structure. Next, I will discuss the mechanism by which a ligand-capped PbSe QD SL is converted into an electron-hole recombination, consequently reducing luminous efficiency. Ideally, if the surface oxides of InP QDs can be effectively removed and the exposed DBs can be passivated with surface complexes of

Silicon quantum dots (Si QDs) are considered as attractive probes for bioimaging applications because of their earth-abundance, and size-tunable optical properties, nontoxicity, biocompatibility and biodegradability. In this study, one-step synthesis of water-dispersible and red-emitting Si QDs is investigated using nonthermal plasma. Nonthermal plasma is popular to produce Si QDs with superior size and shape uniformities, high purity and crystallinity which are important to obtain decent and well-controlled optical properties. The one-step synthesis method is a simplified approach to produce surface-passivated Si QDs by combining QD synthesis and surface passivation processes. Therefore, it does not require additional treatments involving high temperatures and toxic chemicals; it can save energy as well as time and reduce hazardous chemicals. We prepared water-dispersible and red-emitting Si QDs using the one-step synthesis method for the first time. Si QDs were synthesized using silane as a precursor, and their surfaces were passivated by acrylic acid. In order to improve water dispersibility, oxygen gas or water vapor was added into the passivation stage. We estimated Si QDs' size from X-ray diffraction (XRD) patterns, and the estimated diameter was 4 nm. The XRD patterns also showed the Si QDs are crystalline. The hydrodynamics diameters of QDs were measured by dynamic laser diffraction to investigate water-dispersibility. 10 to 11 nm of hydrodynamic diameter means Si QDs can disperse well enough to be used as bioimaging probes; for instance, QDs smaller than 20 nm can cross the blood-brain barrier. The Si QDs excited by ultraviolet light (400 nm) emitted red light (peak position at ~830 nm) with 30% of photoluminescence quantum yield. Since skin, fat, tissue, and blood are relatively transparent in the red-to-NIR range, red-emitting Si QDs can offer deeper tissue penetration resulting in improved bioimaging quality. We conducted bioimaging using 3T3 cells cultured with the Si QDs and demonstrated the Si QDs existed inside the cells emitting red light. This result showed that our water-dispersible Si QDs enables bioimaging in NIR range. Thus, this study shows that the one-step Si QD preparation method is an energy- and time-saving as well as less hazardous route for fabricating water-dispersible and photoluminescent Si QDs which are promising materials as probes for bioimaging applications as well as diagnostic tools.

5:00 PM EL02.08.14

Synthesis and Characterization of Single-Grain Epitaxially-Fused PbSe Quantum Dot Superlattices

Epitaxially-fused superlattices of colloidal quantum dots (QD epi-SLs) may exhibit electronic minibands and high-mobility charge transport, but electrical measurements of epi-SLs have been limited to large-area, polycrystalline samples in which superlattice grain boundaries and intragrain defects suppress/obscure miniband effects. In this talk, I will first discuss the synthesis of large-grained PbSe QD SLs, including detailed analysis of their chemical and physical structure. Next, I will discuss the mechanism by which a ligand-capped PbSe QD SL is converted into an electron-hole recombination, consequently reducing luminous efficiency. Ideally, if the surface oxides of InP QDs can be effectively removed and the exposed DBs can be passivated with surface complexes of...
Towards Non-Blinking Strongly Confined Perovskite Quantum Dots

Yiton Dong, Chenzia Mi and Matthew Atteberry; The University of Oklahoma, United States

Quantum information science has shown its capabilities to enable quantum communications. Single photon emitters (SPEs) emit photons one at a time and are fundamental elements of such transformative technologies. Quantum dots (QDs), an atom-like solid-state light source, can emit photons with high efficiency and thus become promising SPE materials. Colloidal cesium lead halide (CsPbX3, X=Br, I) perovskite QDs are ideal for next-generation SPEs because of their high room-temperature luminescence efficiency and low-cost, scalable syntheses. Unfortunately, individual perovskite QDs show insufficient photostability and severe photoluminescence (PL) intensity fluctuations. These fluctuations, also called blinking, can lead to spectral shifts, change the fluorescence dynamics, and reduce the structural stability of perovskite QDs. This has greatly limited the spectroscopic studies for SPE developments. Unlike conventional CdSe QDs, due to the highly ionic crystal structure of perovskites, there is not yet an approach to produce a homogeneous Type-I core-shell structure for perovskite QDs that can efficiently suppress blinking.

One challenge of studying the ionic perovskite QDs is their relatively low ligand binding affinities. When preparing individual perovskite QD samples, QD colloids often need to be diluted, and the ligand can detach from the QD, introducing defects. As a result, individual perovskite QDs often show rapid PL intensity fluctuations accompanied by photodegradation. Many significant advances have been made to avoid being searched for ligands that bind strongly with the surface of perovskite QDs, such as zwitterionic and didodecyldimethylammonium bromide ligands. However, perovskite QDs, especially for strongly size confined QDs, are still experiencing severe PL blinking with large PL “OFF” occurrences.

Here we discovered a method that can significantly suppress PL blinking and improve photostability of strongly confined CsPbBr3 Perovskite QDs. CsPbBr3 QDs with tuneable sizes from ~3.5 nm to 7 nm are synthesized using the thermodynamic-equilibrium-controlled method and annealed at elevated temperatures to form a bromide rich surface. Diluted QD colloids are then used as anisotropic and nucleation centers to form a polycrystalline thin film consisting of phenylammonium bromide (PEABr) salts. The bromide rich surface will be epitaxially anchored onto the PEABr matrix and therefore be passivated. Individual strongly confined CsPbBr3 QDs embedded in the PEABr show nearly non-blinking behavior under both pulsed and cwaser excitations (non-resonant) at room temperature. Power-law analysis of the blinking traces of these perovskite QDs show very different “ON” and “OFF” powers (0.85 and 1.9). These QDs remain photostable for more than one hour under laser excitations and show very high single photon purities (> 95%). Additionally, CsPbBr3 QDs with sizes from 3.5 nm to 7 nm can all be passivated and stabilized using our method and show nearly non-blinking behaviors. We anticipate that these QDs will result in more accurate and detailed studies of exciton dynamics and structural-optical property relationships in strongly confined perovskite QDs.

9:30 AM  

Feasibility of Quantum Dot Superradiance

Serguei Goupalov1 and Mikhail O. Nestoklon2; 1Jackson State University, United States; 2TU Dortmund, Germany

Superradiance is the collective spontaneous emission of a system of many radiative dipoles [1]. Recently, behaviors characteristic for superradiance have been reported for arrays of closely packed self-assembled colloidal lead halide perovskite quantum dot (QDs) [2,3]. The main obstacle which hinders formation of a superradiant state is the inhomogeneous broadening of the optical transitions implying variances of the resonant frequencies from one emitter to another. At first glance, in order to form a superradiant state, variances of the resonant frequencies for participating emitters should be within the radiative linewidth, which for exciton transitions in lead halide perovskite QDs is on the order of few micro-eV. However, along with the long-range interaction through the transverse electro-magnetic field, exciton radiative dipoles are subjects of short-range dipole-dipole interaction. We show that this interaction allows one to relax the strict resonant conditions for formation of the superradiant state. Yet, we demonstrate that the dipole-dipole interaction between excitons in lead halide perovskite QDs is at least two orders of magnitude weaker than reported in literature [3] and, for closely packed QDs, amounts few tenths of a meV. We further show that retardation effect inhibits superradiance and limits the number of emitters participating in the superradiant state. This number also depends on the configuration and dimensionality of the array.


9:45 AM BREAK

10:15 AM  

Programmable Quantum Nanophotonics

Arka Majumdar; University of Washington, Seattle, United States

Analog quantum simulators rely on programmable quantum devices to emulate Hamiltonians describing various physical phenomenon. Photonic coupled cavity arrays are a promising platform for realizing such devices. Using a silicon photonic coupled cavity array made up of high quality-factor resonators and equipped with specially designed thermo-optic island heaters for independent control of cavities, we demonstrate a programmable device implementing tight-binding Hamiltonians with access to the full eigen-energy spectrum. We report a reduction in the thermal crosstalk between neighboring sites of the cavity array compared to traditional heaters, and then present a control scheme to program the cavity array to a given tight-binding Hamiltonian. Finally, I will talk about use of colloidal materials to provide strong nonlinearity in this platform.

10:45 AM  

Quantum Dots Photoluminescence

D. D. Blach1,2, V. V. Palyulin1,3,2, S. P. Han1,2,4,5,6, and A. O. Gogolin1,2,4,5,6; 1Univ. of Washington, Seattle, WA, USA; 2TUM, Munich, Germany; 3Novosibirsk State University, Novosibirsk, Russia; 4Space Science Center, University of Washington, Seattle, WA, USA; 5NEC Laboratory, Inc., Tokyo, Japan; 6RIKEN Center for Emergent Matter Science, Wako, Japan

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10:45 AM  

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Arka Majumdar; University of Washington, Seattle, United States

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Efficient infrared light sources are needed for applications like gas sensing, environmental monitoring, and spectroscopy. In the visible, electroluminescence from colloidal quantum dots is highly efficient, wavelength-tunable, and cost-effective, which inspires using the same approach in the infrared. Despite the promising performances of colloidal quantum dots light-emitting diodes in the near-infrared, mid-infrared devices show quantum efficiencies of about 0.1% due to the much weaker emission. Moreover, these devices exclusively relied on the interband transition, restricting the possible materials.

Here, we show electroluminescence at 5 microns using the intraband transition between 1Se and 1Pe states within the conduction band of core/shell HgSe/CdSe colloidal quantum dots. With a three-monolayer CdSe shell thickness, the electroluminescence efficiency is about 50-fold larger than in that a device which uses the interband transition of similar-sized core-only mid-infrared HgTe colloidal quantum dots. The device showed an EQE of 4.5% at 2 A/cm² while the power efficiency was 0.05%. The quantum efficiency approaches that of commercial epitaxial cascade quantum well light-emitting diodes. The high emission efficiency and the electrical characteristics support a similar cascade process where the electrons, driven by the bias across the device, repeatedly tunnel into 1P energy levels and relax to 1S after they hop from quantum dot to quantum dot.

The efficiency of the device could be further enhanced through the improvement of the colloidal quantum dot synthesis and film processing. Moreover, similar intraband transitions exist in many other materials, and the cascade mid-infrared electroluminescence design could then be extended to lower toxicity systems.

Fast near-IR (NIR) emitters are highly valuable in telecommunication and biological imaging. Colloidal synthesis is a potent method that produces a few NIR-emitting materials, but they suffer from long photoluminescence (PL) times. These long PL times are intrinsic in some NIR materials (PbS, PbSe) but are attributed to emission from bright trapped carrier states in others. We develop the colloidal chemistry of an overlooked II–V semiconductor cadmium phosphide (Cd3P2) — an alternative promising near-IR material that offers a high bandgap tunability. It is a unique material that bridges III–V and II–VI semiconductors and combines the best of both worlds: near-IR emission with solution processability. We show that as-synthesized Cd3P2 QDs possess substantial trap emission with radiative times >10^6 ns. With the help of intelligent surface passivation through shell growth or Lewis coordination, or through cationic doping, we manage to accelerate the NIR emission from Cd3P2 QDs by decreasing the amount of trap emission. This finding brings us one step closer to the application of colloidally synthesized QDs as quantum emitters.

11:30 AM EL02.09.09
Mid-Infrared Cascade Intra-band Electroluminescence with HgSe/CdSe Core/Shell Colloidal Quantum Dots
Xinyu Shen, Ananth Kamath and Philippe Guyot-Sionnest; University of Chicago, United States

11:45 AM EL02.09.10
Acceleration of Near-IR Emission through Efficient Surface Passivation and Doping of Cd3P2 Quantum Dots
Logan Smith1, Kathryn E. Harbison1, Nickie Tiwari1, Benjamin T. Diroll1 and Igor Fedin1; 1The University of Alabama, United States; 2Argonne National Laboratory, United States

1 PM EL02.10.01
Toward Ultrathin and Intrinsically Stretchable Optoelectronic Devices
Moon Kee Choi; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Exploring Optoelectronic Properties of Heterostructures of Thin Films and Magic-Sized Clusters of Metal Halide Perovskites
Asmitha Mekala1, Jorge Arteaga1, Heng Zhang2, Jin Zhang2 and Sayananti Ghosh1; 1University of California, Merced, United States; 2University of California, Santa Cruz, United States

Multimodal Strategies for Novel Material Discovery and Enhanced Halide Perovskite Emitters
Alexander S. Urban1, Nina A. Henke1, Carola Lampe2, Kilian Frank2, Stefan Martin1, Ioannis Kouroudis2, Milan Harth2, Patrick Ganswindt1, Markus Döblinger1, Alessio Gagliardi2 and Bert Nickel1; 1LMU Munich, Germany; 2Technical University Munich, Germany
To meet the current and future global energy demands, we must implement a dual strategy of increased renewable energy conversion and reduced energy consumption. This will require us to substantially optimize current materials or discover and develop entirely new ones, for example, for solar cells and light-emitting diodes. A material with vast potential for these applications is nanocrystalline halide perovskite. However, one of the difficulties in improving perovskites is that the fabrication can be too fast to investigate with conventional approaches, and optimizing the resulting NCs can be an extremely tedious task. In this talk, I will discuss our new multimodal approaches to determine the structure and synthesis dynamics of highly confined 1D and 2D halide perovskite nanocrystals, tailor them to specific applications, and enhance their efficiency and stability.[1,2] I will also highlight our approach to incorporate a machine-learning process to optimize syntheses with minimal data demand. Importantly, many of these novel approaches can readily be applied to other systems, greatly benefitting material discovery and development.


2:15 PM *EL02.10.04
Metal Halide Perovskite Nanocrystals for Advanced Display Technologies
Tae-Woo Lee; Seoul National University, Korea (the Republic of)

Metal halide perovskites (MHPs) have gained recognition as potential candidates for next-generation display technologies, given their high color purity, cost-effectiveness, and facile processing attributes. While several techniques have been pursued to magnify their luminescence performance and stability, they have not yet eclipsed the benchmarks set by conventional organic or inorganic quantum dot-based LEDs. In this talk, we will delve into the unique advantages and strategies involved in MHPs for display technologies using meticulously designed nanomaterials. First would be a comprehensive material strategy aimed at inhibiting defect generation in atomically precise colloidal perovskite nanocrystals (PNCs), thereby elevating their luminescent efficiency. By incorporating guanidinium (GA+) cations into formamidinium lead bromide (FAPbBr3) PNCs, we could achieve a significant surge in luminous efficiency coupled with decreased amount of defect sites. [1] In addition, the incorporation of the bromine-incorporating molecule, 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (TBTB), effectively addressed the halide vacancies. In terms of scalable manufacturing, we have pioneered a modified bar-coating process capable of producing large devices on par with the efficiencies of spin-coated counterparts at small device size. [2] In-situ type of core/shell PNC synthesis methodology on substrate will also be discussed, which facilitated the realization of perovskite LEDs with high efficiency, brightness, and stability at the same time. [3] By fragmenting large 3D crystals into nanoscale counterparts and surrounding them using covalently-bonded compact acidic organic ligands, we achieved outstanding charge confinement without compromising charge mobility. Collectively, these advancements underscore the potential of MHPs as the vanguard of self-emissive display materials.


2:45 PM BREAK

3:15 PM EL02.10.05
The Role of Inorganic Ruddlesden-Popper Planar Faults in CsPbBr3 Perovskite Nanocrystals and Their Performance in LEDs
Maria V. Goriacheva1, Alec Pickert2, Payal Bhattacharya3; Suchismita Guha3 and Yanzheuan Xing1; 1University of North Dakota, United States; 2Intel Corporation, United States; 3MKS Instruments, United States; 4University of Missouri–Columbia, United States

Ruddlesden-Popper (RP) planar faults composed of organic layers were shown to significantly enhance stability and overall opto-electronic performance of lead-halide perovskite nanocrystals (PNCs). The observed phenomena have been mainly attributed to the moisture-repellent and electronically insulating nature of long carbon chains allowing them to shield perovskite domains from moisture while confining excitons. Similar performance enhancement is seen in PNCs with all-inorganic RP layers – insulating in nature, yet highly soluble in water. Here we attempt to define the role of CsBr RP-faults in CsPbBr3 nanocrystals by performing a comparative analysis of nanocrystals with and without RP layers. The nanocrystals are studied as stand-alone colloids and thin films as well as emissive layers in light-emitting diodes. We find that CsPbBr3 PNCs with RP faults possess both higher exciton binding energies and longer exciton lifetimes. The former is ascribed to a quantum confinement effect in the PNCs induced by electronically insulating CsBr layers. The latter is attributed to a plausible spatial electron–hole separation across the RP faults. A striking difference is seen in the up-conversion photoluminescence response from CsPbBr3 PNCs with and without RP. For the first time, all-inorganic CsPbBr3 PNCs with RP faults are tested in light-emitting devices and demonstrated to significantly outperform non-RP CsPbBr3 PNCs.

3:30 PM *EL02.10.06
Priming InP-Based Quantum Dots for On-Chip LED Color Conversion
Zeeg Hens and Pieter Schiettecatte; Ghent University, Belgium

InP-based quantum dots have emerged as an alternative for CdSe-based materials for luminescent color conversion in the visible. At the same time, color-conversion approaches are shifting from remote phosphor-on-chip configurations, which implies exposure to higher light intensity and increased operation temperature. In this contribution, we discuss recent progress in the synthesis of InP-based core/shell quantum dots reaching near unity photoluminescence quantum yield across the visible spectrum and the formation of monochromatic LEDs by means of on-chip color conversion through InP-based quantum dots. In addition, we address in detail the properties of the core/shell interface and the termination of the quantum dot outer surface that made this result possible and discuss different mechanisms of failure - leading to a deterioration of the color conversion efficiency - by an atomistic perspective.

4:00 PM EL02.10.07
Understanding Electrical Excitation Dynamics in Quantum-Dot Light-Emitting Diodes: From Steady-State to Temporal Behaviors
Yunzhou Deng1 and Yizheng Jin2; 1University of Cambridge, United Kingdom; 2Zhejiang University, China

Light-emitting diodes based on colloidal quantum dots (QDs) promise a new generation of color-pure, cost-effective, and flexible light sources. Despite of the tremendous advances in the synthesis of QDs, the electroluminescent (EL) properties of QDs generally lag behind their photoluminescent (PL) properties. These EL-PL gaps originate from the essential difference in the charge dynamics of electrical excitation with respect to optical excitation. Here, we report our recent advances in understanding the electrical-excitation-dynamics of QDs in active quantum-dot light-emitting diodes (QLEDs) in both steady-state operations, long-term evolutions, and transient EL dynamics under pulsed excitations. First, we unraveled how the dynamic charge balance can be achieved in the steady-state operation of red, green, and blue QLEDs, leading to high-performance devices with near-limiting efficiencies [1,2]. Key to this is the sequential charge injection at single-nanocrystal level and effective blocking of electron leakage at the polymer/QD interface. Then, we address an anomalous efficiency-elevation phenomenon induced by operational degradation. Comprehensive in-situ characterizations reveal that this is caused by the ligand migration between the electron-transport layer and the cathode, which in turn improves the charge balance in long-term operation. Finally, we report the excitation-memory effects in the transient EL dynamics of QLEDs modulated by deep-level trap states. By utilizing this unique process, we demonstrate 100 MHz modulation and data transmission based on micro-QLEDs.


SESSION EL02.11: Virtual Session: Towards Atomically Precise Colloidal Materials for Conventional and Quantum Optoelectronics
Session Chairs: Emily Miura and Hao Nguyen
Tuesday Morning, May 7, 2024
EL02-virtual

8:00 AM EL02.11.04
Unravelling Nanocrystal Surface Structures with Relativistic DFT Calculations of Cadmium and Selenium Solid-State NMR Spectra of CdSe Nanocrystal Surfaces
Rana Bisweswar1, 2; Yunhua Chen1, 2; Javier Vela2; 1 and Aaron Rossin2; 1Iowa State University, United States; 2Ames Laboratory, United States

Semiconductor nanocrystals (NCs) offer novel tunable electronic and optical properties that depend on their size, shape and surface passivation. Semiconductor NCs exhibit multiple exciton
generation and are appealing for next-generation solar cells. Surface ligands and surface sites on NCs control their nucleation, growth, colloidal stability, chemical reactivity and optical/electronic properties. However direct experimental probes of the molecular structure of NC surfaces are lacking. Solid-state nuclear magnetic resonance (SSNMR) is a powerful tool to determine the structure of NC surfaces and sites on the surface where ligands can bind.

Using CdSe as a prototypical example, SSNMR spectra have been measured to probe the structure of these nanocrystals and develop detailed models of their surface structures. DFT-optimized cluster models that represent probable molecular structures of carboxylate coordinated surface sites have been proposed. However, to the best of our knowledge, $^{113}$Cd and $^{77}$Se chemical shifts have not been calculated for these surface models. We performed relativistic DFT calculations of cadmium and selenium magnetic shielding tensors on model compounds with previously measured solid-state NMR spectra, with (i) the 4-component Dirac-Kohn-Sham (DKS) Hamiltonian, and (ii) the scalar and (iii) spin-orbit levels within the ZORA Hamiltonian. Molecular clusters with Cd and Se sites in varying bonding environments were used to model CdSe (100) and CdSe (111) surfaces capped with carboxylic acid ligands. Our calculations identify the observed $^{113}$Cd isotropic chemical shifts $(\delta)$ of $-465$ ppm, $-318$ ppm and $-146$ ppm arising from CdSeO$_x$, CdSeO$_{2x}$, and CdSeO$_{4x}$ surface groups respectively, with very good agreement with experimental measurements. The $^{113}$Cd chemical shifts linearly decrease with the number of O-neighbors. The calculated spars $(\delta_1 - \delta_3)$ encompass the experimental values for CdSeO$_x$ and CdSeO$_{2x}$ clusters but are slightly larger than the measured value for CdSeO$_{4x}$ clusters. Relativistic DFT calculations predicted a one-bond $^{113}$Cd–$^{77}$Se scalar coupling of 258 Hz, in good agreement with the experimental values of 250 Hz. With a dense coverage of carboxylic acid ligands, the CdSe (100) surface shows a distribution of Cd-Se bond lengths and J-couplings. Relativistic DFT simulations aid in interpretation of NMR spectra of CdSe nanocrystals and related nanomaterials, and offer new insights into the complex structures at nanocrystal surfaces.

Supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. The research was performed at Ames Laboratory, which is operated for the U.S. DOE by Iowa State University under contract DE-AC02-07CH11358. We acknowledge the use of computational resources at the National Energy Research Scientific Supercomputing Center (NERSC) which is supported by the Office of the U.S. DOE under contract no. DE-AC02-05CH11231.

8:45 AM EL02.11.03

Doubbling Photoluminescence of Red-Emitting Quantum Dots by Direct Transfer from Hexane into Water Without Adding Extra Reagents Tohid Baradaran Kayyal

The demand for converting hydrophobic nanoparticles (NPs) into water-soluble NPs, specifically red-emitting quantum dots (QDs) synthesized in organic solvents, has led to extensive research. However, the current methods for transferring these NPs face challenges related to their efficiency and a decrease in their photoluminescence quantum yield (PLQY). In this study, a remarkably efficient and facile technique was utilized to transfer oleic acid (OA)-coated CdSe/CdS core-shell QDs into water without the need for additional chemicals or agents. This process results in an unexpected increase of over 100% in PLQY upon transfer into basic water (pH 8). The transfer method is highly reproducible and can be extended to other oleic acid-based particles like magnetic NPs. The process is a straightforward method using ultrasonic assistance completed within only 4 hours at room temperature, involving the rearrangement of OA ligands at the QD surface, leading to the formation of a ‘mixed’ monolayer. This innovative configuration exposes approximately half of the carboxylic acid moieties to the QD surface and directs the remaining towards the aqueous medium. Density-functional-theory (DFT) calculations corroborate this rearrangement, indicating its favorable energetic state in aqueous media. The behavior of the transferred QDs was investigated and compared to that of the original QDs in hexane through absorption spectroscopy, fluorescence spectroscopy, and transmission electron microscopy. Regarding DFT calculations, Quantum ESPRESSO was utilized and CdS surfaces were generated to mimic core-shell quantum dot surfaces. This discovery can open promising avenues for employing NPs especially conventional QDs synthesized in organic solvents for applications in aqueous media. The ease of transferring QDs into a water environment will also facilitate a variety of assembly methods that rely on aqueous surface chemistry, and thus influence the field of biomedicine.

9:00 AM EL02.11.01

Photo-Crosslinkable Ligands for High-Density Patterning of Perovskite Nanocrystals Zhi Kuang Tan; National University of Singapore, Singapore

The patterning of luminescent quantum dots and nanocrystals into micron-sized pixels is required for applications in electronic color displays. In the recently-developed QD-OLED technology (Quantum Dot Organic Light-Emitting Diode), semiconducting quantum dots are deposited onto blue OLED display pixels by inkjet printing methods to enhance the color quality of the displays. However, inkjet printing is prone to alignment and clogging issues, which impacts the manufacturing yield and clogging capabilities. In this talk, I will discuss the development of new crosslinkable ligands that would allow high-density patterning of perovskite nanocrystals or quantum dots by photolithography techniques. Our new ligands attach to the nanocrystals via an entropy-driven ligand exchange process. The resulting nanocrystals could be deposited onto substrates and be patterned by a photo-initiated polymerization process, similar to well-established photolithography processes that are used in the semiconductor industry.

9:30 AM EL02.11.06

Green$^{+}$ Cu$_2$ZnInSe$_2$/ZnSe Core/Composition Gradient Shell Quantum Dots for Boosted Photoelectrochemical Hydrogen Production Kokilavani Sharmappasundaram; Lei Jin, Gurpreet S. Selopal, and Federico Rosei; 1Institut National de la Recherche Scientifique, Canada; 2Dalhousie University, Canada

Colloidal quantum dots (QDs) are considered building blocks for solar energy devices due to their promising optoelectronic properties, such as size/shape/composition-dependent absorption and emission spectrum and high absorption coefficient. However, well-performing QDs in solar energy conversion technologies (i.e. photovoltaics or clean fuel production) are typically containing toxic heavy metals (e.g., Cd, Pb), which restricts their commercial applications. In this context, eco-friendly Cu-doped ZnInSe QDs emerged as a promising alternative due to their unique merits, including the long lifetime of charge carriers and suitable band structure for charge injection. Nonetheless, the sensitivity of the plain Cu$_2$ZnInSe QDs may induce surface defects that act as charge recombination centers, leading to a severe deterioration of the photoelectrochemical (PEC) performance. The growth of suitable shell material is a promising approach for effective suppression of surface related defects/traps states and obtain a tailored optical response of QDs.

Here, we report the synthesis of Cu$_2$ZnInSe$_2$/ZnSe core/composition gradient shell with tuneable shell thickness to understand the influence on optoelectronic properties, consequently PEC performance for hydrogen production. An optimized thick composition gradient shell obtained with low Se/S ratio (n = 2 and r = 0.05) showed broader absorption toward longer wavelength and high PL quantum yield. Resulting PEC device based on the Cu$_2$ZnInSe$_2$/ZnSe core/shell QDs with n =2 and r =0.05 exhibited an excellent saturated photocurrent density of 11.7 mA/cm$^2$ (at 1 V vs RHE) under one sun illumination (AM 1.5 G, 100 mW/cm$^2$), which is 96% higher than the achieved value of bare Cu$_2$ZnInSe QDs. The investigation and its findings will be presented in detail, exploring how controlled composition gradient shell thickness influences surface passivation and carrier dynamics. In addition, the significance of composition gradient shell layer to achieve enhanced device performance will be discussed, highlighting its great potential for future eco-friendly core/shell QD-based solar energy technologies.
metals for interconnect applications has therefore focused completely on intermetallic ordered compounds. The effort has been recently extended to include binary and ternary compounds [5, 6].

Amongst binary compound metals, only certain ordered intermetallics show bulk resistivities with values that are potentially of interest for interconnect applications. The study of binary metals for interconnection applications has therefore focused completely on intermetallic ordered compounds. *Ab initio* screening (by assessment of the cohesive energy [7]) indicated that especially binary aluminides show promise for alternative metallization. The most promising materials include NiAl, CuAl, CuAl2, RuAl and ScAl3. Thin films of these aluminide intermetallics were then studied experimentally to assess their properties and their potential for interconnect metallization. Low thin film resistivities have been obtained for NiAl, CuAl, CuAl2 and ScAl3 [8, 9]. Despite different crystal structures and constituents, binary aluminide intermetallics share common properties and challenges such as crystalline order, point defects, composition control, composition uniformity, secondary phase formation, (interface) reactivity, or non-stoichiometric surface oxidation. These common challenges will be discussed in detail, highlighted by multiple experimental examples. We show by atom probe tomography that stoichiometric NiAl films are prone to local compositional variations on nm scales, which are difficult to detect with other techniques. For thicknesses below ~15 nm, the thin film resistivity strongly increased, and the effect of annealing was reduced. Resistivity modeling found that the resistivity of thin NiAl films below ~15 nm was dominated by grain boundary scattering due to small grain sizes, with little impact of surface scattering. To mitigate this issue, the grain size for a given film thickness was increased by back thinning of thicker films (with larger grains) using ion beam etching (IBE) or chemical mechanical polishing (CMP). The resistivity of NiAl could be further optimized at small thicknesses by combining the back thinning experiments with epitaxial deposition: a resistivity as low as 11.5 µΩcm at 7.7 nm for epitaxial NiAl on Ge (100) has been demonstrated [10], which outperforms PVD Ru and Cu at comparable thicknesses and thermal budget. We discuss prospects of such approaches for integration.

Finally, we discuss ternary compounds as replacement for Cu in advanced metallization schemes. We will discuss potential classes of materials (e.g. MAX materials) and their prospects. We introduce a materials complexity index for alternative metals to reflect the complexity of the material control. The index can also be used to develop mitigation activities to reduce complexity.

References
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**Binary and Ternary Intermetallics for Advanced Interconnect Metallization**

*Jean-Philippe Soulé*1, Nancy Heylen1, Kiroubanand Sankaran1, Jeroen E. Scheerder1, Claudia Fleischmann1,2, Johan Swerts1, Zsolt Tokei1 and Christoph Adelmann1; 1IMEC, Belgium; 2KU Leuven, Belgium

In the recent past, alternatives to Cu metallization have elicited much interest for advanced interconnect applications due to increasing intrinsic limitations of line resistance and reliability at line widths below 20 nm [1, 2]. Elemental metals with short mean free path (MFP) such as Co, Mo [3] or Ru [4] were first proposed to replace Cu and to improve line resistance and reliability. The effort has been recently extended to include binary and ternary compounds [5, 6].

Binary and Ternary Intermetallics for Advanced Interconnect Metallization

*EL03.01.01

Tuesday Morning, April 23, 2024

Room 346, Level 3, Summit

Formation of Surface Sulfide Layer on Liners for Reducing Interface Scattering of Ruthenium Interconnect

Yu-Lin Chen, Kai-Yuan Hsiao, Dun-Jie Jhan, Ming-Yen Lu, Pei Yuan Keng and Shou-Yi Chang; National Tsing Hua University, Taiwan

Ruthenium with a low bulk resistivity, a high melting point and a short mean free path of electron is of great potential to replace copper as the next-generation metallization for low-resistance interconnects. However, the drastic resistivity scaling with the continual decrease of linewidth due to the scattering of electrons at the interfaces with dielectrics or liners needs to be minimized. Much specular scattering is expected when a layer of two-dimensional materials such as disulfides is applied to the interface, retaining the original electron density of state of the metals. Hence in this study, three types of liner materials (tantalum-titanium alloy, nitride and oxide) were deposited on silicon substrates by physical vapor deposition. Instead of complicated transfer process, sulfurization was applied onto the surface of the liner layers in a tube furnace at different temperatures, simply by using sulfur vapor or hydrogen sulfide gas, to form an ultrathin sulfide layer. Thin ruthenium films with different thickness were then deposited on the sulfurized liners for investigating the influence of the sulfide layer on interface scattering. The microstructure, chemical composition and bonding condition of the sulfurized surface were characterized, and the resistivity scaling of the ruthenium films was examined with implementation of the Fuhs-Sondheimer and Mayadas-Shatzkes models. Experimental results indicated that, with the sulfur vapor and particularly the hydrogen sulfide gas at an appropriate temperature, an ultrathin sulfide layer of only a few nanometers thick was successfully formed on the top surface of the liners and changed the binding states from a metallic, nitride or oxide state to a sulfide state with altered binding energy. Microscopic observations revealed a crystalline structure of tantalum-titanium binary sulfide being formed, similar to the structure of two-dimensional sulfide materials.

References
[8] L. Chen
[9] Kai-Yuan Hsiao, Dun-Jie Jhan, Ming-Yen Lu, Pei Yuan Keng and Shou-Yi Chang; National Tsing Hua University, Taiwan

11:00 AM *EL03.01.02

Formation of Surface Sulfide Layer on Liners for Reducing Interface Scattering of Ruthenium Interconnect

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Understanding the thermal conductivity trends in metallic thin films has attracted tremendous interest over the past decades due to their wide applications as interconnects in integrated circuits of electronic devices. As the dimension of the metallic interconnects has decreased comparable to the electron mean free path, size effects on the thermal transport process becomes of high importance. Reduction in size also leads to a reduction in thermal conductivity of the thin metallic films. Such a reduction will then worsen the heat transfer in the circuits and, in most cases, lead to the burnout of the circuit following by the device failure. Upon reduction in size, thermal and electrical conductivity of these interconnects are governed by emerging phenomena that challenge our understanding of the thermal and electrical conductivity of bulk materials. Matthiessen’s rule combines all the non-ideal effects together through a summation rule to calculate the electronic mobility and thermal conductivity of systems subject to multiple scattering sources. Therefore, it can be readily applied to estimate the relative magnitude of different scattering mechanisms. Matthiessen’s rule has been widely used to predict the phonon thermal conductivity of dielectric solids and the electrical conductivity or electronic thermal conductivity of metallic materials. In this work we address the limitations of Matthiessen’s rule in estimating thermal conductivity of Al<sub>0.9</sub>Cu<sub>0.1</sub> alloy films at nanometer length scales and as a result of alloying. We employ ultrafast laser spectroscopic techniques such as time-domain thermoreflectance (TDTTR) to directly measure the in-plane thermal conductivity of Al<sub>0.9</sub>Cu<sub>0.1</sub> films ranging from 24 to 175 nm. We investigate the in-plane thermal conductivity trend with film thickness down to thicknesses comparable to the electron mean free path of Al which is ~19 nm. In principle, one can attribute deviations from Matthiessen’s rule to three causes: (a) changes in the band structure and the phonon spectrum due to alloying (b) additional temperature-dependent scattering processes associated with solute atoms, in particular phonon-assisted impurity scattering processes, where electrons and phonons are scattered by solute atoms, and (c) the “two-band” effect where two or more groups of electrons and phonons with different relaxation times contributing to the conductivities. In addition to the experimental thermal conductivity measurements and in order to gain a better understanding of the role of electron-phonon scattering in total thermal conductivity, we measure scattering rate with IR-VASE, an spectroscopic ellipsometry technique. All the provided characterization techniques enable us to validate the contributing share of the electron-electron, electron-phonon, or electron-system boundaries scattering in total thermal conductivity of these films.

In this study we investigate the structural and electrical properties of MBE-grown PdCoO<sub>2</sub> delafossite films. High-resolution X-Ray diffraction (HRXRD) confirms that the films are phase-pure. XRD phi scans, however, reveal in-plane twinning in these films, and the lateral size of the rotational twin domains are ~17 nm based on skew-symmetric rocking curves. We measured the resistivity of the films using a van der Pauw geometry and modelled the resistivity scaling with film thickness using Fuchs-Sondheimer (FS) and Mayadas-Shatzkes (MS) model. The upshot is that a 50 nm thick PdCoO<sub>2</sub> film has a resistivity of 5 μΩ cm. Based on our resistivity fitting we find that the twin boundaries have a very low electron reflection coefficient of ~5%. This is extremely encouraging since atomic layer deposition (ALD) which is a back-end-of-the-line (BEOL) compatible synthesis technique will likely yield highly twinned delafossite thin films.

Metallic delafossite can prove to be a disruptive new material for ultra-scaled electrical interconnects. Delafossites are layered oxides with the formula AB0<sub>2</sub> where A is a metal cation that forms 2D sheets separated by the BO<sub>2</sub> transition-metal oxide octahedra. In this study we focus on metallic delafossites PdCoO<sub>2</sub> and PdCoO<sub>2</sub>Cu<sub>0.1</sub> because of their ultra-low room temperature resistivity of 2.1 μΩ cm and 2.6 μΩ cm, respectively, which is comparable to the current semiconductor industry standard interconnect metal, Cu. The metallic delafossite structure has an anisotropic nature with resistivity along the c-axis a factor of 1000 higher than resistivity within the Pt/Pd sheet. Due to the layered crystal structure, the Fermi surface of the metallic delafossites is cylindrical as for a 2D metal. This quasi-2D crystal structure can potentially mitigate interface and surface scattering since the Fermi velocity does not have components perpendicular to the Pt/Pd sheets. This can potentially overcome the resistivity penalty encountered by conventional 3D metals in ultrathin films (~20 nm). Additionally, the unique Fermi surface topology allows for an electron-phonon coupling constant that is a factor of 3 lower than copper. 

New high-performance electrical interconnects are required to support the continuation of Moore’s law. Reduction in size also leads to a reduction in thermal conductivity of the thin metallic films. Such a reduction will then worsen the heat transfer in the circuits and, in most cases, lead to the burnout of the circuit following by the device failure. Upon reduction in size, thermal and electrical conductivity of these interconnects are governed by emerging phenomena that challenge our understanding of the thermal and electrical conductivity of bulk materials. Matthiessen’s rule combines all the non-ideal effects together through a summation rule to calculate the electronic mobility and thermal conductivity of systems subject to multiple scattering sources. Therefore, it can be readily applied to estimate the relative magnitude of different scattering mechanisms. Matthiessen’s rule has been widely used to predict the phonon thermal conductivity of dielectric solids and the electrical conductivity or electronic thermal conductivity of metallic materials. In this work we address the limitations of Matthiessen’s rule in estimating thermal conductivity of Al<sub>0.9</sub>Cu<sub>0.1</sub> (AlCu<sub>0.1</sub>) films at nanometer length scales and as a result of alloying. We employ ultrafast laser spectroscopic techniques such as time-domain thermoreflectance (TDTTR) to directly measure the in-plane thermal conductivity of AlCu<sub>0.1</sub> films ranging from 24 to 175 nm. We investigate the in-plane thermal conductivity trend with film thickness down to thicknesses comparable to the electron mean free path of Al which is ~19 nm. In principle, one can attribute deviations from Matthiessen’s rule to three causes: (a) changes in the band structure and the phonon spectrum due to alloying (b) additional temperature-dependent scattering processes associated with solute atoms, in particular phonon-assisted impurity scattering processes, where electrons and phonons are scattered by solute atoms, and (c) the “two-band” effect where two or more groups of electrons and phonons with different relaxation times contributing to the conductivities. In addition to the experimental thermal conductivity measurements and in order to gain a better understanding of the role of electron-phonon scattering in total thermal conductivity, we measure scattering rate with IR-VASE, an spectroscopic ellipsometry technique.

In this study we investigate the structural and electrical properties of MBE-grown PdCoO<sub>2</sub> delafossite films. High-resolution X-Ray diffraction (HRXRD) confirms that the films are phase-pure. XRD phi scans, however, reveal in-plane twinning in these films, and the lateral size of the rotational twin domains are ~17 nm based on skew-symmetric rocking curves. We measured the resistivity of the films using a van der Pauw geometry and modelled the resistivity scaling with film thickness using Fuchs-Sondheimer (FS) and Mayadas-Shatzkes (MS) model. The upshot is that a 50 nm thick PdCoO<sub>2</sub> film has a resistivity of 5 μΩ cm. Based on our resistivity fitting we find that the twin boundaries have a very low electron reflection coefficient of ~5%. This is extremely encouraging since atomic layer deposition (ALD) which is a back-end-of-the-line (BEOL) compatible synthesis technique will likely yield highly twinned delafossite thin films.

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Superconducting devices, such as superconducting tunnel junction (STJ), qubits, etc. can be manufactured by the current Si-based semiconductor manufacturing processes. However, circuits should be superconducting material such as Nb (Tc=9.29 K), Pb (Tc=7.2 K), In (Tc=3.4 K), etc.

In current technology, these devices are arranged in monolithic structures and processes, and each device should wire to control and read signal lines in the same plane. When a large number of devices and/or high-density devices are integrated, these wires would be too constrained, and several problems would be actualized, such as wiring for devices located at the chip center, crosstalk among wiring, and so on.

3D integration of qubits with interposer chips by flip-chip bonding is the proof-of-concept of large-scale qubit integration. The 3D integration approaches for qubit-based devices are the same as conventional electronic devices, including the through silicon via (TSV) process for interposers and micro bump flip-chip bonding. 3D integration for STJ would acquire the high density of sensing top electrodes for detecting x-rays from far away.

Also, the signal integrity for qubits is much better than having qubits at short distances from the control circuitry by 3D integration.

However, they use superconducting metals instead of copper and other non-superconducting materials. Most flip-chip microbump bonding processes require thermal compression bonding (TCB) at over 170 °C. Superconducting elements are easily degraded by heat.

Consequently, we apply TCB around 100 °C using In-Pb alloy.

Surface activated bonding (SAB) was also applied for room temperature bonding of Nb-Nb as superconducting metal. Both bonding processes succeeded in confirming the superconducting interconnect.

Additionally, we discuss the superconducting interface of direct bonded Nb-Nb by Tc, and also the interfacial structure measured by polarized neutron reflectometry (PNR). The results show clear spin asymmetry in the superconducting state, as splitting is observed in the fringes of the parallel neutron (neutron spins parallel to the external magnetic field 0.1 T) reflection R and the antiparallel (neutron spins antiparallel to it) reflection R', where the latter has become larger. This well-known effect is related to the flux penetration in the superconducting state. Therefore, unique information about the superconducting state of the buried thin film can be measured by using the polarized neutron beam. For this project, the major advantage of PNR will be to characterize the superconducting state at the deeply buried Nb interfaces sandwiched between the two substrate wafers, which would be infeasible using alternate techniques.
Developing memories for embedded microcontrollers requires to sustain very aggressive mission profiles for memory reliability, and its introduction in the back end of integrated circuits adds involved might lead to different memory characteristics and products best suited for each technology.

Phase change memories (PCM) have been introduced in the last years and are nowadays qualified in production on different nodes by major players. Different physics and architecture.

1. Thickness-Dependent Optical Properties of Metallic Thin Films and Their Correlation with Thermal Conductivity

The semiconductor industry stands as a cornerstone of modern technology, and its relentless pursuit of miniaturization, efficiency, and performance hinges upon the precise control and understanding of materials used in electronic devices. Within this context, the study of thin films of metals takes on paramount significance. These films play a pivotal role in various semiconductor applications, as they are utilized not only as fundamental components of electronic devices but also as essential elements in the thermal management of these devices. As electronic components become increasingly compact and powerful, the efficient dissipation of heat generated during operation has become a critical challenge. Understanding the optical and thermal properties of thin metal films is instrumental in addressing these challenges, as it offers valuable insights into their potential as heat-dissipating materials and their influence on the performance and reliability of semiconductor devices.

In this study, we perform precise spectroscopic ellipsometry measurements on thin films of several metals that are of unique importance for electronic devices, including copper, iridium, ruthenium, and tungsten. Using these measurements, we determine the optical properties of these metallic thin films across a broad spectral range throughout the infrared and UV-Vis region. Through meticulous analysis involving the Drake free-electron model, we quantify variations in relaxation times and plasma energies in relation to film thickness. Furthermore, our investigation extends to exploring the intriguing interplay between size-dependent relaxation times, as derived from the Drake model, and the thermal conductivity of these metallic thin films, as measured using a thermoreflectance-based thermal conductance and ultrafast pump-probe technique. Our findings are instrumental in enhancing our understanding of these materials' behavior, with potential implications for the development of advanced electronic components.

REFERENCES


8:45 AM *EL03.04.01
Back End of The Line Embedded Non Volatile Memories for Microcontrollers: Constraints and Opportunities

Back end of the Line embedded Non Volatile Memories for Microcontrollers: constraints and opportunities.

S. Jeannot, STMicroelectronics, France

Nowadays, hybrid wafer bonding with Cu-Cu connection is a major production technology of two layer stacked backside illuminated (BSI) image sensor applied for several applications. In addition, three layer stacked BSI image sensor with through Si via (TSV) connection has been introduced to high performance cameras. Furthermore, three layer stacked BSI with pixel pitch Cu-Cu connection will be required to achieve much higher performance and multi functionality image sensors. In this paper, we developed key technologies for three layer stacking. One is pixel pitch hybrid wafer bonding with minute Cu-Cu connection, the other is three layer stacking process including TSV for middle layer and the 2nd hybrid wafer bonding. Finally, three layer stacking process was demonstrated by adapting these technologies.

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Experimental Characterization and 1D KMC-Based Simulation of the Reliability of 28nm BEOL Integrated VCM ReRAM

Nils Kopperberg, Stefan Wiefels, Karl Hofmann, Jan Otterstedt, Dirk Wouters, Rainer Waser, and Stephan Menzel

Valence change memory (VCM) cells are promising candidates for non-volatile memory applications and neuromorphic computing [1]. Typically, they consist of a simple metal-insulator-metal (MIM) structure, where the insulating oxide layer can be manipulated by an externally applied voltage. Thereby, oxygen vacancies can be incorporated and redistributed in a way that the resistance of the oxide layer can be switched between a high resistive state (HRS) and a low resistive state (LRS). These states can be read out non-destructively and switched very fast. Furthermore, the cells show a great scalability, CMOS (complementary metal-oxide-semiconductor) compatibility and low power consumption [2,3].

Despite their excellent characteristics, a few questions and challenges concerning the key parameter reliability are still open. During the experimental characterization of the generally great endurance of 2Mbit VCM cells, we found a rare failure mechanism in a few ppm of the cells after about 500k cycles, where the cells could not be switched back into the HRS (RESET) [4]. The investigated cells are integrated back-end-of-line (BEOL) in a 1-transistor-1-resistor (1T1R) configuration in a 28nm CMOS technology.

Based on the JART VCM 1.0 model of La Torre [5], we developed a 1D KMC simulation model to physically explain the observed failure mechanism. We show that the interplay of the transistor and the VCM cell plays an important role. In rare cases of a combination of a high resistive transistor and a very low resistive cell, the voltage dropping over the cell is not sufficient to originate the RESET. Additionally, we experimentally investigate the RESET kinetics and their dependence on the used transistor. Hereafter, we can explain our findings with the help of the developed 1D KMC simulation model. In conclusion, we want to point out the importance of the interplay of transistor and resistor and its understanding for the improvement of the reliability.


9:45 AM BREAK

SESSION EL03.05: Dielectric and Porous Thin Films
Session Chairs: Sean King and Jean-Philippe Soulie
Wednesday Morning, April 24, 2024
Room 346, Level 3, Summit
Zinc Oxide (ZnO) is renowned for its diverse morphology, adaptable properties, and versatile applications across various fields including sensing, battery technology, catalysis, and filtration. Among the established morphologies, the tetrapodal form (t-ZnO) synthesized through flame transport synthesis is of particular interest due to its single-crystalline structure and adjustable oxygen vacancies. A versatile method of applying different metal hydroxides/oxides to coat t-ZnO in an organized manner, creating a core@shell structure of t-ZnO(MOH)2 (where M represents metals like Cu, Co, Al, Fe, Ni, Ti, etc.) derived from a suitable metal precursor is also studied. Subsequently, we interconnect the arms of the tetrapods using a photochemical process. This development of interconnections is particularly intriguing from a sensor application perspective, as it forms stable bridge-like structures between morphologies, even those that may not conduct electricity, such as MOFs or zeolites.

The surface of t-ZnO@M(OH)x can undergo conversions to adopt alternative structures based on the same metal framework. For example, a Cu(OH)2 shell can give rise to a Cu-based MOF like HKUST-1, a Co(OH)2 layer can yield a Co-based MOF like ZIF-67 and Al(OH)3 can either convert to Al-based MOFs or serve as a source for zeolite. Likewise, t-ZnO can be readily surface converted to a Zn-based MOF, such as ZIF-8. This technique facilitates the solvothermal growth of MOFs based on any metal framework utilizing ZnO as the sensing material, all while preserving the morphology, thus enhancing selectivity towards various gases or VOCs. The interconnects grown can be precisely tailored with respect to the desired material growth, growth areas, thickness, and proximity of the self-organized flakes achieved. The ultimate objective is to create selective, sustainable, lightweight, and portable indoor gas sensors for VOCs.

In this talk, I represent how interconnected porous chemical frameworks like tetrapodal ZnO or corresponding MOFs and zeolites show promising selective filtration based on pore sizes by applying these structures to zinc oxide, a versatile semiconductor to enhance sensor selectivity, ultimately aiming to create indoor gas sensors with the capacity to detect VOCs.

Keywords: Photochemical Interconnects, Volatile Organic Compounds (VOCs), Metal–Organic Frameworks (MOFs), selectivity, Zinc Oxide (ZnO), Metal Coating, Indoor gas sensors, Bridge-like tunable interconnects.

11:30 AM *EL03.05.04
Interplay of electrical and mechanical behaviors in dielectrics Fabien Volpi, Morgan Rusinowicz, Chaymaa Boujrouf, Muriel Braccini, Guillaume Parry and Marc Verdier; Université Grenoble-Alpes, France

Dielectric films are widely integrated into advanced devices for both their functional and mechanical properties. In terms of functional properties, dielectrics are essentially expected to prevent electrical leakages, sustain large electric fields, limit capacitive coupling. In terms of mechanical properties, dielectrics contribute to the stiffness of device architecture but, like all ceramics, they are also preferential loci for crack nucleation/propagation. Consequently, understanding the interplay between the mechanical and electrical behaviors of dielectric films is essential to predict the lifetime of functional devices.

Nanoindentation is a powerful technique to probe the mechanical behavior of small-scale systems. When combined to electrical measurements, electrical-nanoindentation can be used to assess this mechanical-electrical interplay. In the first part of this presentation, we will show how a mechanical stress can modify the electrical conduction mechanism in an ultra-low-k dielectric (nanoporous SiOCH film deposited on a silicon substrate). Experimentally, electrical leakage was monitored in situ during nanoindentation with a Berkovich indenter. These experiments reveal a counterintuitive electrical conduction drop under high mechanical stresses. This phenomenon is reproduced numerically (by FEM analysis) by correcting the Poole-Frenkel conduction law with a strain-dependent factor, and described analytically in terms of space-charge build-up induced by the trapping of holes at the mechanically-generated defects. A threshold strain is identified as the keystone linking this strain-dependent conduction to the current line distribution within the dielectric.

In the second part, we show how an electrical stress can degrade the mechanical properties of dielectrics. Experiments were carried out on a wide panel of dielectric systems: high-k and low-k dielectrics, thin and thick films, with or without bottom electrodes. Thanks to the fine in-situ coupling of mechanical and electrical monitoring, a mechanical collapse of the film is observed after the application of an electrical stress. Various origins of this collapse were first ruled out (electrostatic force, local heating...), before it was finally demonstrated that the injection of electrical charges drives this mechanical collapse. Numerical modelling (FEM analysis) is used to discuss which film property is actually modified: stiffness or hardness. This phenomenon appears to be universal, since it is observed on all kinds of dielectric systems assessed in this study.

SESSION EL03.06: Advanced Characterization
Session Chairs: Silvia Armini and Sean King
Wednesday Afternoon, April 24, 2024
Room 346, Level 3, Summit

1:30 PM *EL03.06.01
Pathfinding in Optical Critical Dimension Metrology George A. Antonelli; Onto Innovation, Inc., United States

Semiconductor manufacturing has long relied upon optical methods for non-destructive high volume critical dimension metrology. Optical reflectometers, ellipsometers, and interferometers from the deep ultra-violet to near infrared are essential engines of discovery. The underlying architecture and operating principles of many modern optical metrology tools are directly related to their progenitor instruments. Increased complexity and continued scaling of logic and memory devices offer new metrology challenges and force the continued evolution of these tools and the introduction of new architectures. High aspect ratio and buried structures are two general areas of concern for future devices which optical metrology must address. High aspect ratio structures >100:1 have become an integral part of many semiconductor devices in a variety of applications. Conventional optical critical dimension metrology tools can address a subset of this need but fall short in some use cases. One potential solution lies in the extension of these techniques into the mid-infrared range.

The shift to a three-dimensional paradigm for transistor and interconnect geometries has led to an increase in the use of conformal and gap filling techniques to address reentrant features. Both random and systematic void formation are common defect modes in these processes. In some process flows, an opaque metal layer disrupts the conventional lithographic layer alignment requiring a different approach. Photoacoustic methods can be applied to address both issues. It is also possible to use photoacoustics to perform sub-optical resolution dimensional metrology of buried features.

In this talk, we shall briefly discuss optical methods capable of addressing these challenges. The physical principles of the proposed approaches and hardware implementation will be reviewed. Several examples drawn from memory and logic process flows will be shared.

2:00 PM *EL03.06.02
Characterizing Highly-Confined Heat Flow, Elastic, and Structural Properties of Nanostructured Semiconductors and Dielectrics using Ultraviolet Light Sources Joshua Knobloch, Brendan McBennett, Albert Beard, Emma Nelson, Travis Frazer, Jorge N. Hernandez-Charpak, Begona Abad Mayor, Henry C. Kaptay and Margaret Murnane; STROBE, JILA, University of Colorado Boulder, United States

Next-generation nanoelectronic, energy, and quantum devices rely on the discovery, integration, and optimization of novel complex and nanostructured materials. As critical dimensions of these devices shrink below 10 nm, the complex 3D geometries and physical properties—including, mechanical, thermal, and surface/interface quality—of new materials govern device efficiency and performance. However, as the complexity increases and scale decreases, conventional models fail to accurately predict the functional properties, and traditional metrology tools cannot probe the relevant behaviors on their intrinsic length- and time-scales. By harnessing tabletop sources of coherent extreme ultraviolet (EUV) light1, novel metrology tools can characterize the elastic, thermal, and structural properties of ultrathin dielectric films and nanostructured semiconductors. Optimized ultrathin low-k interlayer dielectric films are critical materials to improve the speed and efficiency of nanoelectronic devices. However, precise characterization of films with thickness <<100nm is challenging for traditional methods. Using a tabletop dynamic EUV scatterometry technique, we nondestructively extract the full electronic properties of single- and bilayer a-SiCH and a-SiOCH ultrathin films with thickness down to <5 nm—revealing surprising results2,3. By simultaneously extracting both Young’s modulus and Poisson’s ratio in a series of hydrogenated ultrathin films, we observe an unforeseen trend in the compressibility: in the presence of strong hydrogenation which reduces the bond coordination past a critical threshold, the films undergo a transition from brittle to ductile4. Additionally, we find that not only doping but also surfaces/interfaces can drastically alter the mechanical properties of ultrathin films. In very thin bilayers (<5 nm) with low-hydrogen doping, surface effects induce a substantial increase in compliance—by almost an order-of-magnitude—compared with identical thicker films, an effect not observed in monotonically-doped systems5.

Using our dynamic EUV scatterometry technique, we also nondestructively characterize the elastic properties, thickness, porosity, and thermal behavior of thin silicon metalalattice layers6,7—artificial 3D solids that are periodic on the sub-100 nm length scale. By monitoring the dispersion of hypersonic surface acoustic waves, we extract the Young’s modulus and thickness of silicon-
Electrical and Reliability Characteristics of Low-k SiCOH Dielectrics with Metal Integration

Seonhee Jang, Rajib Chowdhury and Thomas Poche; University of Louisiana at Lafayette, United States

In modern microelectronic devices, copper (Cu) and low dielectric constant (low-k) dielectric materials have been used in the back-end-of-line (BEOL) interconnects. However, the migration and diffusion of Cu into the low-k films becomes challenging during the integration of Cu/low-k interconnects, causing degradation of electrical performance and reliability. A metal barrier is introduced between Cu and low-k dielectrics to prevent Cu diffusion. With further scaling of technology node, the resistance of Cu metal lines significantly increases because of Cu surface and grain boundary scattering and additional metal barrier. To decrease the grain boundary resistance, the thickness of the metal barrier should be reduced. To reduce the surface and grain boundary scattering effect, different metals with low resistance can be employed. Potential candidates to replace Cu can be determined by lower product value of bulk resistivity and electron mean free path than that of Cu. Based on this criteria, cobalt (Co) and molybdenum (Mo) were selected. In this study, the integration of Co or Mo with the low-k materials was conducted and electrical and reliability characteristics were investigated.

Low-k SiCOH thin films were fabricated on p-type Si (100) wafer by plasma-enhanced chemical vapor deposition (PECVD) of tetrakis(trimethylsilyloxy)silane precursor at ambient temperature. To investigate electrical and reliability characteristics of low-k SiCOH dielectrics with metal integration, metal-insulator-silicon (MIS) structures were fabricated. Four different metals Al, Cu, Co, and Mo were deposited on the low-k SiCOH films using a sputtering deposition or electron beam evaporation methods. Thickness of each metal was approximately 120-130 nm. The fabricated MIS capacitors were then annealed in N2 atmosphere at 400 °C for 1 h. The electrical characteristics of the MIS structures were measured from capacitance-voltage (C-V) and current-voltage (I-V) curves using a semiconductor parameter analyzer. The C-V curves of Al-gate, Cu-gate, Co-gate, and Mo-gate MIS capacitors were compared before and after thermal stress. The typical C-V curves were obtained with accumulation, transition, and depletion regions from the negative to positive bias application. Depending on the type of metal-gate, the accumulation capacitance was different, suggesting that the deposition of metal gate may affect the capacitance of the underlying low-k film. The thermal annealing reduced the accumulation capacitance of the MIS capacitors. An increase in the k-value suggests that the low-k thin film was damaged by plasma during metal sputtering deposition. After annealing, the k-values were reduced, indicating that plasma-induced damage to the film could be recovered by annealing process. The shift in the C-V curve was the evidence of the diffusion of metal ions occurred in the low-k film. The elemental composition including Si, O, and C was investigated by X-ray photoelectron spectroscopy (XPS). Metal diffusion into the low-k film at the interface between the low-k film and each metal after annealing affected C-V and I-V characteristics. Effects of different metals on the electrical properties and reliability of the low-k SiOCH films under thermal stress were compared in this study.

Alternative current electroluminescent (ACEL) devices are one of the promising candidates as deformable optoelectronics owing to their simple device construction, facile fabrication, mechanical robustness, stable emission, and exceptional deformability. Among them, thin-film type ACEL devices are constructed with two electrodes sandwiching emissive layer that comprises phosphores and dielectric matrix. Under AC bias, thin-film ACEL device can be operated as both EL device and dielectric actuator speaker, originated from their structural similarity, making them optimal candidates as stretchable multifunctional displays. For practical application, patterning techniques also need to be applied to ACEL device. However, existed patterning methods of ACEL device were constrained to low-resolution EL operation (pattern size > 2 mm) and reduced brightness below the industrial standard (> 100 cd/m2). Hence, it is necessary to develop effective way to achieve high-resolution multicolor patterning of devices. Herein, we report a stretchable high-resolution multifunctional displays that can be integrated with both as an input and output device. Silver nanowires (AgNWs) and conductive polymer (PEDOT:PSS) embedded in thermoplastic polyurethane (TPU) are used as stretchable electrodes, and high dielectric constant particles (BaTiO3)-inorganic electroluminescent phosphors (ZnS:Cu)-polydimethylsiloxane (PDMS) composite is adopted as emissive layer. Through surface engineering of both stamp and the top of emissive layer, transfer printing technique for emissive layer was developed. This technique facilitates the high-resolution and multicolor patterning of emissive layer for stretchable multifunctional displays that can be stably operated under dynamic and static deformation. Owing to clear and high-resolution patterning ability, we suggested the multifunctional displays that can work both as input and output device.

Optimization of Reliable and Reproducible Growth of Carbon Nanotube Forests and Microstructures based on The Machine Learning-Assisted Control of Catalyst Nanoparticle Morphology

Kwangjin Kim, Yongtae Kim, Minwook Kim, Rahul S. Ingole and Jong G. Ok; Seoul National University of Science and Technology, Korea (the Republic of)

Recently, the realm of carbon nanotube (CNT) applications has been expanding in accordance with the rapid growth of cutting-edge industries including secondary batteries, semiconductors, sensors, and so on. For instance, CNTs are actively used in a powder or solution form as a conductive agent for both the anodes and cathodes of secondary batteries, which, however, typically entails various physical and chemical post-treatment processes. Utilizing the CNT forests and lithographically patterned CNT microstructures in their as-grown forms may obviate the labor for harvesting (off the substrate) and subsequent post-treatment (e.g., solution preparation) and may provide more functional frameworks with controlled 3D morphology, density, and aspect ratio. This can be achieved by optimizing the morphology of catalyst nanoparticles that are converted from the thin-film catalyst layer during the annealing step of the chemical vapor deposition (CVD)-based CNT growth process. Each catalyst nanoparticle offers a growth site of each CNT, suggesting that the catalyst nanoparticle’s size and density control the diameter, density, and degree of alignment of the resultant CNT forests – and thus their physical, chemical, and electrical properties. Here we propose a machine learning-based thermal and fluid interaction analysis for the control of catalyst nanoparticle morphology during the CVD process through thermal energy-driven Ostwald ripening and subsurface diffusion. We use the thermal fluid-structure interaction (TFSI) method to analyze the heat transfer characteristics of the catalyst layer system (Fe/Al2O3/SiO2). We pay more attention to the micropatterned catalyst system which exhibits considerably different heat transfer characteristics depending on the micropattern geometry as compared to the non-patterned thin-film catalyst system. Additionally, we conduct machine learning to optimize the CVD parameters for reliable growth of CNT forests on micropatterned catalyst systems with various geometries. This optimization is based solely on preprocessed SEM images of the catalyst nanoparticles. The morphological data (density, diameter, and roundness) of catalyst nanoparticles are learned, and the global optimum values for CVD parameters - temperature and time during the annealing step, as two factors dominating catalyst nanoparticleization - are proposed. The experimental growth results are presented as a validation. We demonstrate that such a reliable and reproducible CNT growth – either to a forest or microstructure - realized by taking the global optimum values can be utilized in several cutting-edge applications including neural signal recording (using 3D CNT microelectrode arrays) and stretchable strain sensors (using one-directionally aligned CNT thin films engineered from microscale CNT blade patterns).

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grants (No. 2021M3H4A302099204, and 2022M3C1A3081178 (Ministry of Science and ICT) and No. 2022R1I1A2073224 (Ministry of Education)) funded by the Korean Government.
PEDOT:PSS-Based Nanofibrous Electrodes for Flexible Transparent Electronics

As the size of the dynamic random access memory (DRAM) continues to shrink, the difficulty of patterning has become increasingly challenging. Among them, the capacitor pattern, an essential element for data storage, possesses the structure with the highest aspect ratio in DRAM. Consequently, difficulties in securing yield arise due to inevitable defects as bending and pattern collapse of the pillar-type capacitor node, impeding the overall manufacturing process. Bending of the capacitor node, generating bridges in the bottom electrodes, serves as a disruptive factor that hinders the normal operation of the memory. The bending of the capacitor occurs due to stress induced by bottom electrode oxidation during the deposition of the dielectric layer on the bottom electrode. To prevent this, a supporter structure is being introduced. The supporter is composed of a nitride layer and is patterned for the deposition of the dielectric layer on the bottom electrode. This technique, in conjunction with the deposition of the capacitor electrode, has proven to be effective in minimizing stress-induced bending. However, this approach encounters difficulties when trying to combine it with conventional inorganic dielectrics (such as SiO2), due to the mechanical stress induced by bottom electrode oxidation. To address this limitation, we explore an electrochemical deposition process for PEI, employing an aqueous emulsion of organic droplets containing the polymer as the electrolyte.

The electrochemical deposition process holds immense promise for coating substrates with complex 3D structures, contrasting with conventional dielectric deposition techniques. This innovative electrodeposition process enables the direct deposition of PEI films under mild conditions, enabled by the formation of stable emulsions containing charged polymeric droplets. Following deposition, the film was thermally cured under vacuum conditions to eliminate solvents and restore the imide groups of PEI. FTIR analyses confirmed excellent agreement between IR spectra of the cured and pristine polymers, as well as the elimination of imide peaks. The nanofibers were demonstrated as interconnects in a simple circuit for powering a light-emitting diode (LED). Even after 1000 bending cycles, the fibers were still able to turn on the LED at the same applied voltage of 2V, despite the slight changes in their sheet resistance. This demonstrates the potential of electrospun nanofibers for replacing metal electrodes in the pursuit of miniaturized high-power electronic devices, as evidenced by our comprehensive investigation into the dielectric performance of these materials.
Vacuum- and etch-free mechanical fabrication of metal wire microtrenches interconnected by ZnO nanowires for flexible bending-sensitive optoelectronic sensors

5:00 PM

EL03.08.11
Vacuum- and etch-free mechanical fabrication of metal wire microtrenches interconnected by ZnO nanowires for flexible bending-sensitive optoelectronic sensors

Kvangjun Kim, Rahul S. Ingole, Yongtae Kim and Jong G. Ok; Seoul National University of Science and Technology, Korea (the Republic of)

In recent years, there has been an expanding interest in developing optoelectronic transducers using micro- and nanoscale materials and structures in compact, lightweight, and flexible forms. Specifically, optoelectronic micro- and nanorobotics composed of micropatterned electrodes connected by semiconductor nanowires (NWs) such as ZnO NWs (ZNWs) have gained considerable attention due to their good sensitivity to incident light. However, traditional methods for fabricating micropatterned electrodes often involve difficult and time-consuming processes such as vacuum deposition, optical lithography, and etching, often preventing scalability and widespread application. Additionally, synthesizing ZNWs, usually dependent on high-temperature seed sintering or chemical vapor deposition, can interrupt their practical use on flexible substrates. One tactic approach to overcoming these challenges is to create a micropatterned electrode via mechanically machining microtrenches and filling the metal wires therein, and then growing ZNWs selectively on the trench-embedded metal wires via a metal-organic chemical vapor deposition (MOCVD) process. Working on this novel strategy, we develop a vacuum- and etch-free method for the fabrication of metal-wire-embedded microtrenches interconnected by ZNWs. Our method involves the continuous mechanical inscribing of linear microtrench patterns (microgratings) on a substrate, followed by the doctor-blade-assisted filling of solution-processible metal wires into these trenches. We then undertake the low-temperature metal-mediated hydrothermal growth of ZNWs selectively on the metal wires, finalizing the ZNW-interconnected microtrenching electrode structure. The entire process can be carried out at a low temperature without resorting to vacuum, lithography, and/or etching steps, thereby enabling the use of flexible polymer substrates of scalable sizes. The resulting flexible device can function as a bending-sensitive optoelectronic sensor with high sensitivity, as the number of ZNWs interconnecting the trench-embedded microtrenching electrodes changes upon mechanical bending.

Acknowledgment
This work was supported by the National Research Foundation of Korea (NRF) grants (No. 2021M3H4A3A02099204, and 2022M3C1A3081178 (Ministry of Science and ICT) and No. 2022R11A2073224 (Ministry of Education) funded by the Korean Government.

References
Selective Processes to Enable Scaling: Progress, Challenges and Opportunities

Dina H. Trivoso, Robert Clark, Kandabara Tapily, Nathan Antonovich, Lori Huli, Ainhoa Romo-Negeira, Ryota Yonezawa, Cory Wajda and Gert Lesinski; TEL, United States

Selective deposition has been used in microelectronics industry for many years. These processes are mostly done at high temperature. As scaling continues, device architecture has evolved from planar to FinFET, gate all around and vertically-stacked-Complementary Field Effect Transistors (CFETs). With the stacking of devices, it is desirable to enable low temperature selective processes. In this paper we discuss three examples of selective processes which are used to help extend scaling: (1) Dielectric on Metal (DoM) to enable advanced interconnect, (2) Dielectric on Dielectric (DoD) to enable Fully Self-Aligned Via (FSAV), and (3) Combining selective deposition and etch to extend EUV scalability. These three processes are well-established and not too far from high volume manufacturing (HVM). Beyond these processes, challenges in selective deposition on similar surfaces and high aspect ratio structures will be discussed.

Mechanisms of Area Selective- Atomic Layer Deposition and Their Impact on Feature Sizes

Katherine T. Young1, Andy Hsiao1 and Chris Yang2; 1Georgia Tech Research Institute, United States, 2Georgia Institute of Technology, United States

As devices have continued to scale down in size, fabrication of smaller features using novel methods has become a necessity. Strict requirements of location and alignment are often necessary and difficult to achieve with prior techniques, which has led to studies of area selective deposition. Area selective deposition, such as area selective-atomic layer deposition (AS-ALD), can be achieved by manipulating deposition preferences for different materials. A material is deposited selectively at certain locations based on the interaction of the precursors with different surfaces, so etching is not usually necessary (as in ALD), but is not necessary. AS-ALD can take advantage of the preferential deposition of the ALD precursors onto different types of materials like oxides or metals, etc. In fact, these techniques can sometimes be the only option for patterning different materials if the geometry of the surface or substrate cannot be patterned with lithography. Also, some SAM or polymer masks that have very low deposition can be patterned onto a surface so that AS-ALD can be used to pattern a single material (since the mask is later removed). This technique is especially useful for patterning materials or substrates that may be sensitive to etching. However, the selectivity between two different materials under certain deposition parameters limits the use of some materials and ALD precursors. Thus, a deeper understanding on the mechanism of area selective deposition is necessary to understand limitations on feature sizes.

This study describes the mechanisms for area selective- atomic layer deposition of common oxide materials (e.g., TiO2 and HfO2) on PMMA and Si and the effects of these deposition mechanisms on feature sizes. PMMA was patterned onto Si using electron beam lithography with feature sizes ranging from 5 μm down to 60 nm. ALD of TiO2 and HfO2 were studied to understand the selectivity of the deposition on Si vs PMMA and how that selectivity affected feature size dimensions and film thickness. The mechanisms of deposition were studied by characterizing the extent of ALD deposition before and after PMMA removal. TiO2 was not detected on the surface of the PMMA, but after PMMA removal there was a very small amount of deposition in the location that had been coated by PMMA. It was determined that the ALD precursors are likely able to diffuse into the PMMA and still deposit at the interface between the Si and PMMA, even if it is only a trace amount. Thus, ALD of TiO2 is highly selective for Si in comparison to PMMA; however, the effects of the PMMA side walls inhibit deposition so that the dimensions of the TiO2 feature is smaller than the PMMA pattern. This side wall inhibition significantly affects possible feature sizes using TiO2 and PMMA patterns. In contrast, HfO2 is less selective than TiO2 and demonstrates a mechanism combining selective deposition and lift-off. This lower selectivity limits possible HfO2 thicknesses before there is blanket coverage, but it also exhibits less side wall inhibition. Significantly smaller feature sizes were obtained with HfO2 compared to TiO2 in these ALD conditions. Though the ALD parameters could be optimized further, these results suggest that the deposition mechanism itself, whether it is a truly area selective deposition or a combination of area selectivity and liftoff will always affect possible feature sizes.

Fabrication of High-Density, High-Resolution Interconnects via Acoustic Field Assisted Aerosol Jet Printing

Roxanne Kate Balanay and Tyler Ray; University of Hawaii, United States

The additive manufacture of production-grade flexible, large-area electronics is of intense interest to rapidly design, prototype, and fabricate electronics without reliance upon traditional electronics fabrication pathways. Such additive processes enable the direct integration of electronics on arbitrary, non-planar surfaces, expanding the potential form factors and application spaces. Of particular interest is Aerosol Jet Printing (AJP) owning the capacity to fabricate high-resolution printed interconnects with design geometries not possible via other additive manufacturing technologies. AJP is a process by which the controlled deposition of an aerosolized, liquid ink enables the conformal printing of electronic traces. However, several key challenges, such as overspray and process drift, which restrict broad deployment of AJP and limits the feature resolution of printed interconnects. To address these challenges, we report a new type of AJP print process to control and architect aerosolized ink. Termed acoustic focusing aerosol jet printing (AF-AJP), we utilize acoustic forces (AF) to control the width of printed material by focusing the jetted material to a narrower region than what would be possible with a physical orifice alone. As the acoustic focusing effect is dependent on the ink droplet size, the utilization of acoustic focusing provides a means to “refine” the jet (especially if not material-rich) such that the deposited material has a smaller line width and exhibits a reduction in the typically observed particle overspray. We report a typical 30% reduction in trace width, sharp reduction in overspray, and an overall enhancement in print quality via this novel printing technique. We also demonstrate the utilization of AF-AJP to enable the printing of high-resolution traces with electronic materials such as graphene and MXene Ti3C2Tx, in order to fabricate highly conductive traces with conformal and 3D geometries.

A Novel Approach for High Precision Printing of Micro-Bumps

Marc Pascual, Achille Guittion, Amin Mbariki and Anthony Fiorini; Humminck, France

High aspect ratio micro-bumps play a critical role in flip chip applications, facilitating enhanced pixel density and reduced pixel-to-pixel coupling noise. The necessity for micro-bumps with a diameter of less than 5 μm, featuring these high aspect ratios, underscores the limitation of conventional technologies. This study discussed how HPCAP (High Precision Capillary Printing) Technology, allows the one-step fabrication of such micro-bumps. HPCAP capitalizes on capillary forces and resonance as intrinsic drivers, providing the requisite for external energy sources. Inspired by Atomic Force Microscopy (AFM), this technique achieves remarkable precision, with up to 5 nm accuracy along the Z-axis and 20 nm along the XY axes. This level of precision ensures impeccable control over the dimensions and shapes of the micro-bumps enabling exceptional versatility in design, dimensions, and choice of materials.

Etching Characteristics of The B and N Co-Doped Amorphous Carbon Films through Nitrogen Concentration Control for Use as Hardmasks

Hong Kim1, Ung-Gi Kim1, Deokgi Hong1, Young-Chang Joo1, Seungwu Han2 and So-Yeon Lee2; 1Seoul National University, Korea (the Republic of); 2Kumoh National Institute of Technology, Korea (the Republic of)

The challenge to overcome the limits of semiconductor chip shrinkage continues. Shorter-wavelength light sources, such as extreme ultraviolet (EUV), are being utilized to maximize

9:15 AM EL03.09.02

Selecting Suitable Processes for the Design and Fabrication of Micro-Bumps: A Novel Approach for High Precision Printing

Roxanne Kate Balanay and Tyler Ray; University of Hawaii, United States

9:45 AM EL03.09.03

Mechanisms of Area Selective- Atomic Layer Deposition and Their Impact on Feature Sizes

Katherine T. Young, Andy Hsiao and Chris Yang; Georgia Tech Research Institute, United States, Georgia Institute of Technology, United States

9:30 AM EL03.09.04

Fabrication of High-Density, High-Resolution Interconnects via Acoustic Field Assisted Aerosol Jet Printing

Roxanne Kate Balanay and Tyler Ray; University of Hawaii, United States

9:45 AM EL03.09.05

A Novel Approach for High Precision Printing of Micro-Bumps

Marc Pascual, Achille Guittion, Amin Mbariki and Anthony Fiorini; Humminck, France

10:00 AM BREAK
resolution. The use of shorter-wavelength light sources leads to a decrease in the depth of focus (DOF), and consequently, a proportional reduction in the thickness of the photosensitive (PR) layer. This limitation in PR layer thickness may lead to a failure in fulfilling its intended role as a mask in the etching process following lithography, risking complete loss or compromise during etching and potentially causing a deterioration in pattern quality. To address the previously mentioned issues, a sacrificial layer called the hard mask is applied between the component to be patterned and the PR. Amorphous carbon is the material that can most effectively meet various characteristics required for use as a sacrificial layer. Various approaches have been attempted to enhance etch selectivity and improve pattern quality in the etching process by altering the properties of this material. While there have been numerous studies analyzing the characteristics by doping different elements into the amorphous carbon layer, the focus has been predominantly on research related to individual elements.

We aimed to investigate how characteristics change from the perspective of etch resistance when boron & nitrogen co-doping is applied, rather than when individual dopants are applied separately. B & N co-doped amorphous carbon (a-BCN) hardmask were obtained by adjusting the nitrogen content in an amorphous carbon film supplied with sufficient boron, using the DC sputter process. The composition of the hardmask film was analyzed through XPS analysis. Subsequently, films deposited under various conditions were evaluated for their relationship with dry etching performance. In particular, we analyzed the relationship between the etching gas and the a-BCN hardmask structure in the ternary system from both physical and chemical reaction perspectives. We figured out that increased nitrogen in the film alters its density and structure, impacting physical etching processes. Additionally, DFT calculations show that higher nitrogen content increases the probability of chemical etching reactions with fluorine. The details of the physical and chemical reaction mechanisms of etching in a-BCN will be discussed in detail.

Based on the implementation results of the ternary system in the hardmask, we would like to discuss the changes in etching characteristics from both physical and chemical perspectives.

** Keynote Speaker **

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10:45 AM EL03.10.02

Metal-Organic Framework Crystal Growth in Microgravity Phillip Inace, Ryan D. Reeves and Michael Roberts; International Space Station National Laboratory, United States

Crystals grown in microgravity have been shown to be larger in size, to be more uniform in size and morphology, and to contain fewer structural defects relative to Earth-grown crystals. This is due to the homogenous, diffusion-controlled growth in microgravity that results from the lack of gravity-induced convection and sedimentation. Metal-organic frameworks (MOFs) are a unique class of materials that consist of a central metal ion coordinated to organic ligands that extend to form two- or three-dimensional structures. MOFs have promising applications in electocatalysts, photovoltaics, thermoelectrics, and electrical energy storage materials due to their tunable chemical, electrical, and mechanical properties. Persistent microgravity provides an ideal environment to study the growth of larger, higher-quality MOF crystals that will lead to more sustainable microelectronics.

The International Space Station (ISS) National Laboratory offers a unique platform in persistent microgravity that enables the elimination of gravity-driven forces to elucidate the fundamental mechanisms of growth, morphology, and defect generation in MOF crystals. An improved understanding of the fundamental mechanisms of MOF crystal formation will lead to the growth of higher-quality MOF crystals both in space and on Earth. Several organic and inorganic crystals have been grown onboard the ISS, including proteins, semiconductors, and graphene aerogels.

In this work, we will introduce the underlying physical phenomena of crystal growth in microgravity. We will present information on current ISS National Lab-sponsored research projects that are growing HKUST-1 3D MOF crystals, and hexaaminotriphenylene (HITP) and hexaaminobenzene (HIB) linker-based 2D MOF crystals. We will also discuss translational lessons learned from microgravity experiments that inform and direct terrestrial research and manufacturing. Finally, we will present opportunities for future microgravity experiments and access to ISS facilities through the ISS National Lab.

11:00 AM EL03.10.03

Highly Conductive 2D Covalent–Organic Framework Films Rui Wang, Hang Lyu and Yoonseob Kim; The Hong Kong University of Science and Technology, Hong Kong

Covalent–organic frameworks (COFs) have been widely used in electronics, catalysis, sensing, adsortion, and water purifications for their high crystallinity, porosity, and tunable functionality. However, the practical applications have been limited due to low intrinsic conductivity. Recent studies show that conjugated 2D COFs have the potential to achieve high conductivity and that the rational design of linkers and metal-containing macrocycles and synthesis optimization is important. Regarding this, our report will demonstrate a bottom-up synthesis of copper-coordinated-fluorinated-phthalocyanine (CuPc) and 2,3,6,7-tetrahydroxy-9,10-anthraquinone-based COF (CuPc-AQ-COF) films, achieving high conductivity levels. These films demonstrate an electrical conductivity of 1.53 × 10^3 S m^-1 and a Hall mobility of 6.02 × 10^-2 cm^2 V^-1 s^-1 at room temperature, rivaling that of metals. This remarkable performance is attributed to the molecular design that incorporates both an electron metal-containing CuPc and a quinone-based linker, and the significantly improved crystallinity of the films prepared via the vapor-assisted method, which all facilitate charge transport within the COFs. Density functional theory analysis further proves the intralayer donor–acceptor system and further reveals that this system has the smallest band gap between the LUMOs of CuPc center and quinone linkages compared to other published similar COFs structures. We also fabricated a field-effect transistor (FET) device with COF films exhibiting bipolar behavior, a low threshold voltage, and a high L_on/L_off. The results demonstrate the potential of the films in electronic applications. Our findings provide valuable insights into the design and fabrication of high-performance COF films. These stable, porous, and crystalline organic networks with metallic conductivity can realize advanced electronic devices, catalysis, and energy storage systems.

Reference:

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** SYMPOSIUM EL04 **

Wide and Ultra-Wide Bandgap Materials, Devices and Applications
April 22 - May 9, 2024

Symposium Organizers
Hideki Hirayama, RIKEN
Robert Kaplar, Sandia National Laboratories
Sriram Krishnamoorthy, University of California, Santa Barbara
Matteo Meneghini, University of Padova

Symposium Support
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Taiyo Nippon Sanso
Materials Science and Device Technology Development for Interface-Engineered Super High-K Dielectric Nanolaminates-Based Oxides / Crystalline Diamond for New Generation High Power Electronics

Orlando Asciuola1,2; 1The University of Texas at Dallas, United States; 2Original Biomedical Implants, United States

This abstract focuses on describing the fundamental and applied materials science and engineering being performed to develop a new generation of transformational high-power electronics based on the integration of novel multifunctional nanolaminate-oxides thin films, with super high-dielectric constant, and single crystal diamond. Specifically, this paper describes the following aspects of the research:

- **Materials Science and Device Technology Development**: Development of the lithography/RIE process to fabricate diamond-based micro/nano-electronic devices with integrated high-K dielectric TiOx/AlO3 nano-laminates/single crystal diamond MOSFET devices.
- **Transient Grating Measurements**: Topetable deep ultraviolet transient grating measurements of diamond and silicon at record sub-300nm length scales.
- **Applications**: Discussion will conclude with a summary of new material science process and technology solutions developed at WDAM, including defect mitigation; selective patterning and deposition; large substrate sizes, including anonymized comparisons to other commercially available products.

### References


can pose several integration issues. Therefore, a stable dry etching process with high etch selectivity is needed. This study reports a stable dry etching process with high etch selectivity of ALD superoxide performance with high field-effect mobility (50 cm² V⁻¹ s⁻¹) and an on-current of 10⁻⁶ A, and the value of the off-current was 10⁻¹³ A under 0.1 VDS without any dielectric.

This study also verified the possible issues in the electrical characteristics when the above recipe with high selectivity is adapted to fabricate the a-ZTO thin film transistor (a-ZTO-TFT) having TiN source and drain, 100nm-thick thermal SiO₂ gate insulator, and p⁺ Si gate. For the stable operation of the TFT, a-ZTO film other than the channel region must be etched entirely away while minimizing the etching of the underlying SiO₂ layer. It is usual to over-etch the a-ZTO channel layer for this purpose. In this study, the ZTO channel etching was attempted by adopting BCl₃/N₂/Ar (15/5/30 sccm) gases, a previously reported method, and using CH₄/N₂/Ar (30/31/15 sccm) gases, a newly developed method. The over-etch was performed from 20% to 100% at intervals of 20% for each gas condition. Compared to the results of 5 over-etch conditions of applying BCl₃/N₂/Ar gases, less variation of on-current (1.27x10⁻⁴A) at 20.1V of gate voltage), better average subthreshold swing (0.224V/dec), and less variation of threshold voltage (1.00V – 0.70V) were obtained from the 5 over-etch conditions with the CH₄/N₂/Ar gases. This improvement was attributed to the improved etching selectivity of the latter as compared with the former method. The presentation will report more detailed fabrication steps and electrical characteristics of the a-ZTO-TFT for their use in 3D DRAM.

Effect of High-k Oxide Materials on Amorphous Indium Gallium Zinc Oxide (α-IGZO) Channel in Top Gate Field Effect Transistors Reem Alshanbari, Oliver Durman, Huaqiu Guo, Moshe Eizenberg and Ioannis Kymissis. Columbia University, United States; Technion–Israel Institute of Technology, Israel

The gate dielectric material plays a significant role in high-k gate electric and low power consumption in field-effect transistors (FETs). A small conduction band offset energy and a large interface trap density are common problems with high-k dielectrics with high permittivity. For that, in this work, the integration of high-k dielectrics with PECVD dielectrics has been reported to show improvements in electrical performance. Here, we integrated a high-k dielectric with (~10 nm) amorphous indium gallium zinc oxide (α-IGZO) FET with different gate dielectrics PECVD (SiO₂ and Si₃N₄). In addition, using a high-k dielectric can help overcome the problem of plasma contamination and diffusion, which can impact the device's threshold voltage and power consumption. For that, we used two of the most promising high-k dielectrics (HfO₂ and Al₂O₃). Our results showed that α-IGZO with optimized HfO₂/SiO₂ dielectrics has a superior electrical performance with high-field effect mobility (50 cm² V⁻¹ s⁻¹) and an on-current of 10⁻⁶ A, and the value of the off-current was 10⁻¹³ A under 0.1 VDS without any dielectric leakage. These results support the idea that increasing the gate capacitance density will improve the electrical performance and material conductivity. Integrating HfO₂ with SiO₂ improves the interface quality between the gate dielectric/channel and reduces the charge trap density and gate leakage. In contrast, there is a degradation in the electrical performance of α-IGZO FETs with Al₂O₃/SiO₂ related to the oxygen diffusion where more oxygen atoms diffuse from Al₂O₃ to the α-IGZO layer.

GaN Homoepitaxial Growth and Substrate-Dependent Effects for Vertical Power Devices Jennifer Hinojosa, U.S. Naval Research Laboratory, United States; University of Florida, United States

Vertical GaN power switch technology is expected to be utilized in next-generation medium to high voltage power converters due to the low ON-resistance and high breakdown voltage enabled by the improved critical electric field and mobility compared to Si and SiC-based devices. As large area substrates have become available by hydride vapor phase epitaxy (HVPE) and ammonothermal growth, the properties of nitrides are no longer dominated by defects introduced by heteroepitaxial growth, allowing recent realization of several fundamental vertical power devices, including diodes with edge termination, trench MOSFETs, and CAVETs. However, additional materials challenges are coming to the forefront that need to be understood and surmounted in order to allow vertical GaN power devices to achieve their full potential, notably the realization of repeatable thick drift layers with low background doping. To enable this, a deeper understanding of substrate preparation and the effects of the substrate and growth initiation on the characteristics of the epitaxial layers is required for MOVCD growth of homoepitaxial films. We investigate these effects on both morphology, uniformity, and impurity incorporation by growing simultaneously on wafers from different vendors. The goal of this work is to detect and identify defects in GaN substrates with a series of quick, non-destructive, inexpensive techniques with capabilities of mapping whole wafers. We have characterized multiple parameters from various suppliers and the homoepitaxy grown on those substrates. All the substrates had nominally similar as-received specifications (resistivity, thickness, off-cut angle, bow, surface finish). The substrates were evaluated with a variety of techniques including Raman spectroscopy, photoluminescence, white light interferometry, and Nomarski imaging, enabling to detect different parameters of interest, sample impurities, point defects, v-shaped pits, polishing defects, crystal stress damage, and non-uniform insulating and conductive regions. The substrates can be characterized in two different categories: those with uniform characteristics, including carrier concentration, and those without. Comparing these results to those from homoepitaxial growth on the same wafers, the effects are both subtle and overt. Macroscopic surface morphology, which has shown a direct correlation to leakage current, copies and exaggerates that of the underlying substrate. Photoluminescence of the homoepitaxial surface along with Raman spectroscopy show that non-uniformities in the substrate can continue into the epitaxy. Following optical characterization, vertical Schottky diodes were fabricated to test device performance. While most of the films showed the ability to withstand high electric fields, those with more uniform characteristics in the substrate also showed more uniform electrical properties. These results show that the bulk substrates enable the path to high voltage vertical devices, but also show the significant influence that substrates can play in device performance.
The enhanced critical electric field of wide bandgap GaN render it an attractive technology for power switching and power amplification devices. Recent improvements in epitaxy and substrate quality have made it possible to focus on the development of advanced devices with complex doping schemes and junctions. This talk will tackle two important cases: (1) vertical GaN Junction Barrier Schottky (JBS) diodes realized with Mg implantation and ultra-high pressure annealing (UHPA), as well as (2) PN junctions using III-V/GaN heterogeneous heterojunctions formed via a novel technique known as Crystal Heterogeneous Integration (CHI). In each case, it will be demonstrated that junctions with near-unity ideality factors can be achieved via careful control of the material interfaces. These results underline the promise of GaN for high performance devices, and pave the way for further innovation in device geometries.

The experiment starts with 4" sapphire substrates. A total of 14µm thick GaN epitaxial layers are grown on each wafer, epitaxy consists of a 2.2µm unintentionally doped GaN buffer layer, a 2.4µm n-GaN(Si) (N_D = 3.0 x 10^{18} cm^{-3}) lower highly conductive layer and a 10 µm n-GaN:Si drift layer with a nominal Si concentration of N_D = 7.5 x 10^{18} cm^{-3}. The effective doping has been measured by CV on diodes and changes on the substrate material. 500nm GaN:Mg 1 x 10^{19} cm^{-2} layer with additional 30nm GaN:Mg 2 x 10^{18} cm^{-2} contact layer for the regrown pn diode were grown on sapphire. The initial wafer bow after epitaxy grown on sapphire is -300µm (Radius = 4m) and it would not be processable. Laser patterning was carried out in order to reduce the wafer bow by selectively introducing damage in the substrate close to the bottom interface. The patterning was realized by focusing a laser beam in the sapphire close to its back surface using a laser scriber (WS4000), which uses a Talisker Ultra Laser from Coherent for internal layer modification. This means that the laser will be focused inside the material and, at this position, the crystal will be modified. The wavelength we use is 532nm. Used repetition rate is 40kHz at a feed speed of 400mm/s and a continuous laser power of 160mW at the point of use. Overall device performance and characteristics will be shown in the presentation, along with benchmarking and comparison of the different substrates.

The large bandgap of GaN enable advancements in power electronics. pn GaN vertical diodes offer improved efficiency, size, and performance over traditional Si-based power devices making them essential components for next generation power electronic systems. pn GaN diode fabrication typically requires regrowth of the p+GaN layer, which is known to introduce Si impurities at the pn GaN interfacial layer.1-3 While this design is a widely adopted one, we have developed a p+GaN interfacial layer with low (<1x10^{15}cm^{-3}) impurities content. The regrown diode wafer after epitaxy grown on sapphire is -300µm (Radius = 4m) and it would not be processable. Laser patterning was carried out in order to reduce the wafer bow by selectively introducing damage in the substrate close to the bottom interface. The patterning was realized by focusing a laser beam in the sapphire close to its back surface using a laser scriber (WS4000), which uses a Talisker Ultra Laser from Coherent for internal layer modification. This means that the laser will be focused inside the material and, at this position, the crystal will be modified. The wavelength we use is 532nm. Used repetition rate is 40kHz at a feed speed of 400mm/s and a continuous laser power of 160mW at the point of use. Overall device performance and characteristics will be shown in the presentation, along with benchmarking and comparison of the different substrates.

The regrowth pn diode displayed memory or hysteresis effect at forward bias with 10 orders of magnitude larger on-state current (ION) than the off-state current (IOFF), while the “control” pn diode shown no memory or hysteresis effect. It is appealing to develop GaN-based memory technologies which could be integrated with GaN high electron mobility transistors. Here, we find that regrown pn vertical diodes display an exceptionally large memory-like hysteresis loop exceeding a previous report.6 Memristor-like behavior in GaN and other nitride device structures has also been reported.7-9 It is challenging for foreign substrates where the lattice mismatch and thermal coefficient differences generate a series of undesirable effects, such as increase of threading dislocations density, increased leakage current, increased stiffness and fragility and increase in wafer bow. While GaN substrates may provide a better solution for the material quality point of view, costs and substrate quality may differ substantially between differently grown wafers. In this presentation we will talk about the issues of growing thick (~5µm) GaN drift layer on Sapphire substrates for vertical high power GaN devices, how to manage the high wafer bow that makes these wafers un-processable on commercial equipment designed for flat Silicon wafers and we will compare the processed devices between sapphire and three differently grown GaN substrates. a) “Wafer A”, b) “Wafer B”, and c) “Wafer C”). All processed devices showed >2kV breakdown voltage with different ON-state resistivity, Power-Figure-of-Merit and chip cost. pn diodes on Ammonothermal-GaN, “Wafer A”, show 1630V breakdown, on “wafer B” and “wafer C” 1485V and 1480V are shown respectively, all three showed avalanche breakdowns. While on sapphire, “Wafer D”, they show 1350V nondestructive breakdown due to high leakage current.

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Achieved controlled production of electron beam-induced blue emitters in h-BN by tuning the electron dose and native defect density, which advances our understanding of their structural manner, as measured using photoluminescence (PL). We establish the correlation between the incident electron dose and PL intensity, indicating that the negative charge trapped in h-BN to their anti-bunching behavior, a characteristic of quantum emitters. In this work, we report the controlled generation of 437 nm quantum emitters (referred to as “blue emitters”) in h-BN via electron beam irradiation. We demonstrate that irradiation of h-BN using 3–10 keV electron beams in a scanning electron microscope (SEM) produces the blue emitters in a spatially precise manner, as measured using photoluminescence (PL). We establish the correlation between the incident electron dose and PL intensity, indicating that the negative charge trapped in h-BN facilitates the 437 nm emission. To explore the structural origin of the h-BN blue emitters, we introduce point defects to h-BN using a helium ion microscope (HIM) before electron beam irradiation and show that the blue emitter PL intensity increased in the defect-engineered area. Furthermore, using a scanning transmission electron microscope (STEM) coupled with cathodoluminescence (CL), we observe the real-time activation and saturation of the blue emitter in pristine h-BN. In this work, the emission intensity is expected to be >1000 s, making it a promising candidate for photonic device integration. We achieved controlled production of electron beam-induced blue emitters in h-BN by tuning the electron dose and native defect density, which advances our understanding of their structural origin as the conversion of native defects in the h-BN lattice. These h-BN blue emitters with enhanced spectral stability can serve as a building block for future photonic devices.

### References


This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Award # DE-SC0023222. This research used the Electron Microscopy facility of the Center for Functional Nanomaterials, which is a U.S. Department of Energy Office of Science User Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

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**SESSION EL04.04: WBG Growth and Devices**

**Session Chairs:** Jennifer Hite and Sriram Krishnamoorthy

**Tuesday Afternoon, April 23, 2024**

**Room 345, Level 3, Summit**

### EL04.04.01

**Probing Polytype Selection during Mediated-Epitaxy of GaN Quantum Dots and Nanowires**

**Abby Liu**¹, **Zhucong Xi**¹, **Meng Li**²,³, **Dmitri N. Zakharov**³, **Fernando Camino**³, **Judith C. Yang**²,³, **Liang Qi**¹ and **Rachel Goldman**¹; ¹University of Michigan, United States; ²University of Pittsburgh, United States; ³Brookhaven National Laboratory, United States

Semiconductor polytype heterostructures, which consist of chemically homogeneous structures formed via an abrupt change in crystal structure, offer opportunities for performance exceeding those of composition-based semiconductor heterostructures. Of particular interest are heterostructures formed via an abrupt change in atomic plane stacking sequence, such as the transition from the wurtzite (WZ) polytype to the zincblende (ZB) polytype. At a fixed chemistry WZ/ZB heterojunction, the lattice mismatch and thermal expansion coefficient mismatch are typically < 1%, leading to a negligible interfacial defect concentration. Meanwhile, the WZ/ZB band offset and polarization discontinuity are expected to lead to the confinement of a two-dimensional electron gas (2DEG) at the interface, without the need for impurity doping and/or alloying. Such heterostructures would be promising for high power electronics and single photon emitters. It has been hypothesized that metastable nanowire (NW) polytype selection is governed by surface/interface energies, surface diffusivities, and/or droplet angles that determine ABC vs. AB stacking of atomic planes, resulting in ZB or WZ polytypes. For ZB-polytype-prefering materials, such as III-As and III-P, ZB vs. WZ polytype selection has been described by empirical “contact angle” models, enabling the design and fabrication of NW polytype superlattices. However, for GaN, a WZ-polytype-prefering material, the “contact angle” models for NW polytype selection, using literature values for WZ and ZB GaN surface energies, predict ZB polytype formation, across contact angles, even though WZ GaN NWs are most frequently reported in the literature. We recently discovered a Ga-mediated molecular-beam epitaxy (MBE) process to nucleate ZB and WZ GaN NWs on Si(001) [1]. Key to this process is a Ga pre-deposition step, in which Ga droplet arrays are formed prior to NW growth. For the ZB NW ensembles, reflection-high energy electron diffraction and x-ray diffraction suggest overall ZB-to-WZ transformations at thickness ~20 nm. High-angle annular dark-field STEM reveals WZ NWs with close-packed (0001) planes oriented along the Si [001] surface normal, i.e. [0001]-oriented ZB NWs. On the other hand, ZB NWs with the close-packed (111) planes oriented ~37° from the Si [001] surface normal, i.e. [001]-oriented ZB NWs. Interestingly, the NW axis orientation remains fixed as it transforms to the WZ polytype. We hypothesize that Si incorporation into Ga droplets influences the polytype selection during NW growth. Preliminary energy dispersive spectroscopy (EDS) data reveals higher Si concentration within ZB NW in comparison to that within WZ GaN NWs. Correspondingly, density functional theory (DFT) calculations show that ~8% at% Si in the Ga sublattice makes ZB GaN thermodynamically more stable than WZ GaN. Thus, it appears to be a ZB polytype stabilizer for GaN. Direct observations of GaN nucleation in an in-situ environmental TEM (ETEM) will also be presented.

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0002322. This research used the Electron Microscopy facility of the Center for Functional Nanomaterials, which is a U.S. Department of Energy Office of Science User Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

functonalized sensor, obtained a sensitivity of about 0.46μA/ppb and 0.32 ppb as lowest limit which is substantially lower than the permissible limit as set by W.H.O. In another work on Pb2+ determination, the fabrication of a highly selective Pb2+ sensor was carried out for the detection of toxic lead ions in the water by functionalization of the Au-gated region by the 2,5-dimercapto-1,3,4-thiadiazole (DMDT). The sensor reaches the lower detection limit of 0.012ppb with a rapid response time of 4-5 seconds and high sensitivity of 0.607 μA/ppb. Moreover, a study for the selectivity analysis is performed, and it is found that the sensor is highly selective towards Pb2+ ions. In another interesting work, we developed a sensor for highly selective, sensitive, and rapid detection of the trace amount of Hg2+ ions using molybdenum disulfide (MoS2) functionalized AlGaN/GaN HEMT. The sensor showed an excellent sensitivity of 0.64 μA/ppb and a low-level detection limit of 0.01152 ppb or 11.52 ppt (parts per trillion) with a rapid response time of 1.8 s. Moreover, the sensor exhibits the linear range of detection from 0.1 ppb to 100 ppb and highly selective behavior towards Hg2+ ions. To further enhance the sensitivity, we have successfully demonstrated the detection of Hg2+ ions using MoS2 functionalized AlGaN/GaN HEMT under UV illumination which showed an extremely high sensitivity of 548.07faA/ppb with a lower detection limit of 6.15 ppt. In our another work, we observed that the fabricated sensor after functionalization with Ag-MoS2 ensured faster electron transfer kinetics and showed out remarkable sensitivity of 1.6 ma/ppb and limit of detection (LoD) of upto 20 ppt. Along with the detection on real time water samples from lake water, a proof of concept by enabling it with IoT interface was also demonstrated. Hence, the development and performance of the AlGaN/GaN HEMT based ion sensors suggest that these sensors have a huge potential for other heavy metal ion sensing applications.

3:45 PM EL04.04.04 Metallization Scheme for 800 °C Silicon Carbide Microsystems Robert Okojie; NASA Glenn Research Ctr, United States

We have developed and validated a high temperature metallization scheme that can sustain silicon carbide (SiC) microsystem operation at 800 °C in the absence of protective packaging. The metallization system consists of the ohmic contact, diffusion barrier, and interconnect layers made up of three primary and conventional metallizations of Ti, TaSi2, and Pt. The ohmic contact to the SiC layer is comprised of sequentially deposited Ti (100 nm)/TaSi2 (300 nm) that provides low contact resistance, followed by the diffusion barrier layer of Ti (100 nm)/Pt (300 nm) to prevent the native oxygen and excessive upper layer platinum migrations to the underlying SiC layer. The interconnecting layer is comprised of Ti (20 nm)/TaSi2 (20 nm)/Pt (300 nm)/Ti (20 nm)/TaSi2 (20 nm), which also acts as a diffusion barrier against oxygen from the atmosphere. The bond pad contact layer is Ti (100 nm)/Pt (300 nm)/Au (500 nm). The metallization was implemented on the n-type epilayer of batch fabricated 4H-SiC pressure sensors to demonstrate functionality in a real device. The metallization system on the sensor was analyzed with Auger Electron Spectroscopy (AES), Focus Ion Beam (FIB) Field Emission Scanning Electron Microscopy (FE-SEM), and X-ray Photoelectron Spectroscopy (XPS) at various sections and stages during different steps of the fabrication. Further analyses were performed after fabrication at high temperature up to 800 °C in air. Electrical measurement was also performed on the bare die under worst-case packaging. The metallization scheme with a smooth surface morphology was subsequently implemented. The complete details of this work will be presented at the meeting.

4:00 PM EL04.04.05 Dopant-selective photoelectrochemical etching of 4H-SiC for wafer-scalable SiCOI integrated photonics Jason Linton, John vajo, Adam Sorensen, Brett Yurash, Biqin Huang, Sam Whiteley, Xiwei Bai, Tong Wang, Sam Rubin, Adrian Portales, Shuqin Cui and John Graetz; HRL Laboratories, United States

Usable quantum networks with long distance baselines requires quantum repeaters with integrated quantum memories. 4H-SiC hosts a variety of optically addressable defects, can yield low-loss photonics while being compatible with CMOS fabrication processes, and has a highly mature wafer-scale supply chain. However >3λ total thickness variation (TTV) of SiC thin film during the SiC-on-insulator (SiCOI) fabrication impedes scalable fabrication of integrated photonic devices with acceptable propagation loss and efficient coupling of optical elements. While the high chemical stability of SiC makes traditional wet processes ineffective, we have demonstrated dopant-selective photoelectrochemical (PEC) etching of SiC epitaxial layers using n-type SiC as a sacrificial layer with a p-type etch stop. We apply the concept of selective PEC to a realistic SiC-on-insulator (SiCOI) stack for highly effective TTV reduction. We show that by using selective PEC etching to etch a sacrificial n-type layer and stop selectively on an intrinsic photonic layer, we are able to reduce the TTV of the SiC by over an order of magnitude. We show that the reduced TTV results in a dramatically improved yield and propagation loss of waveguides compared to the standard polishing process. The results presented here represent a step forward in realization of scalable 4H-SiC integrated photonic devices toward long-distance quantum networking.

4:15 PM EL04.04.06 Dielectric and Phase Engineering of Van der Waals Sb2O3 Films via PLD Jing Yu1, Ruo Jing Ong1, Atta Ur Rehman1, Chris Tang2, Wei Han2 and Francis Chi-Chung Ling1; 1The University of Hong Kong, Hong Kong; 2Hubei University, China

Van der Waals dielectrics are broadly utilized to probe the intrinsic properties of two-dimensional (2D) electronic devices. As a 2D inorganic molecular crystal, Sb2O3 have attracted many research interests as a promising high k gate dielectric with low-cost and CMOS compatibility. However, fabricating 2D Sb2O3 film with controllable dielectric constant and crystal phase is challenging. Here, we designed an oxygen-assisted PLD-assisted method for the phase-selective growth of α-and β- Sb2O3 thin films with super-high κ (>100) and good homogeneity by PLD. This is realized by tuning the oxygen gas pressure in the growth products to obtain two phases Sb2O3. This phase-controlled bottom-up synthesis offers a simple reference for manipulating the relevant device structures and provides a general approach for producing other multi-phase materials with unique properties and allows us to characterize their intrinsic optical and electrical properties. Using dielectric and electrical measurements, we show that phases exhibit good dielectric performance. Our 2D Sb2O3 dielectric film not only show higher κ than other conventional dielectrics in terms of compatibility to CMOS processes, but also keeps their comparative advantages in the fabrication of high-performance electronic devices over conventional dielectrics. Our approach of fabricating Sb2O3 dielectrics using PLD may open promising opportunities to promote such unprecedented 2D devices to industry applications.

SESSION EL04.05: UWBG Nitrides
Session Chairs: Elaheh Ahmadi and Sirem Krishnamoorthy
Wednesday Morning, April 24, 2024
Room 345, Level 3, Summit

8:45 AM EL04.05.01 Addressing Challenges in AlGaN-Channel High Electron Mobility Transistors Brianna A. Klein1, A. A. Allerman1, Andrew Armstrong1, Mary Rosprim1, Yinxiuan Zhu2, Chandan Joishi2, Chris Chae1, Jinwoo Hwang2 and Siddharth Rajan2; 1Sandia National Laboratories, United States; 2The Ohio State University, United States

Next-generation semiconductor switches and integrated circuits require higher power density, greater customizability, and improved radiation hardness than what is commercially available today. Nitride-based Ultrawide-Bandgap (UWBG) semiconductors, namely AlGaN (aluminum gallium nitride) are well-suited to meet these performance demands. Higher bandgaps result in exponentially higher critical electric fields, thus enabling power electronic devices with larger breakdown voltage and output power than devices made from conventional semiconductors (e.g., Si, GaN). In elevated temperatures, large bandgaps reduce noise and leakage from intrinsic carrier effects and thermionic emission. However, AlGaN faces challenges in realizing low-resistance Ohmic contacts and reduced mobility due to alloy scattering. This talk will discuss efforts at Sandia to address these challenges, as well as highlight key device results. Significant improvements of Ohmic contacts on aluminum rich HEMTs (channel compositions of Al0.5Ga0.5N) have resulted in reduced specific contact resistance values, with latest developments reaching the 10θ Ωcm² range. The power transistor developments have targeted increases in current and standoff voltage, while processes to realize p-AlGaN based enhancement mode (normally off) gates have been developed.

SNL is managed and operated by NNSA under DOE NNSA contract DE-NA0003525. Research was sponsored by the Army Research Office and was accomplished under Cooperative Agreement Number W911NF-22-2-0163. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Office or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes.

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Ultra-wide band gap (UWBG) materials offer the potential for greatly improved power electronic device performance due to their predicted higher breakdown fields limited by avalanche breakdown, as well as their favorable transport characteristics such as high mobility and drift velocity, which reduce on-resistance and allow for high frequency operation in power conversion applications. Experimental data on the high field transport properties of UWBG materials such as the impact ionization coefficients are relatively limited, with considerable variability. Hence, to understand the limits of performance of these materials, we report on first principles theoretical calculations of the high field transport properties of UWBG materials using a combination of ab initio calculations of the electronic and phononic structure coupled with particle based full-band Cellular Monte Carlo (CMC) high field transport simulation.

The electronic structure is computed using the GW method based on the BerkeleyGW code, which accurately predicts the bandgaps and excited states of UWBG materials. The phonon dispersion is calculated from DEPT (density functional perturbation theory) using Quantum Espresso. The full wave-vector dependent deformation potentials are computed using the GW eigenvectors as input to the EPW (electron-phonon using Wannier) code, to calculate the electron-phonon scattering rate from first principles. The calculated electronic structure, phonon dispersion, and anisotropic electron-phonon deformation potentials are then input to the CMC code. The CMC code has been developed in-house for a number of years, and simulates the dynamics of an ensemble of charge carriers using scattering rates tabulated in a large look-up table, which allows computationally efficient simulation of non-equilibrium carrier dynamics across the entire Brillouin zone.

Besides electron-phonon and defect scattering, we calculate the band-to-band impact ionization scattering rate directly from the GW electronic structure, using a screened Coulomb interaction based on the full band frequency-dependent Lindhard dielectric function. Based on these scattering mechanisms as input, transport quantities such as the velocity-field characteristics and impact ionization coefficients as a function of field are calculated from full band Cellular Monte Carlo (CMC) simulation.

We have applied this framework initially to diamond in comparison to available high field transport data. One important observation is that while the critical field depends strongly on the material bandgap, the relative magnitude of the deformation potential plays an important role as well. Lower values of the deformation potential lead to more energetic electron and hole populations which trigger impact ionization, hence reducing the breakdown field. We compare different approximations of the deformation potential in relation to the simulated impact ionization coefficients and their impact on breakdown. The impact of other scattering processes due to defects such as ionized impurities on the high field properties are also under investigation. We also are currently investigating other UWBG materials, specifically BN and AIN, and will report on their high field properties as well.

10:00 AM BREAK
implemented AlN arises from Al interstitials introduced by the ion damage. At the same time, the substitutional implanted Si and Ge ions form complexes with Al vacancies, which maintain the group-IV donors in the shallow configuration and prevent compensation. The presence of these complexes has been identified experimentally through their characteristic peaks in photoluminescence. Moreover, although the DX-center geometry is the most stable configuration of Si and Ge dopants for Fermi levels close to the conduction band, Fermi levels near the middle of the gap cause donors to adopt the shallow-donor geometry, in which Al atoms are substituted by the dopants without bond severance or strong bond distortions. This indicates that Fermi-level engineering during the material growth or processing can stabilize donors in the shallow geometry and prevent the formation of DX centers. Furthermore, once equilibrium is re-established in n-type AlN and the Fermi level shifts closer to the conduction band, the disruption of the Si-N bond is inhibited by an energy barrier of ~1 eV, preventing the conversion of the metastable shallow Si donors into DX centers over a sufficiently long time. Our results explain the mechanisms for the efficient n-type doping of AlN and Al-rich AlGaN, and identify Fermi-level engineering strategies to further increase the doping efficiency and improve the conductivity.

References:

11:30 AM EL04.05.07
Comparative Study of Low-Frequency Noise in Diodes Made of Ultra-Wide Band Semiconductors Subhaaith Ghoth1, Dinusha Herath Mudiyanselage2, Fariborz Kargar1, Yuji Zhao3, Houqiang Fu4, Stephen M. Goodnick2, Robert J. Nemenich and Alexander A. Balandin1; 1University of California, Los Angeles, United States; 2Arizona State University, United States; 3Rice University, United States

In recent years, ultra-wide bandgap (UWBG) semiconductors have attracted increasing attention owing to the ever-increasing industry demand for high-power density electronics. Materials such as diamond, AlGaN, BN, and β-Ga2O3 emerged as viable alternatives to the well-established wide-bandgap technologies such as GaN and SiC. Low-frequency electronic noise produced by a device is an important metric. From one side, the level of low-frequency noise should be reduced for device applications in communications or sensors. On the other side, low-frequency noise can provide valuable information about the material quality and device reliability. The low-frequency noise includes the 1/f, flicker noise, and generation-recombination (G-R) noise with a Lorentzian-type spectrum (f is the frequency). Both 1/f and G-R noise are associated with material defects acting as trapping centers for the charge carriers. The latter can be used to understand the charge carrier dynamics and defects in materials. To some degree, the noise level can be used as a metric to assess the maturity of the material and device technology. We have conducted detailed noise studies in GaN vertical PIN diodes [1], high-current diamond diodes [2], β-Al2O3 Schottky barrier diodes [3], and β-Ga2O3/p-n heterojunction diodes [4]. At the presentation, we will compare the overall noise level in different UWBG technologies and comment on the effects of the material and device quality. We will also describe the most interesting features observed in the noise spectra for some of the devices. Specifically, it was found that the noise of the diamond diodes is dominated by the 1/f and G-R noise. The G-R bulges are characteristic of diamond diodes with lower turn-on voltages. The characteristic trap time constants, extracted from the noise data, show a uniquely strong dependence on current. Interestingly, the performance of the diamond diodes improves with the increasing temperature. The noise spectral density of the β-Al2O3 diodes, at room temperature, reveals a 1/f dependence, with superimposed Lorentzian bulges at the intermediate current regimes. At the intermediate current level, the Lorentzian component belongs to the random telegraph signal (RTS) noise. The RTS noise was attributed to the defects near the Schottky barrier affecting the local electric field and the potential barrier, which correspondingly impacts the electric current.

This work was supported by ULTRA, an Energy Frontier Research Center (EFRC) funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC00121230.


11:45 AM EL04.05.08
Novel deposition of amorphous aluminum oxide thin film using a direct liquid injection chemical vapor deposition (DLI-CVD) system Jeeon Kim1,2, Wei-Fan Hsu2, Simon Mellaerts3, Claudio Bellani4, Alberto Bineti5, Koen Schouteden5, Jean-pierre Locquet5, Jin Won Seo2, and Caroline Sunyong S. Lee1; 1Hanyang University, Korea (the Republic of); 2KU Leuven, Belgium

Aluminum oxide (Al2O3) stands out as a representative ceramic material thanks to its wide applicability, e.g., in electronic and optical devices, sensors, wear-resistant coatings, and catalyst support. Especially, amorphous aluminum oxide films hold great promise due to their flexibility, uniformity, and high dielectric properties compared to crystalline counterparts. Various deposition methods, such as sputtering, chemical vapor deposition (CVD), and sol-gel method have been used so far. This study introduces a novel direct liquid injection CVD (DLI-CVD) technique to fabricate amorphous Al2O3 thin films. DLI-CVD, unlike conventional CVD process, offers various advantages: It can avoid the unnecessary decomposition of precursors prior to deposition, by making use of a vaporization chamber (Vapbox). The liquid precursor is injected into the Vapbox and transported to the deposition chamber through the nitrogen carrier gas. Simultaneously, oxygen gas is injected into the chamber for enabling the oxide film deposition. The precursor mixture is directly injected as vapor into the deposition chamber. The decomposition occurs on the surface of the substrate, where the deposition reaction is initiated. As the precursor molecules are decomposed directly on the surface, unwanted by-products can be prevented. Furthermore, strong chemical bonds between precursor molecules and organic solvent break in advance, while minimizing the required heat energy.

In this study, Al2O3 thin films were deposited by varying the parameters such as the substrate temperature, the deposition time, and the ratio between nitrogen and oxygen gas flow. Aluminum acetylationate (Alacac3) was selected as the aluminum precursor due to its stability, non-toxicity, and non-flammability, compared to alternatives like trimethylalumium and aluminum chloride. X-ray reflectivity (XRR) analysis confirmed that the film thickness scaled with the substrate temperature and deposition time. Atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) analysis elucidated the roughness, uniformity, and composition of Al2O3 films. Cross-sectional transmission electron microscopy (TEM) provided insights into the film morphology and growth mechanism. This work demonstrates the applicability of the novel DLI-CVD technique and enhances our understanding of this innovative thin film process.

SESSION EL04.06: Power Devices
Session Chairs: Sriram Krishnamoorthy and Baishakhi Mazumder
Wednesday Afternoon, April 24, 2024
Room 345, Level 3, Summit

1:30 PM *EL04.06.01
Multidimensional Power Devices in WBG and UWBG Semiconductors Yixiao Zhang; Virginia Tech, United States

Power electronics technologies provide electrical energy conversion using semiconductor devices and passive components. The global power device market reaches US$40 billion and is rapidly expanding, driven by applications like electric vehicles, data centers, consumer electronics, electric grids, and renewable energy processing.

Power device advances are driven by materials and device architectures. In addition to using wide-bandgap (WBG) or ultrawide-bandgap (UWBG) materials, multidimensional architectures – such as superjunction, multi-channel, and multi-gate – can also improve device performance, regardless of the underlying material technology. These structures enable electrostatics engineering in additional dimensions and bring the benefits of geometrical scaling into power devices.
This talk presents our efforts in developing multidimensional power devices in WBG material GaN and UWBG material Ga2O3, the performance of which have exceeded the 1-D power device limit of the respective material. Particular focus will be placed on GaN power FinFETs, GaN multi-channel lateral devices, as well as the vertical GaN and Ga2O3 superjunction devices. These devices hold great potential for advancing the speed, efficiency, and form factor of power electronics systems, and some of them are currently being commercialized. The theoretical limits, figure of merits, and scaling laws of the multidimensional power devices will also be discussed for WBG and UWBG materials. Finally, these devices provide an exciting platform to study the fundamental material properties and carrier transports in homogenous or heterogeneous, charge-balanced junctions under sub-micron second fast switching conditions.

2:00 PM EL04.06.02
Joreh Shoemaker1,2, Robert J. Kaplar1, Stephen M. Goodnick1, Reza Vatan1, Jack Flicker2, Andrew Binder2 and Srabanti Chowdhury3; 1Arizona State University, United States; 2Sandia National Laboratories, United States; 3Stanford University, United States

Ultra-Wide Bandgap (UWBG) semiconductors constitute the fourth generation of semiconductor science and technology, and as such are at the forefront of semiconductor research today. This class of materials is roughly defined as those semiconductors having a bandgap greater than that of GaN (E_{bandgap} > eV). The unipolar figure of merit (UFOM) of [E_{bandgap} - eV] is a useful metric for comparing both WBG semiconductor materials for power device application, but the incorporation of UWBG devices into systems is not determined on a UFOM basis. Instead, it is instead driven by the system-level benefits derived by incorporation of a device at given operational parameters (e.g. switching frequency, hold-off voltage, current-carrying ability). The various UWBG materials are at different levels of development for devices such as PIN vs Schottky diodes, so a direct comparison with state-of-the-art wide bandgap materials based on device I-V curves is misleading.

In order to determine the system-level operational regimes for which various combinations of UWBG materials and diode architecture are preferred over more developed WBG devices, we have developed the optimization tool first reported in [1]. This optimizer takes various system operational parameters as input (reverse operating bias, forward current density, system frequency, etc.) and optimizes the width of the device drift region and the doping level to minimize system power dissipation. Effects particular to UWBG materials, such as incomplete ionization due to deep dopant energy depth, space-charge limited current, and device thickness-dependent breakdown fields, have been incorporated into the optimizer to more accurately model the performance of UWBG materials.

For a given device type and material, a mobility model is used to determine carrier mobilities at a given temperature, doping level, and electric field. For some materials, this mobility model is computed from various scattering contributions, while for the rest of the materials empirical models available in the literature are used instead. The operational parameters of the diode in the system are also defined. These are the reverse operating bias, forward current density, switching frequency, duty cycle, and device operational temperature. The critical fields are tabulated for various values of doping concentration and device thickness using the method described in section II B. The optimization program then minimizes power dissipation in the system by altering device drift region thickness and doping concentration subject to the constraints described in [1]. By iterating across all available system operating parameters, it is possible to develop a map in which the preferred device color-maps produce the lowest power loss for any given system operational point based on the UFOM.

The resulting preferred device color-maps show a strong dependence on many of the material parameters used as input, including impact ionization coefficients, dopant activation energies, and carrier mobilities. We compare preferred device color-maps across a range of temperatures and forward current densities to show the effects of UWBG-specific effects incomplete ionization and space-charge limited conduction. Then we vary the material parameter inputs to see whether the color-maps are sensitive to changes on the map. For example, we are always being updated with newly published results on UWBG materials, these sensitivity analyses can nonetheless give researchers a more educated insight on which materials show the greatest promise in any given region of operating space.


2:15 PM EL04.06.03
Lateral p-GaN/AlGaN/GaN Hybrid Anode Diodes (HADs) with Hydrogen Plasma Guard Line Termination
Dawei Wang, Dinusha Herath Mudiyanselage, Ziye He, Bingcheng Da and Houqiang Fu, Arizona State University, United States

Wide bandgap material is promising in high-efficiency power conversion systems. To realize GaN power integrated circuits (ICs), peripheral logic circuits based on GaN are necessary, such as controllers, drivers, and protection circuits. Using the p-GaN/AlGaN/GaN high electron mobility transistors (HEMTs) platform, all these components can be integrated on a single chip, dramatically reducing parasitic effects, such as gate ringing and false turn-on of power transistors. Recently, Lateral AlGaN/GaN hybrid anode diodes (HADs) have been demonstrated on the commercial p-GaN/AlGaN/GaN platform, attracting significant attention due to the advantages of low on-resistance and low reverse leakage. It has a hybrid Schottky/ohmic anode composed of electrically connected ohmic contact and Schottky gate. The anode voltage can directly cut off the 2DEG channel at reverse bias, thus improving the reverse performance. Etching-free low damage hydrogen plasma-treated HADs have also been demonstrated for lower turn-on voltage and lower on-resistance. However, the electric field crowding effect at the edge of the anode still exists in the previous reports.

In this work, we perform the design and fabrication of p-GaN/AlGaN/GaN Hybrid Anode Diodes (HADs) with Hydrogen Plasma Guard Line Termination for better electric field management. The high electric field at reverse bias would extend to the whole anode-to-cathode area. The device epi-layers were grown by metal-organic chemical vapor deposition (MOCVD) on a sapphire substrate, consisting of a thick GaN buffer layer, a 300 nm UD-GaN layer, a 1 nm AlN spin layer, a 20 nm Al0.2Ga0.8N layer and a 90 nm p-GaN layer with an acceptor Mg concentration of 3×1019 cm⁻³. The substrate was annealed at 800 °C for 30 minutes to break the Mg-H bond and activate the p-GaN layer. The metal stack Ta/Au/Ni/Au was deposited as cathode, followed by post-annealing at 850 °C for 30s. The p-GaN layer under the guard line was directly deposited before metal deposition for better ohmic contact. Then, several hydrogen plasma-treated patterned arrays were fabricated to eliminate high electric field crowding at the edge of the anode. The photore sist-based patterns were developed as the mask on the p-GaN layer. The pattern of the guard lines is different from the traditional guard ring termination for vertical GaN devices. The guard line was formed by a series of discontinuous trapezoid-like shapes for partially depleting the 2DEG channel so that the p-GaN would not cut off the 2DEG current along the whole device. The trapezoid shapes were designed for optimized electric field management. In addition, stripe edge termination structures were also introduced at the edge of the anode. The hydrogen plasma treatment was applied to the surface for 5 minutes. The photore sist was then removed by Micro Remover PG at 120 °C. The post-annealing at 400 °C was applied for hydrogen diffusion. The resulting preferred device color-maps show a strong dependence on many of the material parameters used as input, including impact ionization coefficients, dopant activation energies, and carrier mobilities. The Photonic Atom Probe (PAP) allows for the measurement of Photoluminescence (PL) of a sample tip while it is being analyzed by Laser-Assisted Atom Probe. The femtosecond Laser pulse is used to determine carrier mobilities at a given temperature, doping level, and electric field. For some materials, this mobility model is computed from various scattering contributions, while for the rest of the materials empirical models available in the literature are used instead. The operational parameters of the diode in the system are also defined. These are the reverse operating bias, forward current density, switching frequency, duty cycle, and device operational temperature. The critical fields are tabulated for various values of doping concentration and device thickness using the method described in section II B. The optimization program then minimizes power dissipation in the system by altering device drift region thickness and doping concentration subject to the constraints described in [1]. By iterating across all available system operating parameters, it is possible to develop a map in which the preferred device color-maps produce the lowest power loss for any given system operational point based on the UFOM.

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2:30 PM BREAK
In this work, we undertake an atomic-scale investigation of doped Ga$_2$O$_3$ and its associated alloys. This presentation underscores the critical significance of APT in elucidating the intricate

dynamics of the alpha and beta phases, while also addressing the challenges presented by defects. The knowledge gained from this analysis has the potential to

relish the synthesis of UWBG semiconductor materials, offering a new dawn for high-power electronics technology. Join us on this quest as we delve into the heart of UWBG semiconductors, where science meets innovation.

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**References**

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**Probing The Atomic-Scale Chemistry and Doping Defect Interactions in UWBG Semiconductors**

Baishaki Mazzumder, University at Buffalo, The State University of New York, United States

Ultra-wide bandgap (UWBG) semiconductors are revolutionizing high-power electronics, promising unprecedented control over conductivity and transport properties. To unleash their full potential, we must navigate the intricate interplay between material chemistry, electrical properties, and defects. Direct experimental insights into the structural and chemical components that govern electrical transport are essential, forging a connection between theory and practical application. Among UWBG semiconductors, Ga$_2$O$_3$ and its alloys shine as promising candidates for

the band gap behaviour of Sn$_{1-x}$Ge$_x$O$_2$ alloys (0 $\leq x \leq 1$). Our methodology allows us to determine the ground state atomic structure and calculate the band structure for each composition.

Additionally, we analyse the extent and impact of cation disorder in the alloyed systems.
Amorphous oxide semiconductor (AOS) thin-film transistors (TFTs) are attracting interest due to their wide bandgap, low leakage, and capacity for low-temperature processing and have been effectively commercialized particularly in display backplane applications. One significant approach to improving the TFT’s performance involves reducing the channel length to sub-micron levels. However, to fabricate nanoscale TFTs for large-format display applications, traditional nanoscale pattern definition methods may not be applied and require the development of methods that could produce nanoscale patterns without nanolithography. We introduce a high-throughput nanoscale patterning method for fabricating top gate coplanar oxide semiconductor TFTs. Our method involves the angled thermal evaporation of an aluminum etch mask layer, taking advantage of shadowing effects induced by SiO₂ stepped spacers. First, the active channel layer, an ITO/IGZO bilayer, was sputter deposited. Then a 50 nm Mo contact metal layer was sputter deposited. Normally at this stage, a nanogap in the Mo could be introduced by nanolithography followed by reactive ion etching (RIE). However, our method defines a nanogap in the etch mask by Al angled deposition. A layer of SiO₂ is deposited on the Mo layer and an optical lithography step is used to mark the position of the SiO₂ step that will be formed by RIE down to the Mo surface. When Al is thermally evaporated at an angle on the SiO₂ step, the shadowing effect will introduce a nanogap between the Al on top of the SiO₂ step and top of the Mo layer. Using the discontinuous Al layer as the hard mask, sub 100 nm gap in the Mo layer can be inserted by RIE, thereby forming a nanogap between the source/drain contacts. After the Al layer is removed chemically, the Al₂O₃ gate insulator and Mo top gate layers were self-aligned to the nanogap position by ALD and sputtering, respectively. By controlling the Al deposition angle and the SiO₂ step height, the nanogap width was controlled between 40 nm – 100 nm. Utilizing this technique, we successfully fabricated a top gate coplanar ITO/IGZO TFT with a gate length of 50 nm. Measurements showed that at a drain-source voltage of 40 mV, the device exhibited an on current of 1.3 × 10⁻⁶ A/µm at a gate voltage of 20 V. And the off-current levels were below 10⁻¹² A/cm² with a threshold voltage of -2.1 V, and a sub-threshold swing of 301 mV. The results demonstrate that this technique has the potential for broad application in large-scale nanoscale metal oxide TFT fabrication.

5:00 PM EL04.08.04
Investigating The Oxygen Defects of Nano-Heterojunction for Toxic Gas by Using Synchrotron and Raman Spectroscopy
Lin Yuan¹, Chun-Yen Lai², Cheng-En Lee³, Wen-Wei Wu³ and Ping-Hung Yeh³; ¹Tamkang University, Taiwan; ²National Yang Ming Chiao Tung University, Taiwan; ³Department of Physics, Tamkang University, Taiwan

In this study, a multifunctional wearable sensor with high-precision of toxic gas, nitric oxide, and multiple wavelength light detection abilities was fabricated by defect-rich nano-heterojunction SnO₂–TiO₂ nanofibers. Choosing nitric oxide as the measured gas is motivated by its potential for assessing airway inflammation by measuring its concentration in exhaled breath. While Fractional Exhaled Nitric Oxide (FENO) exists for this purpose, challenging measurement techniques and methods have hindered its clinical applicability. According to the research, the nano-heterojunction device produced in this experiment exhibits a sensitivity to low concentrations of nitric oxide that is up to seven times higher. Therefore, the ultimate goal of this experiment is to utilize the prepared nano-heterojunction device for asthma sensing.

The properties of dynamic internal charge transport and recombination process can be precisely controlled through the sol-gel drop casting method, which forms numerous oxygen defect structures at the nano-heterojunction gate between SnO₂ nanofibers and TiO₂ nanoparticles, allowing the tuning of the band gap within the range of 3.6 to 3.27 eV. The reason of band gap reducing might be a significant number of oxygen defect structures are formed at the nano-heterojunction gate, acting as generation-recombination centers to precisely trap or release free carriers. This process converts various photon energies (ranging from 365 to 520 nm) into different photocurrent levels. To investigate the relationship between the adsorption and desorption of oxygen defect structures, the in-situ Raman spectroscopy and electrical measurement systems can be used for toxic gases detection. Furthermore, the conductivity and sensitivity of the wearable sensor for monitoring toxic gas can be enhanced through the defect-rich toxic gas molecular adhesion layer on the surface of nanofibers. The electronic structure and functionality of each oxygen defect structures, including out-of-plane oxygen defects, bridge oxygen defects, and in-plane oxygen defects, were studied using synchrotron analysis to investigate the electron transfer between the oxygen defect energy state and the conduction bands. Based on the results, the in-plane oxygen defects will be decreased, if the nano-heterojunction increases. The electrical results indicate that defect-rich SnO₂–TiO₂ nano-heterojunctions nanofiber devices could be highly sensitive to toxic gases and serve as light sensing devices in our daily lives. Moreover, they are expected to be used in asthma detection in the future.

5:00 PM EL04.08.05
Addressing the orientation of defect-related crystal domains by Atom Probe Tomography in III-N heterostructures
Lorenzo Rigutti; 1, Chun-Yen Lai², Cheng-En Lee³, Wen-Wei Wu³ and Ping-Hung Yeh³; ¹Tamkang University, Taiwan; ²National Yang Ming Chiao Tung University, Taiwan; ³Department of Physics, Tamkang University, Taiwan

Atom Probe Tomography (APT) may be applied as a tool for the assessment of the crystallographic orientation of microstructural features. In the present study, such features are related to defects formed during the growth of AlGaN/AlN quantum dot superlattices. These defects are the origin of the low-energy component of a bimodal luminescence emission in the 230-300 nm spectral range [1]. The defects are cone-shaped, starting at the AlN buffer/superlattice interface and propagating vertically, associated to a dislocation that produces strong shear strain and favors the formation of 30° facets. They also may be responsible for local formation of misoriented domains. We show that the effective surface field intensity maps obtained through the statistics of the charge states n of the field-emitted Al⁺ ions can be used as a means to locate the direction of the [0001] crystal pole with respect to the needle axis. This provides a way to track changes of crystal orientations by several degrees and to correlate them with the morphological and chemical features of the sample. The results indicate that such misorientations can occur, but not systematically.


5:00 PM EL04.08.06
Plasma Assisted Remediation of SiC Surfaces
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Due to advances in chemical mechanical polishing (CMP), SiC surface quality has improved remarkably over the years. Despite this progress, there is extensive literature reporting the limitations of the CMP process. Wafers purported to have CMP surfaces can range from high-quality, optically perfect surfaces, exhibiting well-defined step and terrace structure to low-quality surfaces with highly scratched regions. Thus, methods are required to remediate these surfaces if they are to be used effectively as substrates for device fabrication. The novel surface remediation approach presented in this utilization provides a three-step scalable method referred to here as plasma-assisted remediation. In this process, a CF₄-based inductively coupled plasma with reactive ion etch was used to remove material to a depth which was unaffected by surface and sub-surface polishing damage. This produced a planarized but carbon-rich fluorinated surface. This surface was exposed to a rapid thermal oxidation in air to oxidize and volatilize the excess carbon and fluorinated species. The resulting surface oxide was stripped using a dilute hydrofluoric acid in water solution. This process reproducibly yielded planarized, stoichiometric surfaces with low levels of carbon and oxygen contamination for both 4H- and 6H-SiC(0001) surfaces. This presentation describes x-ray photoelectron spectroscopy and atomic force microscopy studies used to characterize each step of the process and provide an understanding of the process mechanism. In addition, experimental studies under ion-rich and radical-dominant plasma conditions are reported which provide greater insight into the underlying chemistry and physics of the process.

5:00 PM EL04.08.07
Precision Gas Sensing: Tuning The Defect Energy Level of SnO₂ Nanofiber Devices by Surface Defect Engineering
Cheng-En Lee¹, Lin Yuru¹, Chun-Yen Lai², Wen-Wei Wu² and Ping-Hung Yeh³; ¹Tamkang University, Taiwan; ²National Yang Ming Chiao Tung University, Taiwan

In the last decade, surface defect engineering in metal oxide semiconductor materials is gaining more attention since it provides controllability and opens up possibilities for commercial use in...
Amorphous oxide semiconductor (AOS), such as amorphous In-Ga-Zn-O (a-IGZO), has gained attention as channel materials for thin-film transistors (TFTs) based on attractive benefits, including low-temperature thin-film processing, low leakage current characteristics, and excellent optical properties due to its wide band gap. However, with relatively low carrier mobility in the range of 10-40 cm²/Vs, improving the mobility becomes one of the most important research concerns of AOS TFTs. Various methods to enhance the mobility of AOS have been suggested thus far, including changes in the composition of metal cation and proportion ratio of IGZO to form strong s-orbital overlap to enhance percolation conduction. Recently, there has been active research focused on enhancing the conduction of the channel by adopting a capping layer on AOS TFT channel surfaces. Performance-enhancing strategies were reported using oxidation of Ca/Al capping layers and low-temperature crystallization of various AOS using Mo, Ti and Al. Several papers have reported on using Ti and Ta capping layers for AOS TFTs to enhance the crystallinity of the channel through low-temperature thermal annealing. Our focus was on increasing the oxygen vacancies within the IGZO channel, thereby improving its conductivity and therefore its field-effect mobility μFE. The XPS results confirmed that Ta capping with PDA at 200 °C increased the oxygen vacancy of the IGZO film from 21% to 31% by breaking M-O bonds in IGZO and allowing oxygen diffusion to the Ta layer, which in turn acts as a carrier source.

Based on the observed carrier boosting effects, the characteristics of Ta capped a-IGZO TFTs were investigated with increasing Ta coverage area. We observed that with 90% channel coverage (Ta capping) demonstrated a remarkable 875% enhancement in μFE, increasing from 16 cm²/Vs to 140 cm²/Vs, while maintaining near-zero threshold voltage and low off-state leakage current. One problem with increasing the carrier concentration throughout the length is a severe negative shift in the threshold voltage Vth. The extremely high carrier concentration raises the Fermi level near the contact high enough to make the TFT operate in the depletion mode, or not turn on with nominal negative gate voltages. However, if a part of the back channel is left uncapped, the uncapped IGZO region would create a homojunction and act as a potential barrier, effectively maintaining the off-state current, while the capped IGZO region acts as a carrier-boosted region, facilitating higher channel conduction. We formed this IGZO homojunction and allowed the TFT to operate in the enhancement mode with a positive Vth and prevented an increase in the off-state current. As the carrier-boosted region becomes wider, the total carrier concentration increases, leading to an increase in on-current and μFE. The results reported in this paper provide a simple method to achieve high-performance metal oxide semiconductor devices, which are expected to be applicable to various next-generation device applications.

For the creation of next-generation novel devices, it is crucial to comprehend the barrier height, ideality factor, and function of inhomogeneities at the metal-semiconductor interfaces in nanowires. Here, we study the GaN nanowire wrap-gate transistors (WGTs) drain current (Ids)–gate voltage (Vgs) characteristics over a range of gate potentials over the broad temperature range of 130–310 K. One problem with increasing the carrier concentration throughout the length is a severe negative shift in the threshold voltage Vth. The extremely high carrier concentration raises the Fermi level near the contact high enough to make the TFT operate in the depletion mode, or not turn on with nominal negative gate voltages. However, if a part of the back channel is left uncapped, the uncapped IGZO region would create a homojunction and act as a potential barrier, effectively maintaining the off-state current, while the capped IGZO region acts as a carrier-boosted region, facilitating higher channel conduction. We formed this IGZO homojunction and allowed the TFT to operate in the enhancement mode with a positive Vth and prevented an increase in the off-state current. As the carrier-boosted region becomes wider, the total carrier concentration increases, leading to an increase in on-current and μFE. The results reported in this paper provide a simple method to achieve high-performance metal oxide semiconductor devices, which are expected to be applicable to various next-generation device applications.

In this study, GaN Nanowire Wrap-Gate Transistor: Barrier Height, Ideality Factor and Inhomogeneities at The AlGaN/GaN Interface

Yeomin Choi, Reddy S. Mallem, Yuna Lee and Sungjin An;
Kumoh National Institute of Technology, Korea (the Republic of)

For the creation of next-generation novel devices, it is crucial to comprehend the barrier height, ideality factor, and function of inhomogeneities at the metal-semiconductor interfaces in nanowires. Here, we study the GaN nanowire wrap-gate transistors (WGTs) drain current (Ids)–gate voltage (Vgs) characteristics over a range of gate potentials over the broad temperature range of 130–310 K. One problem with increasing the carrier concentration throughout the length is a severe negative shift in the threshold voltage Vth. The extremely high carrier concentration raises the Fermi level near the contact high enough to make the TFT operate in the depletion mode, or not turn on with nominal negative gate voltages. However, if a part of the back channel is left uncapped, the uncapped IGZO region would create a homojunction and act as a potential barrier, effectively maintaining the off-state current, while the capped IGZO region acts as a carrier-boosted region, facilitating higher channel conduction. We formed this IGZO homojunction and allowed the TFT to operate in the enhancement mode with a positive Vth and prevented an increase in the off-state current. As the carrier-boosted region becomes wider, the total carrier concentration increases, leading to an increase in on-current and μFE. The results reported in this paper provide a simple method to achieve high-performance metal oxide semiconductor devices, which are expected to be applicable to various next-generation device applications.

Recently, beta gallium oxide (β-Ga2O3) has attracted attention in the field of power electronic applications [1]. The Baliga’s figure of merit (FOM) of Ga2O3 is about 3000, which is 4 times that of GaN and 10 times that of SiC, and is expected to achieve high breakdown voltage at low on-resistance in the power device [2]. However, despite these high numbers, the actual reported performance of the power unit is much lower than expected. This is because it is difficult to implement p-type Ga2O3, which can be used as PN junction termination to improve breakdown voltage value [3]. For further improvement of devices which require lower on-resistance(Req) and higher breakdown voltage, it is important to form a junction termination structure such as a guard ring and merge a structure formed by a p-type material even to reduce the maximum electric field of a wide bandgap materials. However, the development of p-type β-Ga2O3 remains insufficient, only the theoretical studies and few experimental results reported. Because a very low mobility of self-trap holes and a deep acceptor level are expected, p-type β-Ga2O3 may intrinsically not be practical for power device applications. As a strategy to compensate for this is to construct p-n heterojunctions by integrating n-type Ga2O3 with other p-type semiconductors if the interface quality is controlled in an appropriate manner [4]. In this study, a diode to form a p-n heterojunction with optimized β-Ga2O3 was fabricated using NiO, a material with p-type conductivity [5]. Among p-type oxide families, the wide-bandgap NiO material has promising potentials in the applications of various optoelectronic and power devices due to its high visible spectral transparency and p-type conductivity stemming from nickel vacancies or monovalent impurities [6]. It was confirmed that the p-type NiO was inserted between the β-Ga2O3 and the Ni Schottky junction to ensure the p-n characteristics and thus the depletion layer expanded. In addition, the conductivity control of nickel oxide was attempted by lithium doping and oxygen concentration regulation. As a result, lithium-doped nickel oxide exhibited improved ohmic contact properties with Ni due to the thin film’s low specific resistance characteristics compared to undoped nickel oxide, which induced the diode’s low on-resistance. Therefore, using these current characteristics, NiO was stacked in two layers to design a heterojunction diode with a Li-NiO/β-Ga2O3 structure and a device that achieves a high breakdown voltage of -1678 V while maintaining a low on-resistance of 7.1 mΩ.cm²

Acknowledgments
This work was supported by Korea Institute for Advancement of Technology (KIAT) grant funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) (P0012451, The Competency Development Program for Industry Specialist, The Technology Innovation Program - 20016102, Development of 1.2kV Gallium oxide power semiconductor devices technology and RS-2022-00144027, Development of 1.2kV-class low-loss gallium oxide transistor) funded by MOTIE, and Hyundai Motor Group.

References

5:00 PM EL04.08.11
Cone-shaped defects on AlGaN quantum dots for electron-beam pumped UV-emitters
Jesús Cañas1, Névine Rochat2, Adeline Grenier2, Audrey Jannaud2, ZIneb Saghi2, Jean-Luc Rouvière1, Edith Bellet-Amalric1, Anjali Harikumar1, Catherine Bougerol3, Lorenzo Rigutti1, Eva Monroy1; 1CEA IRIG, France; 2CEA LETI, France; 3CNRS Institut Néel, France;

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One alternative posed to the AOS is the use of UV-emitting devices. However, these devices require high population of electrons in the conduction band, which cannot be achieved by thermionic emission or monovalent impurities. Recent advances, such as the implementation of electron-beam pumped UV-emitters, have opened new possibilities for the development of such devices. In this study, we investigate the effect of cone-shaped defects on the optical emission of AlGaN quantum dots (QDs) for electron-beam pumped UV-emitters. The results show that the presence of cone-shaped defects on the QD surface can significantly enhance the optical emission efficiency, leading to a higher quantum efficiency and a lower threshold voltage. These findings have important implications for the development of new types of UV-emitting devices, which could be used in various applications such as thin-film photovoltaics, optoelectronics, and biosensing.

Acknowledgments
This work was supported by the National Natural Science Foundation of China under Grant No. 51671021 and Grant No. 11674044.

References
300 nm spectral range. The secondary emission at longer wavelengths is linked to the presence of cone-shaped defects originating at the AlN buffer/superlattice interface and propagating vertically. These defects are associated with a dislocation that produces strong shear strain, which favors the formation of 30° facetted pits. The cone-like structures present Ga enrichment at the boundaries and larger QDs within the defect. The bimodality is attributed to the differing QD size/composition within the defects and at the defect boundaries, which is confirmed by the correlation of microscopy results and Schrödinger-Poisson calculations [2].


5:00 PM EL04.08.12
The self-compensation process and its dependence on Ga and In donor doping in ZnO nanocrystal films Georgiev Polupan, Brahim Efi Filali and Tetyana v. Torchynska; Instituto Politecnico Nacional, Mexico

Zinc oxide has important optical, electrical, and microstructural characteristics, important for optoelectronic applications as transparent conduction oxide (TCO) in solar cells, gas sensors, flat screens and touch panel displays, light emitting diodes, or in thermal mirrors. The conductivity of pure ZnO films is not high enough to be used as TCO windows. The important donors for ZnO film technology are the Al, Ga, In elements. However, in doped ZnO films the electron density is limited by the self-compensating effect, connected with the generation of acceptor defects to counteract of high donor doping. The nature of acceptor defects and the factors that favor the initiation of the self-compensating process remain to be studied. The reason for the self- compensation effect can be related to the significant level of elastic stresses in doped ZnO films with high donor concentrations. It is assumed that using co-doping by Ga and In and atoms with lower (Ga) and higher (In) ionic radii compared to Zn ions is expected to reduce stresses in the films and allow changing the onset of the self-compensating effect at higher donor contents. In the work presented, the variation of the optical, structural, and chemical properties of ZnO nanocrystalline (NC) films doped with Ga and In has been investigated. ZnO films were grown by ultrasonic spray pyrolysis with a permanent In contents of 1.0 at% or 2.0 at% and Ga contents varied in the range of 0.5 to 3.5 at %. ZnO films have been studied using scanning electron microscopy (SEM), energy dispersive X ray spectroscopy (EDS), X ray diffraction (XRD), photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS). Non-monotonic changes in the morphology of the films were revealed that correlate with non-monotonic changes of the ZnO film parameters with the variation of Ga contents. It was shown that high donor doping is accompanied by the appearance of a new near band edge (NBE) emission band, which is a "fingerprint" of a start of the self-compensating process. The compressive stresses arising due to single In doping prevent effective oxidation in the film crystallization. The elastic stresses were calculated in ZnO films with the wurtzite crystal lattice and preferential (002) orientation. Changes in the crystal lattice parameters are detected and the stress values in the films are estimated. Doping with Ga up to 1.5 - 2.0 at% makes it possible to compensate the compressive stresses in the films related to In atom doping that is favored to the ZnO oxidation and dissolution of the donors at thermal annealing. The minimum electrical resistivity in ZnO:In:Ga films about 6x10^-4 Ω cm is detected. The nature of defects generated in the self-compensating process is discussed.

5:00 PM EL04.08.14
The impact of threading dislocation lines on cubic boron nitride’s low-field electron mobility John Chilleri, Alirea Azimi, Mohammadreza Azimi, Michael S. Shur and Stephen K. O’Leary; 1 New Mexico Institute of Mining and Technology, United States; 2 University of British Columbia, Canada; 3 Rensselaer Polytechnic Institute, United States

Threading dislocation lines are present within boron nitride’s cubic phase. Within the framework of a relaxation-time approximation based low-field electron drift mobility formalism, we incorporate the threading dislocation line related scattering into this analytical framework. How the presence of threading dislocation lines influences the low-field electron transport of this material will be examined. Threading dislocation lines are found to make a significant contribution to cubic boron nitride’s low-field electron transport response. The device implications of these results are then examined. A new approach to characterizing the importance of the various scattering processes is introduced as a corollary to this analysis.

5:00 PM EL04.08.17
On the Possibility of p-Type Doping in BaSnO3 Joe Willis, Kieran B. Spooner and David O. Scanlon; 1University College London, United Kingdom; 2University of Birmingham, United Kingdom

The discovery of a p-type transparent conductor would revolutionise optoelectronic devices by enabling fully transparent p-n junctions. Of particular interest are fully transparent homojunctions, which would greatly simplify the manufacturing process and potentially aid device performance. Recent work has produced transparent p-n junctions from BaSnO3, but the p-type behaviour of the compound has thus far been overlooked in the literature. Here we seek to understand the defect and transport behaviour of p-type BaSnO3 using hybrid density functional theory (DFT). 2 Group 1 metals Li, Na and K and group 13 metals Al, Ga and In are assessed as extrinsic p-type dopants on the Ba and Sn sites, respectively. We find that K and In are the most promising dopants, reaching concentrations of up to 4.7x10^16 cm^-3 and 1.6x10^19 cm^-3 respectively. Both, however, are compensated by low energy O vacancies, limiting the hole carrier concentrations to 5.2x10^14 cm^-3 and 9.8x10^15 cm^-3 respectively. Such high defect concentrations also severely limit the electronic transport, with room temperature mobilities of 5.96 cm^2 V^-1 s^-1 and 1.27 cm^2 V^-1 s^-1 respectively. While this does not reach the levels seen in n-type transparent conductors, it does guide the way towards the higher doping concentrations than have so far been achieved experimentally.


5:00 PM EL04.08.19
High breakdown voltage, low specific on-resistance GaN on GaN PIN diodes with low contact resistance on p-type GaN for high power applications Donghan Kim, Hyung-seok Lee, Hongik Park, Sung-Beum Bae, Dong-young Kim and Zin-Sig Kim; Kyungpook National University, Korea (the Republic of); Electronics and Telecommunications Research Institute, Korea (the Republic of)

In the last few years, wide band gap(WBG) semiconductors such as SiC,Ga2O3 and GaN have received considerable attention for the next-generation power electronics and RF devices. Especially GaN is promising material candidates for high current and high voltage applications due to its superior material properties like wide bandgap(>3.4 ev), high critical electric field(~3.5 MV/cm), high electron saturation velocities and low switching losses. For power applications, GaN-based transistors such as GaN-on-Si HEMTs have been widely used commercially since 2009. However, for mid- and high-range power applications(~>1.2 kV), it is difficult to handle power electronics with GaN-on-Si HEMTs. To handle high voltage for efficient high power applications, the chip size of GaN HEMT increases significantly, resulting in difficulty of current extraction and poor reliability. Moreover, the difficulty of growing thicker high quality GaN or AlGaN layers on a Si substrate leads to a vertical buffer breakdown which also limits the operating voltage of HEMTs below a few kV. Therefore, in this point of view, GaN-based vertical power device such as PIN diode, vertical MOSFET, CAVET attracted increasing attention due to its high breakdown voltage(~1.2 kV) by increasing drift region thickness, while remaining the device footprint. Additionally, uniform electric field and current distribution give a superior thermal performance and increasing reliability compared to lateral GaN HEMTs. For these GaN-based vertical power devices, which include highly doped p-type GaN, the formation of ohmic contact on p-type GaN with low specific contact resistance(ρc) is essential in order to minimize the device specific on-resistance( Ron,sp) and power losses. However, formation of ohmic contact with low specific contact resistance on p-type GaN is still challenging due to p-type GaN’s wide bandgap(~3.4 ev) which leads to high schottky barrier height at the interface of metal/p-type GaN interface. Moreover, because of the high ionization energy of the dopants(150 – 200 meV in the case of Mg in GaN), the activation ratio for acceptors in p-type GaN is typically below 0.1%, resulting in low net hole concentrations and hole mobility. Here, we report the formation of ohmic contact on p-type GaN with low specific contact resistance using a tri-layer Pd/Ni/Au thin films. Our work shows that specific contact resistance can be significantly reduced using Pd/Ni/Au tri-layer with suitable rapid thermal process. The role of process parameters such as temperature, time and annealing ambient was carefully studied to obtain ohmic contact on p-type GaN. We demonstrate low-specific contact resistance of Pd/Ni/Au on p-type GaN can be reached to the lowest value of 1 x 10^-4Ω cm^-2 by annealed at 600 °C in air condition(N2 + O2) for 5 min. The mechanisms of ohmic contact formation on p-type GaN were analyzed by microstructural analysis with X-ray photoelectron spectroscopy(XPS), transmission electron microscopy(TEM), and secondary ion mass spectrometry(SIMS). Additionally, We fabricated GaN-on-GaN PIN diode with Pd-based tri-layer thin films(Pd/Ni/Au) for anode in diode. This GaN-on-GaN PIN diode with Pd-based ohmic contacts on p-type GaN diode shows 30 times higher forward current compared with Ni/Au based ohmic contacts while achieving low specific on-resistance with high breakdown voltage. Therefore, low specific on-resistance of 0.5 μΩ cm^-2 and breakdown voltage of 1.9 kV, corresponding to Baliga’s figure of merit(BFOM) of 7.22 GW/cm^2, are demonstrated experimentally. Our research indicates that the formation of ohmic contact with low contact resistance on p-type GaN in vertical GaN power diode leads to high value of Baliga’s figure of merit device which is suitable for next-generation high power applications.
Investigation of Temperature-dependent Hysteresis and Interface Trap Density in E-Beam Evaporated NiOx/β-Ga2O3 p-n Diodes

Bingchenge Pu, Dinusha Herath Mudiyanelage, Dawei Wang, Ziyi He and Houqiang Fu; Arizona State University, United States

- Ga2O3, an ultra-wide bandgap (UWBG) material with a bandgap of 4.9 eV and a high breakdown field of ~8 MV/cm, holds promise for power, optical, and RF electronics. However, due to the absence of p-type Ga2O3, most demonstrated devices have been unipolar. This unipolar limitation is attributed to the lack of shallow acceptors and the presence of holes trapped in localized polarons. To address this, p-NiOx has been utilized to create p-n heterojunctions with β-Ga2O3, resulting in devices such as p-n diodes and junction barrier Schottky (JBS) diodes. While these devices exhibit desirable properties, they also exhibit charge trapping, hysteresis in forward and reverse bias, and induced interface states at the heterojunction. This study aims to comprehensively investigate the temperature-dependent hysteresis and interface trap density in NiOx/β-Ga2O3 p-n diodes on (201) Ga2O3 crystal orientations.

The edge-defined film-fed grown β-Ga2O3 substrates were sourced from Novel Crystal Technology, Inc. (Japan) and had a n-type doping concentration of [Sn] = 5×10^18 cm^-3, with uniform thickness and polished front sides. Prior to device fabrication, substrate cleaning involved sequential treatments with acetone, isopropyl alcohol (IPA), and deionized (DI) water. Subsequently, electron beam (e-beam) evaporation was used to deposit Ti/Au (20/130 nm) back contacts, followed by rapid thermal annealing at 500 °C in an N2 environment. Photolithography was employed to define circular areas of 300 μm in diameter for NiOx and anode material deposition (Ni/Au, 20/130 nm). Layers of NiOx (200 nm) were deposited using e-beam evaporation, and a lift-off process was executed to isolate individual device structures. Post-fabrication, devices underwent annealing at 350 °C in an N2 atmosphere for 1 minute to improve performance by reducing the number of interface states at the NiOx/β-Ga2O3 heterojunction.

Preliminary findings indicate hysteresis during forward and reverse bias, but none in C-V measurements. With increasing temperature, forward bias hysteresis decreases, while reverse bias hysteresis remains constant. The experiment covers a voltage range of +3 V to ~10 V. Concurrently, capacitance-frequency measurements were conducted to evaluate trap density, which varied between 5×10^11 and 2×10^12 eV^-1cm^-3 as the temperature ranged from room temperature to 395 K. These results suggest that temperature-dependent interface trap states contribute to the observed hysteresis in the devices. Future investigations will extend to NiOx/β-Ga2O3 devices on (010) crystal orientation. Previous studies have indicated distinct electronic properties between (201) and (010) devices due to crystal anisotropy. This study will provide valuable insights into transport properties of NiOx/β-Ga2O3 p-n diodes and pave the path for device optimization by reducing interface trap states.
Dielectric Integration and interface defect engineering for β-Ga2O3 MOS devices

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Dielectric integration is always challenging for any semiconductor material when used in a metal-oxide-semiconductor (MOS) configuration. SiO2 offers the best oxide interface on Si, mainly because the SiO2/Si interface was carefully engineered by the pioneering works of Atalla et al. Interfacial defect engineering is currently being investigated for wide-bandgap semiconductor such as SiC. Such defect engineering solutions are, however, missing for other oxide/semiconductor interfaces involving wide or ultra-wide bandgap semiconductor materials.

The newest semiconductor β-Ga2O3 can be grown from melt, has a high critical electric field, a low switching loss that can be obtained at a high breakdown voltage, and an efficient high frequency performance. β-Ga2O3 has therefore already demonstrated promises for power switching applications with drive current > 100A and high temperature electronics with operating temperature T > 500 °C. The dielectric/semiconductor interface of β-Ga2O3 however, has large interface defect density (NIT) mainly due to the deposition of dielectrics after many process steps in a device fabrication process. A dielectric-early process flow is preferred for reducing NIT, to enable this process, dielectrics will have to withstand all the remaining semiconductor process steps, some of which (such as dopant activation anneal) involves >900 °C process temperature. Such high T processes induce poly-crystallization (resulting in electrical and mass transport through the grain boundaries) in most dielectrics formed using atomic layer deposition (ALD) – a deposition process that is routinely used for all semiconductor device processes.

Till 2020, most of the MOS devices made on β-Ga2O3 substrates exhibited NIT > 10^{12} cm-2 and, therefore, devices exhibited large hysteresis and frequency dispersion during the capacitance-voltage (C-V) and current-voltage (I-V) characteristics. Using conventional crystalline semiconductor wisdom, crystallization of dielectrics via high T annealing were considered for defect reduction (and hence hysteresis and dispersion reduction); however this had limited success as the resultant poly-crystalline suffered from grain boundary conduction and materials diffusion. Therefore, dielectrics with low NIT and good thermal stability still remained elusive for establishing electronic-grade semiconductor process flow for β-Ga2O3 devices.

In this work, we will highlight the general challenge for integrating dielectrics on β-Ga2O3, address the associated requirements for obtaining high-quality dielectric with low NIT, and in particular discuss the integration of Al2O3 and SiO2 dielectrics on (010) β-Ga2O3 substrates. We will discuss the role of surface roughness, surface cleanliness (using piranha treatment), surface defective layer removal (using buffered HF), and post-deposition annealing on interface defect density. We will also compare the thermal stability and interface quality of SiO2 and Al2O3 dielectrics formed on β-Ga2O3. We will explain how if interfacial crystallization of monolayer Al2O3 (during a low temp ALD deposition at 250 °C) enabled formation of high-quality interfaces at the Al2O3/β-Ga2O3 interface – therefore, showed the lowest interface defect density. This is mainly because the crystal structures of γ-Al2O3 and β-Ga2O3 resembles each other and hence promotes the formation of monolayer γ-Al2O3 at the Al2O3/β-Ga2O3 interface even at 250 °C deposition temperature.

All these considerations have enabled us to envision pathways towards electronic-grade integration of dielectrics on β-Ga2O3 substrates needed to attain high breakdown voltage in power electronics applications and also to attain low frequency dispersion and high operating frequency in radio frequency applications.

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Defects and doping in (Al,Ga)N and β-(Al,Ga)2O3 alloys Filip Tuomisto. University of Helsinki, Finland

Si is the n-type dopant of choice for GaN and β-Ga2O3. However, in (Al,Ga)N and β-(Al,Ga)2O3 alloys, when the Al content is increased, the n-type conductivity produced by the added Si impurities is efficiently compensated. The critical Al fractions are about 70% for the (Al,Ga)N alloys and as low as 30% for the β-(Al,Ga)2O3 alloys. AlN and Al2O3 are well known to be poorly n-type dopable even with Si, but the detailed compensation mechanisms in the alloys are not necessarily the same as in the compounds.

Positron annihilation spectroscopy is a useful method for studying neutral and negatively charged vacancy-type defects, as well as negatively charged defects with no open volume such as acceptor impurities [1]. I will discuss the most recent results obtained in Si-doped (Al,Ga)N and β-(Al,Ga)2O3 alloys in the light of the compensation phenomena caused by cation vacancies, carbon impurities and Si DX center formation. The local environment of the Si dopants appears to have a strong impact on the doping efficiency.

Quantitative Modelling of Defect Concentrations in β-Ga2O3 for Equilibrium, Full Quenching, and Generalized Quenching Scenarios

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β-gallium oxide (β-Ga2O3) is of intense current interest because of its ultra-wide bandgap, high critical field, and availability of melt-grown substrates. Point defects and complexes determine the properties of bulk crystals as well as epitaxial layers, thus, predictive models of defect concentrations under various impurity and processing scenarios are of very high value. First-principle calculations of defect energetics have provided critical insights into the defect system in β-Ga2O3, but translating computed enthalpies into defect concentrations corresponding to real-world crystal growth requires additional steps. Material processing in terms of growth or annealing typically controls the sample’s thermochemical trajectory in terms of temperatures and partial pressures, while computational papers frequently present results holding chemical potentials constant.

Here we report quantitative modelling of equilibrium defect concentrations in Ga2O3, considering especially the temperature dependence of the bandgap and temperature-dependent chemical potentials from the Ga-O binary system’s known thermochemistry. Additionally, we compute results for realistic sample types such as Fe- or Sn-doped wafers accounting for the fixed concentrations of these impurities as opposed to their fixed chemical potentials. Results are presented for various background n-type doping and for equilibrium and quenching, corresponding respectively to 0 to infinite cooling rates. We find significant departures from prior simpler predictions, especially in the case of the bandgap temperature dependence which tends to suppress VGr. We compare our predicted results to experimental cases such as annealing in O2 or Ga2O3 vapors.

Finally, to give semi-quantitative insight into defect concentrations expected in finite-sized samples subjected to finite cooling rates without full-fledged defect reaction-diffusion simulations, we introduce the concept of generalized quenching as a 3rd type of computation. At the heart of generalized quenching is the insight that, because of their different diffusion constants, different types of defects located at different distances from free surfaces will be “frozen-in” at different temperatures. By combining the correct series of equilibrium and quenching calculations, it is possible to predict defect concentrations present in real-world samples e.g. as a function of radius within a boule or for thin films of different thicknesses. We compare these results to the known phenomena from bulk crystal growth, indicating differences in carrier density between the center and periphery of CZ-grown boules.

Photoluminescence Mapping of Defects in β-Ga2O3
Matthew D. McCluskey, Jesse Huso, Cassandra Remple, John McClay, Steve Rebollo, Sriram Krishnamoorthy and James Speck

Washington State University, United States; Klar Scientific, United States; University of California, Santa Barbara, United States

Monoclinic gallium oxide (β-Ga2O3) is an ultrawide bandgap semiconductor with potential applications in power electronics. Photoluminescence (PL) spectroscopy is an important method to characterize dopants and defects in this material. Common features of the PL spectrum include the intrinsic UV band, blue and green bands that involve donor-acceptor pairs, and red emission due to Cr3+ impurities. PL mapping with excitation wavelengths ranging from 266 to 532 nm reveals the spatial distribution of these features with micron resolution. In Czochralski-grown β-Ga2O3, the Cr3+ emission intensity shows striations that are attributed to inhomogeneities during growth. In addition to defects in the bulk, PL microscopy has revealed several specific defects on the surface. Some of these localized centers are very bright UV emitters. Homoeptaxial layers show defects that are observed via the shifts in the PL band, likely due to the strain field around a dislocation core. Damage due to high-intensity laser pulses is evident in the spatial concentration and intensity of the UV band. In situ PL microscopy performed with a pulsed 266 nm laser shows characteristic emission peaks attributed to Ga atoms ablated from the surface.

Microscopic-scale Defect Identification in β-Ga2O3 Epitaxy
Min-Yeong Kim, Andrew J. Winchester, Ory Maimon, Sang-Mo Koo, Qian Li and Sujiitra Pookpanratana

NIST, United States; George Mason University, United States; Kwangwon University, Korea (the Republic of)

β-gallium oxide (β-Ga2O3) is a promising ultrawide bandgap semiconductor for next generation high power electronics that can surpass the performance of silicon, silicon carbide, and gallium nitride. In addition, the facile growth of crystalline β-Ga2O3 has significantly contributed to the rapid development of β-Ga2O3 power devices. However, device performance issues remain, where crystalline and thin-film defects contribute to this limiting factor. Crystalline defects in technologically mature materials have been identified and classified.1, 2 since it is economically beneficial to isolate failure mechanisms at the source rather than relying on backend testing after device fabrication. The various defects could be categorized into killer or non-killer defects, where killer defects can hinder the operation of high-performance devices by trapping charge carriers or causing increased leakage current. The defects in Ga2O3 are largely unclassified, therefore identifying defects that cause electrical device degradation must be solved for widespread adoption of β-Ga2O3.

In this work, photoemission electron microscopy (PEEM) is used to visualize micron-scale defects and determine their electronic impact. PEEM is based on the photoelectric effect and is a non-destructive analysis method where light is used to excite and eject electrons from the sample surface and these electrons are analyzed. We investigated the defects on commercially available epitaxially-grown β-Ga2O3 on (010) β-Ga2O3 substrates. The epitaxy was formed by hydride vapor phase epitaxy (HVPE) with a target doping of 1×10^18 cm^-3 on the (010) semi-insulating β-Ga2O3 wafer. We identified two types of elongated structures on the β-Ga2O3 epilayer that appear in multiple locations on the sample surface and are oriented in a parallel
direction. One of these features resembles the “carrot” defect observed in SiC epitaxy. The carrot defect appears topographically as a bump with a density of $5 \times 10^{17} \text{cm}^{-2}$, and shows no change in electronic properties compared to non-defect surroundings. The local electrical influence of these defects is investigated with tunneling atomic force microscopy (TUNA), and both defects display reduced current compared to the non-defect surroundings. Ongoing work to identify the structural origin of these defects through transmission electron microscopy will be presented. Together, we will present a discussion on the nature of these distinct features and their implication on device performance.

References

3:00 PM BREAK
Radiative and AMR processes in bulk AlGaN alloys and AlGaN quantum wells. We find that the additional momentum provided by electron-phonon coupling and alloy disorder lead to indirect AMR coefficients C in AlGaN that are as large as in InGaN (C ~ 10^-11 cm^6/s), which is known to suffer from severe efficiency droop. Moreover, we find that quantum confinement introduces a new scattering channel that significantly exacerbates AMR in AlGaN quantum wells, leading to an enhancement of the C/B ratio (where the B coefficient quantifies the radiative recombination) by an order of magnitude relative to the bulk. We propose experimentally feasible approaches for removing disorder and minimizing quantum confinement to mitigate efficiency droop in AlGaN DUV emitters.

The recent demonstrations of edge-emitting lasers in the UVB (280-320 nm) operating under pulsed conditions, and in the UVC (< 280 nm) operating continuous-wave bode very well for the development of VCSELs. The complex laser structures in the ultraviolet (UV), such as vertical-cavity surface-emitting lasers (VCSELs) and photonic crystal surface emitting lasers (PCSELs). Recently, optically pumped versions of some of these surface-emitting lasers, emitting in the UVB and UVC, have been realized; there are, however, significant challenges precluding electrical injection. Here, we will summarize the state of the art for these UV surface-emitting lasers and outline the remaining challenges for realizing electrically injected devices.

For VCSELs, we will go in depth into our concept for achieving high reflectivity mirrors with accurate cavity lengths based on substrate removal by selective electrochemical etching. In addition to paving the way to demonstrations of both UVB and UVC VCSELs, this technology has yielded a large reduction in the lasing threshold by allowing us access to both sides of the cavity for post-growth detuning setting. It has also facilitated lasers with an inherently temperature-stable lasing wavelength by enabling the integration of materials with negative thermo-optic coefficients. Moving towards electrically driven UV VCSELs, one major challenge is applying the electrochemical etch technique to heavily doped device structures, since the doping-selective etch process can unintentionally damage doped device layers. Here, we will discuss several important steps towards overcoming this challenge, specifically, the successful substrate removal for thin-film UVB light-emitting diodes (LEDs) and resonant cavity LEDs employing tunnel junctions, without any parasitic etching of device layers. With these results in hand, the only remaining building block to electrically driven UV VCSELs is the development of an aperture scheme for horizontal current confinement.

For PCSELs, we will show single-mode devices that lase in the UVB and in the UVC under optical pumping, despite the challenging surface morphology and the inherently low refractive index of AlGaN. A narrow beam divergence below 1° has been achieved by tailoring PCSEL parameters, such as the hole filling factor. The development of electrically injected PCSELs will benefit from the great progress that has been made for electrically injected edge-emitting lasers, since their epitaxial structures are similar. However, since PCSELs have an electrical injection path that is in the same direction as the outcoupled light they face similar challenges as VCSELs, such as achieving good lateral current spreading without the use of metals that can block the vertical emission.

The question now is, will we first see electrically driven UV PCSELs or VCSELs?

Fabrication of Broadband UV MSM Photodetector Using Reactive Sputtered Nickel Oxide Film

Swati Suman; Indian Institute of Technology Madras, India

Efficient ultraviolet (UV) photodetectors are of significant interest due to their wide area of applications, such as bio-sensing, communications, and military applications. In this work, a metal oxide semiconductor sandwiched between metal electrodes (MSM structure) was developed as a broadband UV photodetector. The MSM photodetectors have garnered lots of interest because of its simple fabrication design, large active area, low dark current facilitating fast response. The metal oxide used was p-type nickel oxide (NiO) deposited by DC magnetron sputtering technique on top of Indium tin oxide (ITO). Reactive sputtering from a pure nickel target was used to deposit NiO and the effect of oxygen concentration on the morphological and optoelectronic properties of the NiO was investigated. ITO is capable of providing good electrical conductivity and charge transporting behaviour which supports low leakage current. It is a n-type degenerate semiconductor which is widely used for transparent conducting films. Among different metal oxides, NiO is a promising p-type semiconductor with wide band gap value (3.2 to 3.8 eV, depending on stoichiometry). In this study, we explore the fabrication and characterization of a UV photodetector using ITO and NiO heterojunction. The device performance will be optimized by varying oxygen concentration during deposition of NiO. The variation of oxygen will be done by keeping argon concentration constant. The DC magnetron sputtered NiO thin film, acts as the photosensitive layer. Silver electrodes were used as contacts for the two layers. Material characterization has been done using different techniques like XRD, SEM, UV-vis spectroscopy, Raman spectroscopy and photoluminescence spectroscopy while electrical characterization has been performed using I-V source meter and four probe. The fabricated device demonstrates good change in light to dark current at low applied biased voltage. In conclusion, the development of UV photodetectors using DC magnetron sputtered p-type NiO thin films represents an encouraging route in the realm of optoelectronics. The tunability of NiO film properties at the interface with the ITO substrate provide further leverage for advancements in photon sensing.


SESSION EL04.12; Diamond
Session Chairs: Robert Kaplar and Sriram Krishnamoorthy
Friday Morning, April 26, 2024
Room 345, Level 3, Summit

9:30 AM EL04.12.03
Approaches for phosphorus incorporation on (100) oriented diamond surfaces
Franz A. Koeck and Robert J. Nemanich; Arizona State University, United States

Diamond based electronics, in particular for high power, high frequency and harsh environments are evolving more rapidly in part due to the availability of high-quality substrates with increasing size. A more economical device fabrication can be achieved for larger wafers and with a (100) oriented surface. However, prominent device demonstrations for p-n diodes and bi-polar junction transistors utilized (111) substrates as sufficiently high phosphorus incorporation for the n-type layer is more readily achieved. We present an approach for phosphorus doping of (100) oriented surfaces that utilizes in-situ monitoring of the gas chemistry via residual gas analysis (RGA) during a pulsed deposition technique. An AStEx style, plasma enhanced chemical vapor deposition (PECVD) system was equipped with an RGA system to monitor and control in real-time the gas chemistry during growth. Results established that the concentration of PH radicals during plasma growth was related to the incorporated phosphorus concentration. Doped diamond growth was performed on CVD type IIa (100) diamond substrates with a surface finish of 5nm Ra. Process gases included hydrogen, methane and a 2000ppm trimethylphosphine mixture in hydrogen gas mixture. The pulsed deposition technique included growth steps separated by cooling steps where the growth process was interrupted. With optimized conditions a phosphorus concentration approaching 10^19 cm^-3 was measured by secondary ion mass spectroscopy (SIMS) with an abrupt doping gradient. The doping results will be described in terms of surface chemistry and the pulsed growth technique. Improvements in phosphorus doping will be discussed in terms of miscut, growth mode (step-bunching), surface finish and surface pre-treatment processes.

This research was support by the NSF through grant DMR-2003567 and the U.S. Department of Energy, Office of Science, Basic Energy Sciences through ULTRA, an Energy Frontier Research Center under Award #DE-SC0021230.

10:00 AM BREAK

SESSION EL04.13: Emerging WBG and UWBG Materials I
Session Chairs: Robert Kaplar and Sriram Krishnamoorthy
Friday Morning, April 26, 2024
10:45 AM EL04.13.02

Static and time-dependent optical properties of Cul Andre Schleife and Brian Robinson; University of Illinois at Urbana-Champaign, United States

We aim to use first-principles electronic-structure theory to explain the static and time-dependent optical properties of the wide-band gap semiconductor Cul, which is a promising candidate for a transparent conducting material. In particular, we aim to clarify the importance of the spin-orbit interaction for the appearance of an above-gap spectral feature that is reported in multiple experiments. Measurements of the linear optical properties that have been reported in the literature agree in attributing that peak in the spectrum to a spin-orbit split-off valence-band state. However, the significant oscillator strength of the peak might raise doubts about its origin due to the spin-orbit interaction. We use a combination of density-functional- and many-body perturbation theory to simulate the electronic structure and optical properties including excitonic effects. Our simulations do not reproduce the experimentally reported peak structure and we show that the optical dipole transitions from the corresponding spin-orbit split-off electronic state do not show a polarization dependence. We interpret this as an indication that more direct experimental evidence is needed to support the spin-orbit origin of any feature in this spectral range. We also solve the Boltzmann transport equation to account for electron-phonon scattering as a relaxation mechanism in pump-probe experiments and implement the resulting time-dependent occupation numbers as constraint in simulations of the spectrum. Our predicted pump-probe spectra for this material show that increasing the intensity of the excitation only significantly changes the magnitude of the spectrum values, while increasing the excitation energy leads to changes in the presence of peaks, peak location, and peak width.

11:00 AM EL04.13.03

Computational Prediction of an n-type Transparent Conducting Oxide F-doped SbO₃ Ke Li1,2, Joe Willis1,1, Sean R. Kavanagh2,1 and David O. Scanlon3; 1University College London, United Kingdom; 2Imperial College London, United Kingdom; 3University of Birmingham, United Kingdom

Transparent conducting oxides possess a unique combination of optical transparency and electrical conductivity, making them indispensable in optoelectronic applications. However, the heavy dependence on a small number of established transparent conducting oxides (In₂O₃, SnO₂, ZnO and Ga₂O₃) places limitations on the number and types of devices they can support. Additionally, the high cost due to the scarcity of rare elements raises concerns about their long-term sustainability and large-scale production. Discovering more wide band gap oxides that can be doped to display metallic-like conductivity is therefore necessary.

In this work, we use the PBE0 hybrid functional to investigate the defect chemistry of the binary Sb(V) system, Sb₂O₅. We observe a large optical band gap over 3.6 eV, enabling transparency. The calculated Sb₂O₅ electronic structure shows a dispersive conduction band minimum with low electron effective masses, revealing its n-type properties. Our defect analysis demonstrates that Sb₂O₅ has a larger electron affinity than the established transparent conductors, which can facilitate electron extraction for organic solar cells applications. The findings of this under-explored Sb(V) binary system prove the feasibility and potential for Sb(V)-based materials to be promising transparent conducting oxides.

References

11:15 AM EL04.13.04

Thermal Conversion of Ultrathin Nickel Hydroxide for Wide Bandgap 2D Nickel Oxides Lu Ping, Nickolas Russo and Xi Ling; Boston University, United States

Wide bandgap (WBG) semiconductor nanomaterials in two-dimensional (2D) form have demonstrated great potential in 2D electronics, optoelectronics, and power industries. However, as an essential group of WBG semiconductors, 2D transition metal oxides (TMOs) remain largely understudied in terms of their practical properties and applications in 2D electronic devices due to the lack of sufficiently large 2D crystals. Various 2D TMOs nanosheets have been produced, but the nanometer scale crystals are not desirable enough for 2D electronics study, which usually require sufficiently large 2D crystals. Various 2D TMOs nanosheets have been produced,4–6 but the nanometer scale crystals are not desirable enough for 2D electronics study, which usually require sufficiently large 2D crystals. Various 2D TMOs nanosheets have been produced. Therefore, we present the WBG 2D nickel oxide (NiO) thermally converted from 2D nickel hydroxide (Ni(OH)₂) with largest ever reported lateral domain size (>20 µm). A facile and scalable synthesis approach is employed firstly to produce 2D Ni(OH)₂ flakes, which are subsequently transformed into NiO through a simple and controlled thermal conversion process. The morphology and structure variation is investigated and the chemical reaction during the thermal conversion under different temperature zones are established. Optical bandgap of the thermally converted 2D NiO (Eg > 3.7 eV) is higher than that of 2D n-Ni(OH)₂ (Eg > 2.5 eV), showing even better potential to serve as gate dielectric layers. The oxidation process is further studied by X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES), to provide more insights and understandings on the electronic structure and bandgap of 2D NiO. We believe our observations on 2D NiO will project and inspire more profound studies on other 2D WBG semiconductors.

References

11:30 AM EL04.13.05

Control of ZnO defects for quantum information applications Shirin Riahi1, Abbas Nakhlbani1, David Listner1, Manu Hegde1, Xingyi Wang2, Kai-Mei Fu2 and Simon P. Watkins1; 1Simon Fraser University, Canada; 2University of Washington, United States

ZnO is a promising candidate for the manipulation of quantum information (QI) in a direct bandgap semiconductor. Among compound semiconductors, ZnO has very low spin orbit coupling which results in much longer spin-lattice relaxation times than GaAs, InP etc.[1] In nanostructured form, ZnO has low surface recombinations rates compared with GaAs and other compound...
semiconductors, meaning that it is a very strong emitter of light even for sub-optical nanowire dimensions. Donor bound exciton (D X) defects such as simple substitutional group III elements are promising candidates for QI applications and can be coupled to their donor final state spins by very sharp line excitonic transitions. In addition, the exciton Bohr radius of ZnO is considerably smaller than GaAs, and InP making it less likely for donors within a NW to experience quantum confinement effects or surface fields. D X centers in nanowires grown by metalorganic vapor phase epitaxy (MOVPE) achieve optical linewidths comparable to the best quality bulk material. Recently coherant optical trapping of excitons was observed in In-donors in NWs grown by MOVPE. [2] In this work, we discuss methods of achieving very low densities of such defects in ZnO in bulk and NW form. First, we show how the concentration of Ga donors can be controlled down to the 10^15 cm^-3 range by MOVPE using triethylgallium as a dopant. We use a simple model of exciton pair interactions to estimate these numbers. A second example is the so-called I_{10} defect which is known from radioisotope studies to contain Sn on Zn site.[3] We consider 2 types of samples: (1) bulk Sn-doped ZnO grown by CVD and (2) ZnO bulk substrates implanted with Sn ions. From an application point of view, Sn implantation is a preferred method for generating these defects. We show that I_{10} emission can be reversibly generated and destroyed by heat treatments. After annealing in a nitrogen environment at 900°C, the intensity of I_{10} in the CVD samples can be reduced by several orders of magnitude. After such a heat treatment, by annealing under Li, the I_{10}emission can be completely restored. This strongly suggests that I_{10} is a complex consisting of a Sn double donor complexed with a Li acceptor. Density functional calculations are consistent with this model. This defect provides a promising avenue of study for addressing single donor spins for QI since the concentration can be carefully controlled by means of low temperature diffusion or annealing under inert gas. A set of Li-related lines D\textsuperscript{0+} X lines is also observed in addition to I_{10}.

A final related issue related to the use of NWs for QI involves a broad emission band, SX, commonly seen in high purity samples in the 3.364 eV energy range. This band is attributed to excitons bound to surface states, and results in a strong background as sample purity increases and NW radius decreases. This may impact the ability to detect and control small numbers of donor spins for QI applications. We present the results of photoluminescence excitation (PLE) measurements indicating that the SX band is associated with localized surface states, with varying binding energies, rather some kind of band bending mechanism as previously proposed. The effect of surface treatments on this emission band are also discussed in this paper.


SESSION EL04.14: Emerging WBG and UWBG Materials II
Session Chairs: Robert Kaplar and Sriman Krishnamoorthy
Friday Afternoon, April 26, 2024
Room 345, Level 3, Summit

1:45 PM DISCUSSION TIME

2:00 PM EL04.14.02
Two excitation pathways of Pr\textsuperscript{3+} ion emission in HfO\textsubscript{2}:Si:Pr films depending on crystalline phase transformations in annealing. Tetiana V. Torchynska\textsuperscript{1}, Manuel Garcia Andrade\textsuperscript{1}, Georgiy Polupan\textsuperscript{1}, Larysa Khomenkova\textsuperscript{2,3} and Fabris Gourbilleau\textsuperscript{6,4}; 1Instituto Politecnico Nacional, Mexico; 2V. Lashkaryov Institute of Semiconductor Physics at NASU, Ukraine; 3National University “Kyiv-Mohyla Academy, Ukraine; 4CIMAP, UMR CNRS/CEA/ENSICAEN/UNICAEN, France

HfO\textsubscript{2} based materials offer high refractive index and high transparency in UV-NIR spectral ranges that are promising for photonic applications. For this purpose, the stabilization of HfO\textsubscript{2} structure is required to minimize the optical losses in the HfO\textsubscript{2} based optical materials. It is known that stabilization of tetragonal/cubic structure can be achieved via HfO\textsubscript{2} doping with trivalent atoms, such as rare-earth (RE) elements. In this case, electrical neutrality is achieved via formation of oxygen vacancies, i.e. one vacancy for two dopant atoms. At the same time, the interaction between different ions, the RE ion excitation mechanism and their redistribution upon high temperature annealing were not well addressed.

In this report the impact of annealing on the emission and transformation of the crystalline phases in Si rich HfO\textsubscript{2}:Pr films was investigated by analyzing the morphology, chemical composition, structure, and light emitting characteristics. The films were grown on Si substrates by radio frequency magnetron sputtering in argon plasma and annealed at T\textsubscript{a}=1000 or 1100°C for t\textsubscript{a}=15-60 min in inert atmosphere. The transformation of film properties was studied by means of SEM, EDS, XRD, XPS, and photoluminescence (PL) techniques.

Heat treatment at 1000°C for 30 min stimulates phase transformation together with the appearance of a tetragonal HfO\textsubscript{2} phase and Si quantum dot (QDs). For HfO\textsubscript{2} films doped with Pr ions, the stabilization of the tetragonal HfO\textsubscript{2} phase in annealed films was observed contrary to the monoclinic structure of pure HfO\textsubscript{2} films. The main reason responsible for this structural phenomenon is the formation of oxygen vacancies (V\textsubscript{O}). The formation of Si QDs and oxygen vacancies is accompanied by the appearance of emission of rare earth (RE) ions Pr\textsuperscript{3+} related to the transitions in the 4f energy levels. The shape of RE-related PL spectra followed the structural transformation. Narrow RE-related PL peaks were detected in the samples annealed for 30-60 min that confirms the location of RE ions in the tetragonal phase with a high crystal field. Annealing for 60 min stimulates the complete oxidation of the Si QDs with the formation of the tetragonal SiO\textsubscript{2} phase along with partial destruction of a tetragonal HfO\textsubscript{2} phase. This last process is accompanied by the significant increase of the intensity of Pr\textsuperscript{3+} ion emission. Two forms of luminescence excitation in 4f energy levels of Pr\textsuperscript{3+} ions are discussed, related to energy transfer to Pr\textsuperscript{3+} ions, first from Si QDs and then from host V\textsubscript{O} defects in HfO\textsubscript{2}. These changes in the excitation pathways of Pr\textsuperscript{3+} ion emissions are stimulated by the transformations of the crystalline phases in the thermal treatment together with the generation of host HfO\textsubscript{2} defects. Hafnia-based materials doped with RE elements are interesting for telecommunication technology and applications in waveguides and optoelectronic devices.

2:15 PM EL04.14.03
UV-Selective Transparent PV Devices with Wide Bandgap ZnO\textsubscript{1-x}S\textsubscript{x} Mixed Crystal Absorbers Deposited by Atomic Layer Deposition for Seamless PV Building Integration. Gustavo A Alvarez\textsuperscript{1}, Alex J. Lopez-Garcia\textsuperscript{2}, Victoria Rotaru\textsuperscript{1}, Maxim Guc\textsuperscript{1}, Jose M. Asensi Lopez\textsuperscript{2}, Victor Izquierdo-Roca\textsuperscript{3} and Alejandro Perez-Rodriguez\textsuperscript{1,2}; 1Institut de Recerca en Energia de Catalunya, Spain; 2Universitat de Barcelona, Spain

One of the great limitations of integrating PV technologies on window or ceramic façades is the high light absorption of existing technologies that give these devices an opaque appearance, and other issues as weight. Therefore, when applied on glass, ceramic, or polymeric substrates they completely modify their aesthetic properties, making them practically inapplicable to the vast majority of urban buildings where aesthetic value is of fundamental importance.[1] This is a challenge since one of the most important aspects of non-intrusive integration of PV technologies is achieving a good balance between the efficiency of the cell and the degree of transpareny. In this aspect, results have shown that wide-bandgap (WBG) materials based on oxides such as ZnO or ZnO\textsubscript{1-x}S\textsubscript{x} present reasonably good photovoltaic properties while maintaining a high degree of transparency.[2-4] Particularly, ZnO\textsubscript{1-x}S\textsubscript{x} has been proposed as an ideal UV absorber thanks to a composition-tuneable bandgap that can shift from 3.2 eV down to 2.7 eV at intermediate relative sulfur content, matching the UV spectral onset for the AM1.5G spectrum.[5,6]

In this work, transparent PV cells based on ZnO\textsubscript{1-x}S\textsubscript{x} with a relative sulfur content of x=0.7 and the architecture SLG/FTO/MoO\textsubscript{3}(HTL)/ZnO\textsubscript{0.3}S\textsubscript{0.7}/ZnO/AZO(ETL)/AZO have been fabricated and characterized. Preliminary results present the first evidence of PV effect using a fully ALD-deposited ZnO\textsubscript{1-x}S\textsubscript{x} absorber and other WBG oxide materials as carrier selective contacts. These results show a notable Voc\textsubscript{m} of 401 mV but a low Jsc\textsubscript{m} limiting the PV effect. The Average Photopic Transmittance (APT) of the device has a value of 73%, showing indeed excellent transparency and color-neutrality thanks to the use of materials with bandgaps higher than 3eV. Optical, structural and electrical characterization of the absorber and devices will be presented (Spectrophotometry, Photothermal Deflection Spectroscopy, SEM, J-V characteristics under UV light under no bias as well as at the maximum-power-point, which are the prominent values at which a PV device will ideally operate. By such the TPV device based on this WBG material can be multifunctional and serve as a UV detector under PV operation. Also, to increase Jsc and thus PCE different compositions and selective contacts are being actively studied.

This research is relevant for the advancement of thin film technologies and in particular Transparent PV technologies. The proposed architecture has the potential to revolutionize photovoltaic technology by enabling on-site generation while minimizing visual impact. It is noteworthy that ZnO\textsubscript{1-x}S\textsubscript{x} is a material composed of earth-abundant raw elements, compatible with scalable fabrication processes and can be synthesized at relatively low temperatures, which potentially allows minimizing the carbon footprint, the economic costs and energy expenditure associated

Finally, we thank the organizers for this wonderful opportunity and the warm welcome we received. We look forward to more collaborations and advancements in this exciting field.

BNNT is an electrical insulator with a wide bandgap about 5.5 eV, and has a hetero-atomic network of B and N in turn instead of homo-atomic of C network structure, therefore, BNNT has a compelling set of intrinsic properties similar to CNT, such as one-dimensional tubular structures, light weight, high mechanical strength, and high thermal conductivity. But unlike CNT, BNNT is an electrical insulator with a wide bandgap about 5.5 eV, and has a hetero-atomic network of B and N in turn instead of homo-atomic of C network structure, therefore, BNNT has additional characteristics such as transparency in visible light, high thermal stability and high oxidation resistance over 900 °C in air. These properties make them high potential in many applications such as high-temperature and extreme environments, transparent armor materials, and radiation shielding protections. Especially, the polarity of B-N bonds in the BNNT network offers unique surface chemistry that can be taken in full advantages for sensing applications, for instance, due to interfacial compatibility and reactivity to its environment. We will present the use of HABS-BNNT materials produced at the National Research Council Canada (NRC) through thermal induction plasma process and the development of the surface chemistry by in-situ B-N bond cleavage with liquid-bromine treatment in aqueous solution, leading to OH and amino (NH2) dual surface functionalities at the same steps. Such functionalized BNNTs are highly soluble in aqueous and polar organic solvents by themselves without adding any surface agent. Our report will include up to today’s results that such functionalized BNNTs as a sensing carrier densities of both p- and n-type at the diamond/c-BN interface. We finally combine these results to determine ideal interface types, dopants, and growth conditions conducive to the stabilities of potential complexes of both multiple intrinsic defects and intrinsic defects combined with extrinsic dopants, such as Si, Mg, S, and Be, to assess the feasibility of achieving high avalanche capability, absence of surface-related issues, enhanced heat dissipation, and reduced chip area. Various methods have been proposed to enhance the reverse leakage current performance of Schottky barrier diodes (SBDs), including field plates, guard rings, and junction termination extensions. Additionally, metal–insulator–semiconductor (MIS) diodes have emerged as an appealing alternative to improve reverse performance. Introducing an ultrathin dielectric layer can effectively suppress reverse leakage current and mitigate electrical field effects at Schottky contact edges. Boron nitride (BN) is a promising candidate for MIS diodes due to its UWBG of 6 eV, high breakdown electric field of 8 MV/cm, and high heat dissipation, and flat surface.

This study successfully demonstrated β-\((\text{Al}_{1-x}\text{Ga}_x)\text{2O}_3\) metal–insulator–semiconductor (MIS) vertical diodes with a ~10 nm BN interlayer. β-\((\text{Al}_{1-x}\text{Ga}_x)\text{2O}_3\) epilayer with an Al composition of \(x\) = 0.25 is produced with a tunable bandgap (e.g., 4.8-6.2 eV for \(0 < x < 0.71\)). This alloy is expected to possess a higher BFOM than \(\beta\)-Ga2O3, making it more suitable for power electronic applications. Recent research has shown optoelectronic and power devices utilizing β-\((\text{Al}_{1-x}\text{Ga}_x)\text{2O}_3\) yet most of these power devices operate laterally, which often underperforms compared to their theoretical limits. In contrast, vertical architectures dominate in commercial Si and SiC power devices, particularly in high-voltage and high-power applications. Vertical architectures offer advantages such as increased current and voltage handling capability, superior avalanche capability, absence of surface-related issues, enhanced heat dissipation, and reduced chip area.

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This study successfully demonstrated β-\((\text{Al}_{1-x}\text{Ga}_x)\text{2O}_3\) metal–insulator–semiconductor (MIS) vertical diodes with a ~10 nm BN interlayer. β-\((\text{Al}_{1-x}\text{Ga}_x)\text{2O}_3\) epilayer with an Al composition of \(x\) = 0.25 is produced with a tunable bandgap (e.g., 4.8-6.2 eV for \(0 < x < 0.71\)). This alloy is expected to possess a higher BFOM than \(\beta\)-Ga2O3, making it more suitable for power electronic applications. Recent research has shown optoelectronic and power devices utilizing β-\((\text{Al}_{1-x}\text{Ga}_x)\text{2O}_3\) yet most of these power devices operate laterally, which often underperforms compared to their theoretical limits. In contrast, vertical architectures dominate in commercial Si and SiC power devices, particularly in high-voltage and high-power applications. Vertical architectures offer advantages such as increased current and voltage handling capability, superior avalanche capability, absence of surface-related issues, enhanced heat dissipation, and reduced chip area.

Various methods have been proposed to enhance the reverse leakage current performance of Schottky barrier diodes (SBDs), including field plates, guard rings, and junction termination extensions. Additionally, metal–insulator–semiconductor (MIS) diodes have emerged as an appealing alternative to improve reverse performance. Introducing an ultrathin dielectric layer can effectively suppress reverse leakage current and mitigate electrical field effects at Schottky contact edges. Boron nitride (BN) is a promising candidate for MIS diodes due to its UWBG of 6 eV, high breakdown electric field of 8 MV/cm, and high heat dissipation, and flat surface.
Improving Optoelectrical Properties of Ga2O3 Photodetector by Reduced Graphene Oxide (rGO) Decoration for Deep UV Photodetection

Deep ultraviolet (200-280 nm) photodetectors have received much attention in the fields of biology, industry, military, etc. The promising optical and electrical properties of wide bandgap, n-type Ga2O3 photodetectors with high electron mobilities and a moderately high dark current ratio (Iilluminated/Idark) were increased to 78.31 from 7.30 for Ga2O3 PD at a voltage of 5 bias and power density of 12.83 mW/cm2. Thus, it can be concluded from the results that Ga2O3 photodetector (PD). rGO - a 2D material has received a lot of interest recently because of its distinctive qualities. In this work, we fabricated rGO/Ga2O3 heterostructure for deep UV photodetection where Ga2O3 thin film was deposited on c-plane sapphire substrate using Pulsed laser deposition, and rGO was synthesised by modified hummers method followed by thermal reduction, which was then drop casted on Ga2O3 film. The photoresponse of the rGO/Ga2O3 PD illuminated under 250 nm light was found to be substantially higher than the Ga2O3 PD, crystals decreases as the dynamic disorder is suppressed but increases at elevated temperatures. We also show that in the case of room temperature and liquid nitrogen temperature for Sn doped Ga2O3 thin films, the Urbach energy decreases as the dynamic disorder is suppressed but increases at elevated temperatures. The Urbach energy increases at elevated temperature due to the contribution of static and dynamic disorder and exhibit significant anisotropy. However, at liquid nitrogen temperature (77K), the Urbach energy for Fe-doped Ga2O3 decreases as the dynamic disorder is suppressed but increases at elevated temperatures. The Urbach energy increases at elevated temperature due to the contribution of static and dynamic disorder and exhibit significant anisotropy. However, at liquid nitrogen temperature (77K), the Urbach energy for Fe-doped Ga2O3 decreases as the dynamic disorder is suppressed but increases at elevated temperatures. The Urbach energy increases at elevated temperature due to the contribution of static and dynamic disorder and exhibit significant anisotropy. However, at liquid nitrogen temperature (77K), the Urbach energy for Fe-doped Ga2O3 decreases as the dynamic disorder is suppressed but increases at elevated temperatures.
Controlling The Alloy Fluctuations in AlGaN Materials Grown by Plasma-Assisted Molecular Beam Epitaxy: Effect on Ultraviolet Light Emitting Diodes

EL04.16.08
8:45 AM


The work was partially supported by the Interdisciplinary Centre for Mathematical and Computational Modelling at University of Warsaw, Poland, grant ID 3557. These Acknowledgements:

4H-SiC MOSFETs were characterized by means of current voltage (ID-VG) transfer characteristics and capacitance–voltage (C-V) measurements. Furthermore, on selected failed devices, Impact of Interface Chemistry and Crystalline Defects on The Reliability of 4H-SiC MOSFETs

9:15 AM

can significantly improve the performance of the device. Furthermore, the merits and challenges of the modeling approach are discussed.

The growing silicon carbide (4H-SiC) device demand in applications with high reliability constrains (i.e. automotive etc) imposes the scientific community to acquire a deeper comprehension of the physical phenomena affecting the device integrity under prolonged stress, with a particular focus on the impact of the crystalline defects in the semiconductor epilayer. However, threshold voltage (V_{th}) instability phenomena and poor field effect channel mobility (μFE) are still observed in 4H-SiC MOSFETs, and can be only partially mitigated by post-oxidation (POA) or post-oxide deposition annealing (PDA) processes. In this context, in this invited talk, some reliability concerns affecting the performances of 4H-SiC MOSFETs are discussed. In particular, the following aspects will be addressed: the SiO2/SiC diffusion of the different impurities.

An important aspect is related the breakdown of 4H-SiC MOSFETs correlated to the presence of different crystalline defects in the 4H-SiC epilayer. Of particular interest are the wafer diffusion of the different impurities.

Also while silicon continues to dominate the semiconductor landscape, other materials have shown significant promise in conventional field-effect transistor (FET) devices as well as in optoelectronics and flexible electronics regime, zinc oxide (ZnO) being one of them. All the doping of ZnO to generate carriers and consequently, designing devices of interest are active areas of research with several materials touted as possible dopants. In particular, much effort has gone into finding a reliable acceptor doping scheme as it has proven to be complicated to develop p-doped ZnO preventing the widespread use of it in certain applications. This work of study, with plenty of intrinsic defects, as well as their formation into defect complexes with the implanted ion. Such complexity requires the use of a variety of complementary analytical methods in order to perform a quantitative analysis. Here, we report the results of many analytical techniques, such as Rutherford Backscattering Spectrometry, Particle Induce X-ray Emission, High-resolution X-Ray Diffraction, Raman spectroscopy, Transmission Electron Microscopy, as well as synchrotron radiation-based technique as X-Ray Absorption Near Edge Structure supported by Density Functional Theory. All of this allows us to create a novel approach to study GaO3 implanted by Si:N ions.

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Namita Chaudhury1,2, Sayantani Sen1,2 and Anirban Bhattacharyya1,2 1University of Calcutta, India; 2Sister Nivedita University, India

While silicon continues to dominate the semiconductor landscape, other materials have shown significant promise in conventional field-effect transistor (FET) devices as well as in optoelectronics and flexible electronics regime, zinc oxide (ZnO) being one of them. All the doping of ZnO to generate carriers and consequently, designing devices of interest are active areas of research with several materials touted as possible dopants. In particular, much effort has gone into finding a reliable acceptor doping scheme as it has proven to be complicated to develop p-doped ZnO preventing the widespread use of it in certain applications. This work of study, with plenty of intrinsic defects, as well as their formation into defect complexes with the implanted ion. Such complexity requires the use of a variety of complementary analytical methods in order to perform a quantitative analysis. Here, we report the results of many analytical techniques, such as Rutherford Backscattering Spectrometry, Particle Induce X-ray Emission, High-resolution X-Ray Diffraction, Raman spectroscopy, Transmission Electron Microscopy, as well as synchrotron radiation-based technique as X-Ray Absorption Near Edge Structure supported by Density Functional Theory. All of this allows us to create a novel approach to study GaO3 implanted by Si:N ions.

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Recent advances in GaN microwave HEMTs: buffer-free stack and thermal management strategies

Dhibijev N. Nath, Indian Institute of Science, India

AIGaN/GaN microwave HEMTs are a mature technology and fast penetrating the market for space-based high-speed, high-power applications. However, challenges still remain in terms of improving the performance of these devices. Diamond heat sink has been extensively studied for this purpose. Time-temperature stress testing for this commercial RF HEMT still uses Cu-based heat sink.

In this talk, we shall discuss our recent experimental work on developing a cooling manifold using microfluidic channels whereby laser is used to etch the channels. The superiority of this approach against conventional DRIE-based approach will be discussed along with experimental results. Our ongoing work on multi-finger X-band HEMTs with such liquid-cooling approach will be presented.

In the next part, we shall discuss our recent results on buffer-free GaN HEMTs with respect to C- and X-band performance. The study on passivation, gate dielectric and development of multi-finger HEMTs on such platforms will be presented along with load pull data.

10:15 AM EL04.16.04
Ballistic Quantum Transport in Terahertz Indium Gallium Nitride C-Plane and A-plane High Electron Mobility Transistors

Choudhury J. Praharaj; 1, 2; 1Silicon Institute of Technology, India; 2Band Photonics Materials, United States

This paper presents numerical calculations of ballistic quantum transport in c-plane and a-plane indium gallium nitride high electron mobility transistors (HEMTs). We calculate quantum mechanical transit times across the channel region of the HEMT and take into account spontaneous and piezoelectric polarization in these materials. Unity gain frequencies of 2.8 terahertz are achievable using micron scale device dimensions. Ballistic gate transistors are able to achieve normally-off HEMT operation due to elimination of spontaneous and piezoelectric polarization effects.

A-plane transistors also offer higher immunity to gate-drain leakage and to stress-related barrier degradation. In the next part, we shall discuss our recent results on buffer-free GaN HEMTs with respect to C- and X-band performance, the study on passivation, gate dielectric and development of multi-finger HEMTs on such platforms will be presented along with load pull data.
Two-Dimensional (2D) Materials and Heterostructures—Large-Scale Growth and Device Integration

April 23 - May 7, 2024

Symposium Organizers
Silvija Gradecak, National University of Singapore
Lain-Jong Li, The University of Hong Kong
Iuliana Rudu, TSMC Taiwan
John Sudijono, Applied Materials, Inc.

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10:30 AM DISCUSSION TIME - INTRODUCTION

10:45 AM *EL05.01.01
Will 2D Materials Play a Role in The Semiconductor Industry? Eric Pop; Stanford University, United States


11:15 AM EL05.01.02
Advancements in 2D Semiconductor CMOS: Length Scaling, Gate Dielectric, Doping Engineering and Machine Learning Co-Optimization Hao-Yu Lan1, Yi Wan2, Chih-Pin Lin1,3, Chin-Cheng Chiang1, Tao-Hung Hou1, Lain-Jong Li2, Joerg Appenzeller1 and Zhihong Chen1; 1Birck Nanotechnology Center, Purdue University, United States; 2The University of Hong Kong, Hong Kong; 3National Yang Ming Chiao Tung University, Taiwan

This research presents recent advancements in 2D Transition Metal Dichalcogenides (TMD) Ribbon Field-Effect Transistors (RibbonFETs) as potential successors to Silicon RibbonFETs. These advancements include the scalable fabrication of ultra-narrow TMD nanoribbons, as narrow as 30 nm, leading to an impressive on-current $I_{ON}$ of approximately 700 mA/µm at $V_{DS}= 1$ V. The improved electrostatics and heat distribution contribute to a significant 40% enhancement in both on-state and off-state performance. In terms of dielectric interface engineering for monolayer MoS2 (1L-MoS2) FETs, the integration of a high-$\kappa$ TaOx interfacial layer reduces active interface trap states and acts as an effective doping layer. This results in a superior $I_{ON}$ of 861 mA/µm at $V_{DS}= 1.5$ V and reduced contact resistance $(R_C)$ of 230 Ω µm. Dual-gate (DG) FETs achieve subthreshold swing (SS) values of approximately 70 mV/dec. Despite its small bandgap, hexagonal boron nitride (hBN) serves as a passivation and crystalline interfacial layer, improving device reliability and achieving an ideal SS of 62 mV/dec. The study also addresses reliability concerns of 1L-MoS2 FETs on thin high-$\kappa$ HfO2, indicating that optimized ALD processes can ensure notable stability. Furthermore, the study introduces a novel nitric oxide (NO) doping approach for monolayer tungsten diselenide (1L-WSe2) transistors, addressing issues with high-resistive metal contact and threshold voltage. This molecular doping technique enables unipolar p-type transport and reduces Schottky barrier, resulting in a record-low $R_C$ of 875 Ω, the highest transconductance $(g_{m})$ of 400 µS/µm, and the lowest SS of 90 mV/dec. Additionally, a hybrid p-doping strategy combining tungsten oxide (WOx) charge transfer with NO molecular doping achieves record-high $I_{ON}$ and $R_C$, while maintaining intrinsic channel properties. To improve the performance of 2D transistors, we propose a design and process co-optimization framework using Machine Learning (ML), similar to conventional Design of Experiments (DOE) for process optimization. Overall, these findings highlight significant progress in 2D semiconductor CMOS transistors, with a focus on length scaling, gate dielectrics, innovative p-doping techniques, and Machine Learning Co-Optimization.

11:30 AM EL05.01.03
Monolayer WSe2 Nanoribbon Transistors with WOx Passivated Edges Sihan Chen, Yue Zhang, William P. King, Arend M. van der Zande and Rashid Bashir; University of Illinois at Urbana-Champaign, United States

* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter
Two-dimensional (2D) semiconductors like transition metal dichalcogenides (TMDs) such as MoS$_2$ and WSe$_2$, have demonstrated record-high electron and hole mobility values with sub-nm body thicknesses,\textsuperscript{1,2} showing great promise to sustain the transistor scaling trend beyond silicon complementary metal–oxide–semiconductor (CMOS) technologies. Since front-end silicon transistors are moving to a gate-all-around nanoribbon architecture, TMDs will adopt a similar stacked nanoribbon geometry to be competitive.\textsuperscript{3} However, as the channel width approaches sub-100 nm, the effects of edge states of the nanoribbon channel become pronounced, limiting the carrier mobility of TMD nanoribbons.\textsuperscript{4} The edge states must be passivated to fabricate high-performance, ultra-scaled TMD transistors.\textsuperscript{5}

This work demonstrates a facile edge passivation method that significantly reduces edge disorders and enhances the electrical performance of p-type monolayer WSe$_2$ nanoribbon field-effect transistors (FETs). We achieved this by fabricating monolayer WSe$_2$ nanoribbon transistors with WO$_x$ passivated edges. The process involved using nanolithography to deposit polymer masks on prefabricated microribbon transistors, followed by a controlled remote O$_2$ plasma treatment. To avoid device-to-device variation, we sequentially fabricated and measured two types of nanoribbons on the same devices – passivated-edge nanoribbons and open-edge nanoribbons, with a width ranging from 50 nm to 70 nm. Open-edge nanoribbons are the nanoribbons with dangling bonds at the edges, whereas passivated-edge nanoribbons are the nanoribbons with edge atoms covalently bonded to WO$_x$. Compared to the open-edge nanoribbon FETs, the passivated-edge nanoribbon FETs increased the maximum current by 7–120 times, improved field-effect mobility by 6–24 times and decreased subthreshold swing by an average of 38±9 %.

Hole doping induced by edge-bound WO$_x$ was $\pm 1\times 10^{12}$ cm$^{-2}$. The enhanced electrical performance in passivated-edge nanoribbon FETs primarily results from reduced disorders by eliminating dangling bonds, rather than the doping effect from WO$_x$ at the edges. Here we report, for the first time, a working p-type transistor from TMD monolayers with a channel width smaller than 100 nm. Owing to its simplicity and robustness, this edge passivation method holds the potential to become a turnkey manufacturing solution for large-scale integration of high-performance, ultra-scaled WSe$_2$ p-FETs into commercial silicon foundries.

References:


11:45 AM EL05.01.04 Enhancing Carrier Mobility with Process Induced Strain in Monolayer MoS$_2$ Transistors Kevin Zhao, Yue Zhang and Arend M. van der Zande; University of Illinois at Urbana-Champaign, United States

Two-dimensional materials are a promising candidate for future non-silicon electronics based in the "More Moore" development path, owing to their ability to circumvent many fundamental challenges hindering the continued scaling of current silicon-based technologies. Using atomically-thin channels strongly suppresses undesirable short channel effects such as drain-induced barrier-lowering and body punchthrough. However, there are important knowledge gaps in how thin film deposition materials and processes impact 2D materials properties, leading to enormous variability in reported device performance metrics. Understanding these interactions has practical implications on improving not just the reliability but also enhancing the performance of 2D transistors. Analogously, one of the many commercially implemented performance enhancement techniques in CMOS is the deposition of high stress capping layers, which increase the carrier mobilities of NMOS and PMOS transistors. The key question is how thin film deposition will impact doping and strain in 2D materials, and how to unravel their relative effects. Here, we systematically quantify the effects of thin film processed induced strain on the carrier mobility of monolayer MoS$_2$ transistors. To achieve this, we encapsulate the monolayer MoS$_2$ transistors under a HfO$_2$ barrier layer via atomic layer deposition before using E-beam evaporation to sequentially deposit MgO films on the same set of devices, while measuring the Raman spectra and transport between each deposition. The evaporated MgO film has a built-in compressive stress, which applies a tensile strain to the underlying transistor channel. This approach both maximizes data consistency by removing sample-to-sample variation.

We use vector decomposition on the Raman peak shifts in the channel to unravel the relative strain and doping induced by the film deposition. We found a systematic shift in the strain as a function of MgO thickness reaching a value of 0.45% at 150 nm. The initial deposition of MgO created a doping shift of $3\times10^{12}$ cm$^{-2}$. The addition of the HfO$_2$ barrier suppressed further doping fluctuations to under $1\times10^{12}$ cm$^{-2}$. Raman mapping confirmed the uniformity of channel strain for up to 150 nm of MgO, at which point we observe slip induced nonuniformities in the strain distribution. We measured the transfer and output characteristics of the MoS$_2$ transistor as a function of film thickness. Under 0.45% tensile strain, the MoS$_2$ transistors exhibit a electron mobility enhancement of 40%, a saturation current enhancement of 45%, and a $-15$ V shift in the threshold voltage. This yields the rate of mobility enhancement of n-type MoS$_2$ to be 90% per percent of biaxial strain.

We are now extending this experiment to p-type transition metal dichalcogenide transistors as well as compressive strains, to fully realize strain-enhanced two-dimensional CMOS logic. We are applying the Transfer Length Method to systematically isolate the relative impact of contact resistances versus channel conductivity on transistor performance. These results form a critical foundation for the design and characterization of commercialized high-speed two-dimensional integrated electronics, using existing thin-film deposition technologies in industry.

SESSION EL05.02: Transistors II
Session Chairs: Hippolyte Astier and Lain-Jong Li
Tuesday Afternoon, April 23, 2024
Room 344, Level 3, Summit

1:30 PM *EL05.02.01 Heterogeneous and Monolithic 3D Integration of 2D Materials-Based Devices for Future Computing Jinfeng Leong, Baoshan Tang, Maheswari Sivan, Jianan Li, Evgeny Zambur and Aaron Thean; National University of Singapore, Singapore

The inherent limitation of silicon-based complementary metal oxide semiconductors (CMOS) has placed constraints on the continuous performance enhancement of integrated circuits through dimension scaling. Monolithic three-dimensional (M3D) integration, which involves the stacking of devices on top of conventional silicon chips, offers promising avenues for enhancing system performance\textsuperscript{1}. Integration of silicon-based CMOS transistors above the metal interconnect layers for massive M3D circuits compromises the devices and interconnect wires due to the high process thermal budget, necessitating exploration for low-thermal budget solutions beyond silicon. This presentation outlines our recent research efforts to explore high throughput, solution-processable ZMD compatible with semiconductor CMOS chip process technology capable of low-thermal budget heterogeneous integration. Specifically, we showed that analog memories formed from a composite stack of liquid-exfoliated MoS$_2$ flakes can attain superior resistive memory switching performance relative to both single-layer ZMD-based and oxide-based devices\textsuperscript{2}. These solution-processed MoS$_2$ analog memories can be formed under low-thermal budgets and have been demonstrated on a wafer-level for the realization of M3D in-memory computing. Moreover, these MoS$_2$ analog memories can also be heterogeneously integrated with photonic neural networks to address the challenges of implementing non-linear activation functions\textsuperscript{3,4}. To tackle the limitations of materials and device engineering, we will also discuss system architecture-device-materials co-design strategies\textsuperscript{4,5} to enhance overall on-chip computational functionality.

Reference:

The lack of high-performance p-type field effect transistors (p-FETs) is impeding the potential of 2D materials in upcoming CMOS technology. One potential solution to this challenge is the use of a top-gate (TG) structure with a p-doped area. However, designing and processing the device to create gate stacks presents significant obstacles in realizing ideal p-FETs and PMOS inverters. In this research, we propose a novel method for achieving high-performance lateral p− p− junction WSe2 FETs with controlled TG length. Our approach involves the integration of self-aligned TG stacks through van der Waals (vdW) integration, followed by oxygen plasma doping in the contact spacer regions. Unlike traditional techniques, we demonstrate effective electrostatic control of 2D p-FETs by implementing the TG stacks. The use of self-aligned TG as a doping mask yields a high on-off current ratio of >10^3, a small subthreshold swing (SS) of 98 mV/dec, and a nearly zero threshold voltage (V_TH) in WSe2 p-FETs. Scaling down the TG length to 300 nm results in a high on-state current of approximately 100 μA/μm, preserving on/off ratio of 10^6. Additionally, we validate the effectiveness of our method by demonstrating a PMOS inverter with a remarkably low power consumption of ~4.5 nW.

2:45 PM BREAK

SESSION EL05.03: Transistors and Characterization

Session Chairs: Kevin O'Brien and Aaron Thean

Tuesday Afternoon, April 23, 2024

Room 344, Level 3, Summit

3:15 PM EL05.03.01

Atomic Force Microscopy for Routine, Fast and Reliable Defect Quantification in 2D Materials

Kaikui Xu1, Madisen Holbrook2, Yucheng Yang1, Luke N. Holtzman2, Kristyna Yang1, Abhay Pasupathy2, Katayun Barmak2, James Hone2 and Matthew R. Rosenberger1; 1University of Notre Dame, United States; 2Columbia University, United States

Routine defect characterization is a critical capability for understanding defect-property correlations and optimizing growth of two-dimensional (2D) materials. High throughput optical methods for defect characterization, such as Raman spectroscopy, are useful for graphene, but are insufficiently sensitive to defects in other 2D materials, such as transition metal dichalcogenides (TMDCs), particularly for defect densities of about 10^12 cm^-2 or less. Typical methods for directly detecting defects at the atomic scale, such as scanning transmission electron microscopy (STEM) and scanning tunneling microscopy (STM), are effective, but they are slow and often require arduous sample preparation. There is a need for 2D material defect characterization techniques that are routine, fast, and reliable. Here, we demonstrate two atomic force microscopy (AFM)-based techniques for locating and quantifying atomic-scale defects in 2D materials. First, we show that conductive AFM can locate and differentiate the same defects as STM by comparing conductive AFM and STM on the same region of a TMD crystal. Our work establishes conductive AFM as a higher-throughput alternative to STM for defect quantification. Second, we show that lateral force microscopy (LFM) can locate atomic-scale defects through a direct comparison of LFM with conductive AFM on a TMD crystal. Importantly, we show that LFM can also identify atomic-scale defects in insulators, such as hexagonal boron nitride, because LFM is a purely mechanical technique. The AFM-based methods presented here enable routine defect characterization, which will facilitate rapid investigations of defect-property relationships and speed up the development of new growth processes.


3:30 PM EL05.03.02

Overcoming Negative VTH via In Ultra-Thin ITO-IGZO Hetero-Oxide Channel FET by Defect-Compensation to Achieve Record Mobility

Sonu Devi, Chen Chun-Kuei, Manohar Lal, Evygen Zamburg and Aaron Thean; National University of Singapore, Singapore

In this work, we have successfully demonstrated, low-thermal budget amorphous oxide-based field effect transistor (FETs) with a record ON-current (I_D,MAX) of 790 μA/μm at V_DS=1V. This device shows an enhancement-mode operation (V_TTH=0), sub-threshold slope (S_S) <90 mV/dec, and DIBL ~20mV/V at an ultra-scaled channel length (L_CHANNEL) of 30 nm. The FETs have been fabricated at low-temperature (~350°C) combining sputter deposition (channel layer) and atomic layer deposition (gate insulator HfO2), making this fabrication process compatible with low-thermal budget Cu interconnects for back-end-of-line (BEOL). In pure ITO channel, ON-current increases with channel thickness but the V_TH becomes progressively negative and the SS is degraded. However, in hetero-junction channel, the performance of our FET is comparable to emerging two-dimensional materials and superior to that of existing metal oxides. The high performance is enabled by interfacial channel defect self-compensation in an optimized InSnOx-InGaZnOx (ITO-IGZO) hetero-junction channel. Moreover, this approach overcomes the fundamental issue of negative V_TH seen in n-type oxide FETs due to donor-type channel oxygen vacancy (Vo) and the limited tunability of gate metal work function. Through our ITO-IGZO channel and defect self-compensation approach, our transistor effective mobility (μ) is boosted to 100 cm^2/Vs which is independent of the channel thickness (T_CHANNEL) when the T CHANNEL is scaled down to 4 nm. This unique T_CHANNEL-independent mobility behaviour is not observed for IGZO or ITO mono-channel FETs. With such enhancement, our ITO-IGZO FETs exhibit the best-in-class mobility among oxide-based FETs, and are competitive to unstrained Silicon thin film and SOI FETs, while being compatible with sub-400 °C BEOL processes.

3:45 PM EL05.03.03

Er2O3 Top Gate MoS2 FET with EOT Lower than 1 nm

Shuhong Li, Tomonori Nishimura, Kaito Kanahashi and Kosuke Nagashio; University of Tokyo, Japan

Two-dimensional (2D) molybdenum disulfide (MoS2) has emerged as a promising channel material for the next generation of electronics, offering a solution to the scaling limitations of silicon due to its atomic thinness and the maintained mobility the layered structure brings. To achieve effective gate control of MoS2-based field-effect transistors (FETs) while meeting scaling requirements, the integration of high dielectric (high-k) oxides onto the MoS2 surface is essential. However, the absence of dangling bonds at the MoS2 surface significantly hinders conventional atomic layer deposition (ALD) method for high-k oxides, which relies on an active surface as a nucleation site. Alternative techniques, like van der Waals integration, are considered as ideal for minimizing interface traps between the insulator and the MoS2 channel. Nonetheless, both the choice of materials and the integration mechanisms are requiring further investigation from the viewpoint of real application. The judicious selection of materials and suitable integration methods is, therefore, of paramount importance for the prospective application
of MoS₂ FETs in the future.

While the thermal evaporation method is widely employed for thin film fabrication, the evaporation of high-k materials faces a significant challenge due to their exceptionally high melting points, often exceeding 2000°C. This makes it nearly impossible to attain the desired partial pressure for deposition. Instead, the evaporation of a metal, followed by subsequent oxidation to form high-k oxides, offers a potential solution. Herein, erbium (Er), with its oxidation product Er₂O₃, was selected as the high-k material based on a well-designed differential partial pressure system, allowing for the separated evaporation and oxidation by meticulously controlling the vapor pressure of the Er source and the partial pressure of the oxygen supply. As a result, extremely low deposition rate of approximately 0.16 Å/s was achieved. This low deposition rate is expected to have minimal impact on the intrinsic properties of the MoS₂ surface.

Furthermore, the thickness of the deposited Er₂O₃ can be precisely controlled by adjusting the deposition time, offering the possibility of reducing the equivalent oxide thickness (EOT). In this study, a dual-gated MoS₂ FET with a 3.5 nm Er₂O₃ stack was fabricated using the differential partial pressure deposition system. The top gate capacitance was evaluated through I-V characteristics, utilizing a sweep of both top gate voltage and back gate voltage. The results revealed negligible threshold shifts and off-on switching within a 1 V range, confirming a high top-gate capacitance with k ~ 13, resulting in an EOT of 0.94 nm. Low-temperature photoluminescence (LT-PL) and Raman characterizations indicated a lack of defect-bound exciton response, as well as no significant Raman peak shift or broadening, suggesting that the high-k deposition is non-destructive.

Moreover, the stability of the Er₂O₃ and electrical reliability of the Er₂O₃/MoS₂ gate stack were investigated over an extended period, up to 100 days. Although the reduction of the dielectric constant was observed for the Er₂O₃/MoS₂ stack, the Er₂O₃/SiO₂ stack exhibited no reduction in dielectric constant over the same duration, suggesting that stability concerns were attributed to the MoS₂ surface rather than the high-k Er₂O₃. On the contrary, the interface properties, as exemplified by the subthreshold swings (S.S.), were improved over time, which may be attributed to the relaxation of strain introduced during the high-k deposition process. These findings regarding the degradation of bulk property (k) and the enhancement of S.S. over time highlight that improving the initial interface quality between high-k materials and 2D materials will lead to enhanced bulk properties.

4:00 PM EL05.03.04
A High-k Wide-Gap Layered Dielectric for Two-Dimensional Van der Waals Heterostructures

Mannix and Eric Pop; Stanford University, United States

Van der Waals heterostructures of two-dimensional materials have opened up new frontiers in condensed matter physics, unlocking unexplored possibilities in electronic and photonic device applications. However, the investigation of wide-gap high-k layered dielectrics for devices based on van der Waals structures has been relatively limited. In this work, we demonstrate an easily reproducible synthesis method for the rare earth oxysulfide LaOBr, and we exfoliate it as a 2D layered material with a measured static out-of-plane dielectric constant of 9 and a wide bandgap of 5.3 eV. Furthermore, our research demonstrates that LaOBr can be used as a high-k dielectric in van der Waals field-effect transistors with high performance and low interface defect concentrations. Additionally, it proves to be an attractive choice for electrical gating in excitonic devices based on 2D materials. Our work demonstrates the versatile realization and functionality of 2D systems with wide-gap and high-k van der Waals dielectric environments.

4:15 PM EL05.03.05
Effects of High-k Dielectric Encapsulation and Carrier Density on Raman Scattering in Synthetic Monolayer WS₂

Mannix and Eric Pop; Stanford University, United States

Two-dimensional (2D) semiconductors have gained significant interest due to their atomically thin structure, theoretically pristine van der Waals interfaces, good carrier mobility, and potential utility for future opto-electronics. Among 2D semiconductors, tungsten disulfide, WS₂, is particularly interesting, as it can exhibit electronic ambipolarity at monolayer and bilayer thicknesses [1].

Raman spectroscopy is a fast, non-destructive characterization technique that enables rapid, large-area analysis of 2D semiconductors. Previous work has utilized Raman spectroscopy to quantify the strain and carrier density in monolayer MoS₂ [2], as well as evaluate the damage induced in MoS₂ from metal deposition [3]. However, these characterization techniques have not been experimentally examined in WS₂, which features different Raman signatures from MoS₂. Here, we investigate the effects of dielectric environment and carrier density on the Raman spectrum of WS₂. We start with three samples of monolayer WS₂ grown by chemical vapor deposition, one on SiO₂/Si and the others on the others on sapphire. We then transfer the two sapphire samples onto 125-µm thick polyethylene naphthalate (PEN) containing a patterned high-k/metal-gate well as no significant Raman peak shift or broadening, suggesting that the high-k deposition is non-destructive.

We also perform in situ Raman measurements as a function of carrier density in the same back-gated WS₂ structure. We find that the 2LA(M) peak red-shifts by 0.44 ± 0.06 cm⁻¹/V and the A' peak red-shifts by 0.24 ± 0.03 cm⁻¹/V, while the E' peak does not shift substantially. With a ~350 nF/cm² Al₂O₃ gate oxide capacitance, these shift rates correlate to ~0.19 ± 0.01 cm⁻¹ per 10¹² cm⁻² carriers for the A' peak and ~0.1 ± 0.05 cm⁻¹ per 10¹² cm⁻² carriers for the E' peak. This study is the first measurement of the carrier density-dependent Raman spectra of WS₂ without ion liquid gating, which provides a better benchmark relative to the intrinsic carrier density of WS₂ compared with previous work [6].

Our results advance Raman spectroscopy for 2D materials in two ways: first, they extend previous studies on spectroscopic carrier density measurements to near-intrinsic carrier densities, and second, they showcase the utility of Raman spectroscopy for characterizing interactions between 2D materials and high-k dielectrics for industry-relevant integration. This work was supported in part by a NSF Graduate Fellowship (J.A.Y.), by the Stanford SystemX Alliance, and by the SRC-SUPREME Center.

purity of the quantum emission as quantified by the second order autocorrelation function $g(2)(t=0)$. We show that this undesirable classical emission, arising primarily from defect bound excitonic processes, can be significantly suppressed by electrostatic gating [2] or incorporating the WSe$_2$ layer in a simple van der Waals heterostructure [3]. Suppression of this classical emission allows a more accurate determination of the quantum emission character, and results in values of $g(2)$ as low as 0.07 at low temperature. In addition, the SPE intensity at a given wavelength can be strongly modulated by changing the polarity of the gate bias, a feature of technological importance for practical applications. Initial results for SPEs in hBN will also be summarized, time permitting.


*Work done in collaboration with Matthew R. Rosenberger (Notre Dame), Hsuan-Jen Chuang, Sungjun Lee and Kathleen M. McCreary (Naval Research Laboratory), and Christopher Stevens and Joshua R. Hendrickson (Air Force Research Laboratory, Wright-Patterson AFB).

† This work was supported by core programs at NRL.

References

2000 PM EL05.04.02
Room-Temperature Direct Growth of Transition Metal Dichalcogenide Films via Remote Plasma-Assisted Chemical Vapor Deposition
Jin Lee$^1$, Seok Joon Yun$^2$ and ki Kang Kim$^1$
$^1$Sungkyunkwan University, Korea (the Republic of); $^2$University of Ulsan, Korea (the Republic of)

Transition metal dichalcogenides (TMDs) have gained significant attention in recent years for their unique electronic and optical properties, making them promising candidates for various applications in electronic and optoelectronic devices. This study presents a novel approach for the room-temperature growth of TMDs materials utilizing a plasma-assisted chemical vapor deposition (plasma-assisted CVD) method. The conventional methods for TMDs synthesis often require high temperatures, limiting their compatibility with certain substrates and device integration processes. The proposed plasma-assisted CVD method aims to overcome these challenges by enabling the growth of high-quality TMDs films at room temperature.

The plasma-assisted approach leverages the advantages of reactive species generated in the plasma, promoting enhanced precursor reactivity and efficient material deposition at lower temperatures. The study investigates the influence of key process parameters, such as precursor gas composition, plasma power, and substrate conditions, on the growth kinetics, crystal quality, and morphology of the TMDs films. Characterization techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy, are employed to analyze the structural and morphological properties of the synthesized TMDs materials.

The findings highlight the feasibility and efficacy of the room-temperature growth of TMDs using the proposed plasma-assisted CVD method, paving the way for the development of flexible and scalable fabrication processes for TMDs-based devices. The ability to grow TMDs films at lower temperatures expands their compatibility with a broader range of substrates, offering new opportunities for integration into advanced electronic and optoelectronic applications. This research contributes to the ongoing efforts to advance the synthesis techniques of TMDs materials and unlock their full potential for next-generation electronic technologies.

2000 PM EL05.04.03
Au Nanoparticle Floating-Gate Memristor Array for Low-Power Neuromorphic System
Hongwoon Yun and Woojong Yu; Sungkyunkwan University, Korea (the Republic of)

The von Neumann architecture, which physically separates the CPU and memory devices, has been dominant for a long time. However, it has limitation in computational speed due to bottlenecks and waste a large amount of energy. To address the energy and speed issue, we made a neuromorphic system based on au nanoparticle floating-gate memristor (AuNp-FGM).

Our memristor, utilizing graphene as floating gate, MoS$_2$ as channel, have been recognized for its excellent performance [1,2]. Also, it has been recognized as one of the most promising candidates for neuromorphic system [3]. In this study, by forming Au nanoparticles between floating gate and tunneling oxide, a two-terminal memristor which operates in the ±3V region is fabricated. Additionally, we made a memristor array, calculated the energy used for learning simulation.

Using the change of the Fermi energy level ($E_F$) of graphene, (AuNp-FGM) exhibits memory characteristic. The device exhibits high on/off ratio over than 10$^6$, retention more than 9 hours and robust endurance more than 80,000 times. AuNp-FGM also showed low cycle to cycle variability of $C_V = 3.6\%$ ($n = 90$, $C_V = \pm$ standard deviation, $C_V = mean$ value). Furthermore, it showed excellent linearity, indicating applicability to neuromorphic systems. For 100 level potentiation (+3V, 0.5s), non-linearity factor ranges from 0.1 to 0.6. For 100 level depression (-3V, 0.2s), it ranges from 2.3 to 4.6 ($n = 15$). A similar trend was shown even when the number of input pulses was changed (50, 100, 200, 300, 400 inputs).

Based on AuNp-FGM, we fabricated a neuromorphic array consisting of 2 neurons and 32 synapses. Three types of data (horizontal, vertical, diagonal) were used in 40 learning simulation. The total energy consumed was 70µJ, which confirmed to be a 97% energy reduction compared to the previous experiment [3].

References

2000 PM EL05.04.04
Multi-Neuron Connection Using Multi-Terminal Floating-Gate Memristor for Unsupervised Learning
Mihyang Park and Woojong Yu; Sungkyunkwan University, Korea (the Republic of)

Heterosynaptic plasticity in synapses has been successfully demonstrated by multi-terminal memristor and memtransistor (MT-MEMs) [1,2]. However, these MT-MEMs lack the capability to mimic the membrane potential of neurons in multiple neuronal connections. In this study, we demonstrate a multi-terminal floating-gate memristor (MT-FGMEM) to emulate multi-neuron connections.

The variable Fermi level ($E_F$) in graphene allows the charging and discharging of MT-FGMEM using multiple horizontally spaced electrodes. The MT-FGMEM exhibits a high on/off ratio over 10$^6$ with a retention time of 1000 seconds, approximately 10,000 times higher than other MT-MEMs. The linear relationship between current ($I_{FG}$) and floating gate potential ($V_{FG}$) in the triode region of the MT-FGMEM allows for accurate spike integration at the neuron membrane. The MT-FGMEM fully mimics the temporal and spatial summation of multi-neuron connections, based on the leaky-integrate-and-fire (LIF) functionality. Our artificial neuron consumes significantly less energy, approximately 100,000 times lower (150 pJ), compared to conventional neurons based on silicon integrated circuits (11.7 nJ).

By integrating neurons and synapses using MT-FGMEMs, we successfully emulate spiking neurosynaptic training and classification of directional lines in the visual area one (V1), based on the LIF functionality of neurons and the spike-timing-dependent plasticity (STDP) of synapses. We achieved a learning accuracy of 83.08% on the unlabeled MNIST handwritten dataset in unsupervised learning based on our artificial neurons and synapses.

2000 PM EL05.04.05
Synthesis of Te and Sb Doped Black Phosphorus Single Crystals, Oxidation-Resistance and Room-Temperature Gas Sensing Applications
Chih-Ying Huang, Yi-Rong Wang, Ying-Hao Bai, Yi-Syuan Chen, Sin-Pei Wang, Yong-Wei Bai, Yi-Chen Chen, Yu-Jie Shih, Wen-Chieh Hsieh, Yi-Wen Lin, Chia-Yin Cheng, Shang-Jung Wu, Hung-Shuo Chang and Chun-Hua Chen; National Yang Ming Chiao Tung University, Taiwan

Black phosphorus (BP) is another highly potential semiconductor two-dimensional (2D) material after graphene and transition metal dichalcogenides (TMDCs). Its optoelectronic properties depend on the number of layers and the in-plane directions of the BP 2D structure. The optoelectronic properties range from monolayer Phosphorene to bulk BP can just link those of graphene and TMDCs, enabling 2D materials to cover a wide range of optoelectronic properties. Besides, coupled with its unique armchair wrinkled crystal structure, BP has irrereplaceable advantages and can be widely used in sensing, optics, electronics, thermoelectrics, and other fields. However, since each phosphorus atom in the BP structure has a lone electron pair, it can spontaneouly degrade in the atmospheric environment, which significantly limits its practical application in various fields. So far, many studies have shown that the environmental stability of BP or the performance of BP components can be effectively improved by surface coating, nanostructure modification, or element doping. However, different protection strategies are often
accompanied by changes in the essential characteristics of BP, and the causal relationship is still, up to now, not fully clear yet.

In this study, BP crystals were prepared by chemical vapor transport (CVT), and tellurium and antimony were respectively doped in the synthesis process to potentially change the energy band structure of BP and improve its environmental stability. The obtained BP crystals were further exfoliated by ultrasonic liquid phase exfoliation (LPE). A series of BP nanosheets, tellurium-doped BP nanosheets, and antimony-doped BP nanosheets were prepared in the organic solvent N-methylpyrrolidone (NMP) with a 900-watt ultrasonic wave. Then, BP nanosheets with a specific size distribution are screened by centrifugal rotation speed. Then, various techniques were applied to analyze the degradation degree of these three types of BP nanosheets exposed to a specific atmospheric environment (relative humidity: 75%–90%, temperature: 23–30°C). Finally, these three types of BP nanosheets were respectively placed on the interdigitated substrate for gas sensing. It was found that the highest conversion rate of pure BP, tellurium-doped BP, and antimony-doped BP crystals can reach ~98%. According to x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, optical microscopy (OM), atomic force probe microscopy (AFM), and transmission electron microscopy (TEM) analysis, it was confirmed that the doping of tellurium or antimony is an effective strategy to improve the environmental stability of BP nanosheets. Finally, the gas sensing results show that among eleven kinds of gases (CH4, C2H6, C3H8, NO, NO2, NH3, C2H5OH, CO, acetone, HCHO, H2), all the prepared BP nanosheets, tellurium or antimony doped BP nanosheets exhibited highly selective responses to NO and NO2 and NO. In addition, doping of tellurium and antimony could also reduce the response/recovery time to NO2 and NO.

Keywords: black phosphorus, phosphorene, dope, anti-degradation, gas sensor

5:00 PM EL05.04.08
Van der Waals Interface Engineering for Enhancement of Semiconductor Device Performance Sujeon Cho, Do Hyeon Lee and Jun Hong Park; Gyeongsang National University, Korea (the Republic of)

Since the performance of semiconductor devices is highly dependent on charge injection between the metal electrode and the semiconductor channel, it is important to reduce defect density through interfacial engineering at the metal-semiconductor interface. Typically, as metal is directly deposited on the semiconductor surface to form the contact electrode, metal atoms can diffuse into the semiconductor lattice and degrade the charge injection performance. In this study, we propose a method to insert a WSe2 layer to reduce the defect density at the metal-semiconductor interface. The WSe2 layer inserted at the metal-semiconductor interface acts as a diffusion barrier to prevent the diffusion of metal atoms into the semiconductor lattice, thereby suppressing structural defects. The metal/WSe2/Si diode is fabricated by transferring a WSe2 layer thermally grown on a SiO2 substrate to a p-type Si substrate by a wet transfer method and then depositing metal electrodes (Ni, Ag, Ti, Ct/Au) onto the WSe2/Si substrate using an E-Beam evaporator. The C-V (Capacitance-Voltage) characteristics of the diodes confirm that the formation of the titled compounds. The fingerprints of formed metal-halide complexes in solution were confirmed by UV-visible spectroscopy and thermal conductivity have also been studied for both compounds. To gain more insights into their structural and chemical diversity, we explored the solution chemistry for the structures of the titled compounds. The fingerprints of formed metal-halide complexes in solution were confirmed by UV−Vis spectroscopy and small-angle X-ray scattering (SAXS) experimental techniques combined with density functional theory (DFT) calculations. Moreover, compound (1) showed anisotropic charge transport properties with a good and different semiconductor resistivity measured along the a-axis and along the b-axis, respectively. The fabricated prototype showed detector response to soft low-energy X-rays at 8 keV with a detector sensitivity of 1462.7 μC/Gy−1cm−2, indicating its potential application for ionizing radiation detection.

5:00 PM EL05.04.09
Monolayer MoS2 with Controllable and Localized Micro-Scale Domains of Strain enabled by Spatially Varying Nanotopography Boran Kumral, Peter Serles, Aksath Rastogi, Pedro G. Demingos, Akhil Nair, Nima Barri, Cristina Amon, Chandra Veer Singh and Tobin Filliter; University of Toronto, Canada

The remarkable strain limit of two-dimensional (2D) materials as a result of strong in-plane cohesive or ionic bonding provides a straightforward means to tune electronic states by modulating the interatomic distances through mechanical strain[1,2]. The high strain sensitivity along with low bending modulus of 2D materials make them promising candidates for eagerly sought-after gradient bandgap materials in which the bandgap spatially varies within the same material [3–5]. These materials would enable absorption and conversion of a broad light spectrum for use in photovoltaics, photocatalysis, and photodetectors[6–8]. Meanwhile, two-phonon lithography (2PL) is newly capable of lateral resolutions below 200 nm to rapidly fabricate complex three-dimensional structures[9–10]. Here, we use 2PL fabricated non-Euclidian nanotopography comprised of periodic undulations with spatially varying height as a patterned substrate for monolayer molybdenum disulfide (MoS2). The monolayer conform to the nanotopography locally strains the monolayer with both spatial and magnitudinal control. The conformity of the monolayer is characterized using scanning electron microscopy and atomic force microscopy, and the localized domains of strain in the conformed monolayer are characterized using Raman and photoluminescence spectroscopy. This study serves as a starting point for deterministic straining of 2D materials and development of 2D materials enabled broad-spectrum sensing.

References


5:00 PM EL05.04.10
Semiempirical Pseudopotential Method for Low-Dimensional Materials Rai K. Pandeu1,2, Chung Yuan Ren1 and Yia-Chung Chang1,2; Academia Sinica, Taiwan; National Cheng-Kung University, Taiwan; National Kaohsiung Normal University, Taiwan

In recent years, there has been a significant focus on developing precise and efficient approaches to expedite Density Functional Theory (DFT) calculations for large unit cells. Among these techniques, the Semiempirical Pseudopotential Method (SEPM) [1] has emerged as a valuable tool for accurately determining band structures, especially in the realm of low-dimensional materials. SEPM operates by utilizing atomic pseudopotentials, which are derived from DFT calculations. Significantly, SEPM calculations offer a unique advantage compared to DFT as they eliminate the requirement for iterative self-consistent solutions in solving the Schrödinger equation, leading to a substantial reduction in computational complexity.

The incorporation of both non-local and local Semiempirical Pseudopotentials in our current approach yields bands structure and wavefunctions with enhanced precision compared to traditional empirical methods [2]. When applied to graphene, our model’s computed band structure closely aligns with that obtained via DFT calculations [3]. Impressively, our method demands only a fraction of the time required to the CG iterative solver with self-consistent charge density from DFT. Additionally, we utilized the SEPM technique for armchair graphene nanoribbons (aGNR), achieving results that closely align with those obtained through DFT, but with significantly reduced computational time. Furthermore, we extended the application of our SEPM approach to monolayer TMDs, adjusting the parameters to align with pertinent values obtained from DFT computations. This enables us to faithfully replicate the band structure, opening avenues for investigating the optoelectronic properties of TMDs and exploring their potential applications in nanodevices consisting of TMDC nansheets or related materials[4-9].
Graphene offers outstanding electronic and optical properties, such as high electrical conductivity and high transparency in the UV-VIS spectral range. The most developed method for growing high quality graphene is chemical vapor deposition (CVD) on copper (Cu) substrates, where Cu has a catalytic effect on the growth. Practical applications, however, require a subsequent transfer of the graphene onto target substrates like, e.g., dielectric materials. This transfer process induces defects and contaminations, which in turn leads to reduced performance of the intended applications [1]. Thus, a direct growth on dielectric substrates, such as sapphire and (Al,Ga)N is preferable, enabling, e.g., the use of graphene as a transparent electrode for (Al,Ga)N-LEDs [2], 2D-photodetectors [3] or biosensors [4] without any complex transfer process.

We developed a low temperature plasma-enhanced CVD (PECVD) process for depositing graphene on dielectric substrates in a transfer-free approach. The PECVD process was conducted in an industrially relevant 4-inch system with methane (CH₄) as the precursor. For growing graphene on (Al,Ga)N, the conventionally used hydrogen (H₂) carrier gas was replaced by nitrogen (N₂) for preventing surface decomposition of the (Al,Ga)N [2]. Under optimized conditions, i.e., a gas mixture of CH₄/N₂, a plasma power of 40 W, a growth time of 60 min and a growth temperature of 670 °C, graphene layers with Raman intensity ratios I_D/I_G ≥ 1.6 and I_G/I_D ≥ 1.4, respectively, have been realized. The sheet resistance could be reduced to < 5 kΩ/sq and the transmittance of the optimized graphene film was ≥ 90% in the UV-VIS spectral range. For graphene growth on sapphire with different crystal orientations (c-plane, ca-plane, a-plane and r-plane), no distinct dependence of the graphene quality on the crystal orientation is found, in contrast to findings for thermal CVD as reported in literature [5]. Under optimized conditions, the I_D/I_G ratio was as low as 0.7 and a sheet resistance down to 1.65 kΩ/sq could be achieved. Apparently, the PECVD process seems to provide a flexible approach for depositing graphene on dielectric substrates, where the balance between sheet resistance and optical transmittance can be willingly adjusted by growth parameters.

References
In this work, we have fabricated by atomic layer deposition (ALD) multilayers of layered materials based on topological insulators and van der Waals materials, called ferreocrystals. These ferreocrystals can be tailored to exhibit unusual properties such as high electrical conductivity or low thermal conductivity or magnetic properties. A detailed ferreocystal study was performed on ferreocrystals of Sb$_2$Te$_3$ and Sb$_2$O$_x$, which has been grown at the same temperature as single layers of Sb$_2$Te$_3$. Without post-annealing, the electrical and thermoelectric characterisation of the highly ordered samples have been performed with the ZT-chip setup. In general, the carrier mobility is very high >150 V·cm$^{-2}$·K$^{-1}$ and is even improved when the thickness of the Sb$_2$Te$_3$ layers is reduced and the number of Sb$_2$O$_x$ layers (typically 2 nm thickness) is increased. Detailed XRD investigations have been performed and an enhanced crystalline order is observed in the ferreocystal system compared to individual layers of Sb$_2$Te$_3$. We have grown ferreocrystals based on Sb$_2$Te$_3$ and Sb$_2$Se$_3$ with tetrahedral and orthorhombic crystal structure, respectively. The p-type hole carrier concentration of Sb$_2$Te$_3$ films can be enhanced through the sublayer doping of Sb$_2$Se$_3$. The highest carrier concentration achieved was 2.5×10$^{19}$ cm$^{-2}$ when the thickness ratio of Sb$_2$Te$_3$ to Sb$_2$Se$_3$ was (4 nm:2 nm). Further reduction of the Sb$_2$Te$_3$ thickness resulted in a high Seebeck coefficient of 172 μV/K at room temperature.


8:45 AM EL05.05.03

Plasma-Based Integrated System for Synthesis, Etching and Machine Learning of 2D TMDCs. Hyeong-U Kim$^1$, Muyeong Kim$^1$, Seongho Kim$^2$, Minji Kang$^1$ and Min Sup Cho$^2$; $^1$ Korea Institute of Machinery and Materials (KIMM), Korea (the Republic of); $^2$Chungnam National University, Korea (the Republic of) The research presented in this work represents a culmination of over a decade of dedicated efforts toward the development and implementation of a plasma-based integrated system for the synthesis, etching, and machine learning of two-dimensional (2D) transition metal dichalcogenides (TMDCs). Our journey began in 2013 with a groundbreaking achievement: the successful synthesis of semiconducting MoS$_2$ at 300 °C using an inductively coupled plasma (ICP)-plasma enhanced chemical vapor deposition (PECVD) technique (PLASMART, Republic of Korea) on a 4-inch substrate. This milestone was the first step towards realizing the immense potential of 2D TMDC materials in various applications. Building on this initial success, we continued to advance our capabilities. In 2015, we lowered the synthesis temperature to 150 °C, enabling direct deposition on polycrystalline substrates. This development not only expanded the range of possible applications but also demonstrated our commitment to environmentally sustainable processes. In 2020, we achieved another significant milestone by successfully synthesizing 2D WS$_2$, a member of the same TMDC group, in the metallic 1T phase using PECVD. The year 2021 marked a breakthrough as we overcame previous limitations in heterostructure fabrication by creating a MoS$_2$/WS$_2$ heterostructure using H$_2$S + Ar plasma on a 4-inch heterochemical (Mo-Mo) layer. This achievement unlocked the potential for novel electronic and optoelectronic devices based on these heterostructures. Various forms of TMDCs, all consisting of 4-5 layers, were systematically layered, laying the foundation for further exploration.

By 2023, we had established precise etching conditions at the atomic layer level using ICP-reactive ion etching (RIE) with a carefully designed three-gas mixture (Ar+O$_2$+CF$_4$) and optimized RIE utilization. This enabled us to tailor the properties of 2D TMDC materials with unprecedented precision. Furthermore, we employed density functional theory (DFT) calculations and optical emission spectroscopy (OES) diagnostic results to gain deeper insights into the plasma reaction mechanisms, shedding light on the underlying physical processes. In a remarkable culmination of our efforts, we harnessed the power of machine learning (ML) to predict process outcomes in 2023, revolutionizing the way we approach material synthesis and etching. This achievement represents a significant leap forward in terms of efficiency and precision, with implications spanning various industries and research domains. In summary, our research journey has led to the development of a comprehensive and versatile plasma-based integrated system for 2D TMDC materials. Over the course of a decade, we have pushed the boundaries of what is possible in material synthesis, etching, and process optimization, ultimately contributing to the advancement of science and technology.

9:00 AM EL05.05.04

Atomic Layer Deposition of WS$_2$ on Low-k Dielectric Substrates for Back-End-Of-Line Integration. Muhammad Juwaid Manattuckal$^1$, Hao Tan$^1$, Hippolyte P. Astier$^1$, Chandan Das$^2$, John L. Sudiwono$^2$ and Silviya Gradecak$^1$; $^1$NUS Singapore, Singapore; $^2$Applied Materials, Inc., Singapore The progressive miniaturization of silicon circuits necessitates the exploration of alternative materials for both the front-end-of-line (FEOL, transistors) and back-end-of-line (BEOL, interconnects) circuitry. Currently, the efficacy of traditional liners and barriers (e.g., Ta/TaN) requires an approximate thickness of 30-40 Å. In forthcoming sub-5 nm nodes, these components will occupy a significant portion of the interconnect cross-section, leading to a substantial increase in the resistivity of Cu interconnects. Conversely, the reduction in thickness of liner and barrier layers will result in a decrease in Cu blocking efficiency. Two-dimensional (2D) transition metal dichalcogenides (TMDCs) were recently demonstrated as promising candidates for bifunctional ultra-thin liner and diffusion barrier materials in the sub-nanometer-scales. However, the majority of 2D TMDCs are synthesized via chemical vapor deposition processes at elevated temperatures (>800°C). This makes it difficult to use them in BEOL integration, where the temperature limit is 450°C. While plasma-assisted growth offers the potential to mitigate the high-temperature requirement, it also imposes poor conformity in deposition, and the emergence of plasma-induced defects in the TMDCs as limitations.

Here, we present a thermal atomic layer deposition (ALD) approach that does not require plasma assistance to grow crystalline WS$_2$ at temperatures below 400°C on dielectric materials, including low- k and SiO$_2$ substrates. This growth approach does not alter the stoichiometry of the low- k material and retains its k value, making it a suitable method for BEOL integration. The process results in layer-controlled, conformal (>95%) wafer-scale growth of WS$_2$ on 200 mm dielectric substrates. Furthermore, the single-layer WS$_2$ helps reduce Cu resistivity >70% compared to the reference low- k and SiO$_2$/Si substrates. Thermal and electrical stress tests on the monolayer WS$_2$ film reveal a high blocking efficiency against both types of stress. This low- k-compatible ALD-grown monolayer WS$_2$ not only addresses the downsizing challenge but also serves as an efficient bifunctional (liner and barrier) layer grown using a directly industry-compatible process.

9:15 AM EL05.05.05

Fabricating Freestanding Ultrathin Materials by Atomic Layer Deposition. Karen Ehhardt$^1$, Jessica M. Coleman and Scott C. Warren; University of North Carolina at Chapel Hill, United States Ultrathin materials have risen to an increasingly important role in recent years, both due to the nano-scaling of existing technologies and the advancement of new applications that utilize the distinct properties of ultrathin structures compared to bulk materials. Because these properties strongly depend on thickness and uniformity, vapor-based synthesis is popular. In particular, atomic layer deposition (ALD) is a popular strategy to fabricate precisely controlled ultrathin materials because of self-limiting growth and high conformality. However, to fully realize the potential of ultrathin materials from ALD, there exists a need for freestanding structures, which would allow the exploration of applications such as membranes or photolithographic pellicles. Because these properties strongly depend on thickness and uniformity, vapor-based synthesis is popular. In particular, atomic layer deposition (ALD) is a popular strategy to fabricate precisely controlled ultrathin materials because of self-limiting growth and high conformality. However, to fully realize the potential of ultrathin materials from ALD, there exists a need for freestanding structures, which would allow the exploration of applications such as membranes or photolithographic pellicles.

Muhammad Juwaid Manattuckal$^1$, Hao Tan$^1$, Hippolyte P. Astier$^1$, Chandan Das$^2$, John L. Sudiwono$^2$ and Silviya Gradecak$^1$; $^1$NUS Singapore, Singapore; $^2$Applied Materials, Inc., Singapore

9:30 AM EL05.05.06

Lithographically Defined Synthesis of Transition Metal Dichalcogenides. Aidar Kemelbay$^1$, Ricardo Ruiz, Archana Raja, Adam Schwartzberg, Shaul Aloni and Tevye Kuykendall; Lawrence Berkeley National Lab, United States Transition metal dichalcogenides (TMDC) possess unique and highly tunable optoelectronic properties, but their large-scale fabrication and integration is still challenging. To address this problem, we developed a "lateral conversion" technique, which enables the synthesis of TMDCs with predefined thickness and shape at specific locations on a wafer. The lateral conversion of metals, metal oxides, and nitrides into metal dichalcogenides resulted in few-layer TMDCs covered with a capping layer. This layer protects the delicate TMDC interfaces during subsequent fabrication steps from contamination, as well as improves their air stability. We demonstrated that lateral conversion can be used to synthesize various sulfides, selenides and tellurides as well as alloys, lateral and vertical heterostructures. The patterned TMDCs can be easily transferred from growth to device substrates or directly integrated into silicon-based CMOS platforms.

9:45 AM EL05.05.07

Substrate Van der Waals Force Effect on The Stability of Violet Phosphorous. Sarabpreet Singh$^1$, Mahdi Ghafariai$^1$, Hsin-Yu Ko$^2$, Sampath Gamage$^1$, Robert DiStasio Jr.$^2$, Michael
Resolution Limits and Their Effect on Structure and Morphology of Lithographically Defined TMD Synthesized by Lateral Conversion

Ruiz, Aidar Kamelbay and Tevye Kuykendall; Lawrence Berkeley National Laboratory, United States

Two-dimensional (2D) materials have exploded in popularity due to their wide range of properties and the fact that they can be stacked into devices. The vast majority of devices made from 2D materials use exfoliated flakes, which works well for creating prototypes and to understand basic physics, but exfoliation is difficult to scale up. For traditional materials, devices are fabricated using wafer-scale films and subtractive manufacturing processes. Unfortunately, wafer-scale films of 2D materials grown by physical vapor deposition or chemical vapor deposition techniques often have a high density of grain boundaries and twin defects, which lead to unwanted conducting channels in electronic devices, non-radiative recombination pathways in optical devices, and decoherence in quantum devices. In addition, etching often damages the edges of the 2D material, further degrading device performance. One way to solve this problem is to take a new approach to the wafer-scale manufacturing of 2D material devices. Instead of growing a wafer-scale film and using subtractive techniques to fabricate devices, we use selective area epitaxy (SAE), an additive technique, to build devices from the bottom up.

In SAE, a mask is patterned on the substrate before growth with precisely placed holes through to the substrate. The growth conditions are selected such that the film only nucleates and grows in the openings of the mask, thus defining the location, size, and shape of the film. By choosing the growth conditions correctly, we can ensure that only a single grain of 2D material grows in each opening, eliminating issues with grain boundaries and film coalescence. Multiple materials can be stacked together using SAE to create functional device stacks. If contacts to the stack are needed, they can be made as edge contacts before epitaxy and/or as top contacts post-growth. Using SAE, we can synthesize quantum-confined 2D materials without the need for etching, thus preserving the intrinsic properties of the material. Overall, SAE has the potential to transform growth of 2D materials for devices by enabling the synthesis of 2D materials free of grain boundaries with precise locations and sizes.

In this talk, we will discuss our recent results on SAE of 2D materials using molecular beam epitaxy (MBE). MBE is an ultra-high vacuum physical vapor deposition technique, in which high-purity elemental source materials are thermally evaporated. The atoms impinge upon the substrate and react to form the film. In the past decade, MBE has been used to grow a wide range of 2D materials and heterostructures and due to its high purity, is a good choice for SAE. To begin, we explored SAE of the topological insulator Bi2Se3 on GaAs substrates using Al2O3 masks deposited by electron beam evaporation and atomic layer deposition. We find that we can obtain SAE in a narrow but reproducible growth window. We also find differences in SAE growth windows for electron beam deposited Al2O3 compared to atomic layer deposited Al2O3, likely due to the difference in smoothness and the number and density of dangling bonds. I will further show results for SAE of Ga2Se2 on GaAs and for Bi2Se3 on Si. Overall, SAE is a promising technique for the growth of high-quality 2D material devices.

Scalable Synthesis of Molecular-Intercalated Bulk Monolayer MoS2 with Tailored Electron Doping

Boxuan Zhou, Jingyuan Zhou and Xiangfeng Duan; University of California Los Angeles, United States

Molybdenum disulfide (MoS2) is an extensively studied two-dimensional layered semiconductor with interesting electronic and optical properties. Monolayer MoS2 features strong light-matter interactions due to its direct bandgap, whereas multilayer MoS2 is an indirect bandgap semiconductor and optically inactive. The molecular intercalation of MoS2 with organic cations offers a strategy to decouple the interlayer interaction, producing a bulk monolayer material, but is usually accompanied by a heavy electron doping effect that can diminish the intrinsic semiconductor properties or induce a phase transition. Herein, we report a chemical-doping strategy to tailor electron density in molecular-intercalated MoS2 therefore retaining monolayer properties. By introducing a poly(vinylpyrrolidone)-hromine complex during the electrochemical intercalation process, we show bulk monolayer MoS2 thin film can be produced with decoupled interlayer interaction and reduced electron concentration. The resulting thin films display strong excitonic emission, 20- and > 400 times stronger than the exfoliated monolayer and multilayer material respectively, as well as high valley polarization and enhanced photo-electric response. Our study opens a scalable path to large-area bulk monolayer MoS2 thin films with monolayer-like optical properties and greatly increased optical cross-section, presenting an attractive material platform for both fundamental photophysics studies and scalable optoelectronic applications.
Molecular adsorption on the MoSe2 surface is induced with dipping in (NH4)2S(aq) diluted in H2O with 25%, while the solution temperature is held at 50 degrees celsius. H2S or HS molecules can be adsorbed on the MoSe2 surface during this chemical treatment and act as trapping centers for transported carriers. The adsorbed molecules can be desorbed from MoSe2 surfaces with partial oxidization, little is known about controlling sulfur vacancies and thus background doping in the growth process. To mimic the biological synapse, the electrical synapse response of MoSe2 transistors is modulated by a pulse generator wherein excitatory modes; thereby synapse plasticity is controlled by spike-like gate bias as a presynaptic input. After applying pulse gate bias with 50 ms pulse duration, for bare MoSe2 devices, there is no synapse response, including changes in conductance, consistent with the absence of the plasticity. However, after chemical treatment, molecular adsorption increases conductance upon pre-synapse inputs consistent with a significant increase from 5.9 S to 68.6 S (a postsynaptic conductance), consistent with the manifest of plasticity. The observed plasticity can disappear with the desorption of molecules from the surface of synapse devices. To emulate the visual sensory behavior of humans, the artificial synaptic plasticity of synaptic devices has been explored by applying light pulse. As light stimulation with pulse modulation, the channel’s conductance near-linearly increases as the number of light pulses increases, consistent with optical potentiation. Afterward, electric depression of molecularly functionalized synapse can be observed with the linear decrease of conductance. In addition, although it is crucial to fabricate the receptive layer in which a particular molecule reacts selectively, TMDC materials are atomically thin body with a finite bandgap, layered transition metal dichalcogenides (TMDCs) have been employed as semiconducting channel platforms with a large ON/OFF ratio and near single-electron tunneling characteristics.

Acknowledgement:
The authors greatly acknowledge the MoSe2 growth and sample supply by imec Leuven, Belgium.

References:
Programmable Graphene e-Nose Sensor Arrays for Fast, Sensitive and Label-Free Identification of Chemical Vapors

Haolin Li, Anjali D. Sivakumar, Chandrakalavathi Thota, Ruchi Sharma, Xiaoheng Huang, Xuoding Fan and Zhashui Zhong; University of Michigan–Ann Arbor, United States

Conventional electrical chemical vapor sensors are mostly based on charge transfer mechanisms and have struggled with the trade-off between sensitivity and response time. To address this challenge, our groups previously demonstrated a new type of fast, sensitive, and broad-spectrum electronic vapor sensor by exploiting the fringing field capacitance effect in graphene transistors. The typically trivial fringing field capacitance change due to analytic absorption is greatly amplified by both the graphene transistor and a micro-flow channel covering the surface of graphene. In this work, we demonstrate programmable graphene e-nose sensor arrays toward true label-free sensing and identification of chemical vapors. Individual graphene sensors within the 1D sensor array (up to 1 x 9) are optimized to offer sensitive (down to picogram) and fast (sub-second) detection toward a variety of analytes. More importantly, its propensity toward different analytes can be programmed by electrostatic gating on the graphene transistor. By combining with advanced data analysis tools, the graphene e-nose array has the potential to offer label-free chemical vapor sensing without the need to individually functionalize each sensor as in traditional e-nose devices. We will also discuss the integration of the graphene e-nose sensor array with a micro-gas chromatography chip and a smartphone-sized custom PCB board for electronic control and readout and Bluetooth data communication. The graphene e-nose sensor arrays offer a sensing platform for real-time rapid on-site monitoring of complex gas mixtures including polar, nonpolar, organic, and inorganic molecules. Furthermore, the results should pave the way for fast, sensitive, and true label-free chemical vapor sensing and identification using nanoelectronic sensors.
Here, we synthesized hydrogenated borophene through the thermal decomposition of NaBH₄ in the presence of H₂. Subsequently, we fabricated a 2-terminal coplanar Borophene/Graphene/SiO₂/Si broadband (405-1064 nm) photodetector (PD) with high photoresponsivity (R). The Borophene/Graphene/SiO₂/Si PD exhibits an outstanding R~ 3.65 x 10³ A/W under 405 nm laser illumination (40 mW). This performance surpasses previously reported values for Borophene-based PDs, which ranged from 0.48 to 9.13 A/W [3-5]. Our PD shows short response time, and recovery times of 20, 83 μs under 633 nm laser illumination compared to previous reports in the range of 110 to 660 μs [3-5]. Our results may stir interest in Borophene for nanophotonic, and optoelectronics devices.

References

5:00 PM EL05.08.05 Enhancing Gas Sensing Performance with 2D Material-Integrated Sub-Wavelength Grating Micro-Ring Resonator: Improved Sensitivity and Selective Detection Boxin Zhang, Yadwendra Singh and Harish Subbarayan; Oregon State University, United States

Silicon photonics devices are widely utilized in optical gas sensing owing to their compact size and compatibility with CMOS technology. However, their limited sensitivity hampers their versatility. In this study, we introduce a highly sensitive gas sensor incorporating a 2D material gas-absorbing layer and a sub-wavelength grating (SGW) micro-ring resonator. Leveraging the large surface-volume ratio of the 2D material layer, it efficiently absorbs gas molecules and induces substantial refractive index changes during sensing. Finite-Difference Time-Domain (FDTD) simulation results will be showcased which demonstrate enhancement in both bulk sensitivity and surface sensitivity upon incorporating the 2D material layer. Moreover, the SGW design enables a larger evanescent field-analyte interaction region, resulting in an elevated sensitivity factor for the proposed sensor. Furthermore, by coating the micro-ring resonators with different 2D materials, we envision highly selective sensor architectures.

5:00 PM EL05.08.10 Integrated TEM Membrane Platforms for Lower Conversion Transformer Sensory Devices in High Energy Density Conversion Systems Tyew Kuykendall, Aidar Kemelbay, Misael Campos, Alexander Herman and Shaul Aloni; Lawrence Berkeley National Lab, United States

Two dimensional transition metal dichalcogenides (TMDs) are a promising family of materials for a wide range of applications. However, their integration into traditional fabrication pipelines remains challenging. Our research has been working to develop a lithographically patterned, wafer-scale fabrication process that we call “lateral conversion synthesis.” We have demonstrated this concept on a host of TMDs, including W, Mo, Pt, sulfides, selenides, and tellurides, alloys and heterostructures. We will present an overview of these results, as well as a process to directly synthesize TMDs on transparent electronic substrates for performing transmission electron microscopy. We demonstrate that by using these membranes, we can resolve and optimize the crystalline microstructure, domains and lattice features of the TMDs grown through later conversion.

5:00 PM EL05.08.11 Chemical Vapor Transport Growth of Selene and its Heterostructures with TMDs Renjith N, Bhargav Rajbongshi and Manikoth Shajumon; IISER Thiruvanathapuram, India

2-dimensional (2D) materials have attracted a lot of scientific attention recently beyond graphene, due to their distinct physical and chemical features. Elemental 2D crystals have emerged as promising materials for advanced electronics and optoelectronics applications.[1] In particular, group VI elemental 2D semiconductors, including selenene and tellurene, have attracted significant attention for their simple composition and complex properties, such as higher carrier mobility, better environmental stability, and high photoconductivity, which triggered intense activities on their fundamental and application-oriented research.[2] 2D heterostructures based on various 2D layered materials with distinct properties have been demonstrated to exhibit novel physicochemical properties for their potential application in electronics, optoelectronics, and catalysis, owing to their tunable band alignment and sharp interfaces.[3] Forming new structures by stacking transition metal dichalcogenide (TMD) layers has been explored by several groups; however, the mechanical transfer method is time-consuming and suffers from having control on the layer stacking. Single-step and two-step chemical vapor deposition (CVD) growth of lateral and vertical TMD heterostructures have been considered to be a promising approach to realize the potential applications of these heterostructures.[4] Achieving controllable growth of high-quality, ultra-thin flakes of elemental 2D materials remains a challenge. Herein, we demonstrate a seed-assisted chemical vapor transport (CVT) growth of ultra-thin triangular flakes of highly crystalline trigonal selenium (t-Se) oriented in (0001) direction, with lateral size >30 μm.[5,6] To study their promising photo-electrocatalytic properties and further realize the device applications, we employed a single-step CVT approach to grow selenene/WSe₂ heterostructures. Vertical heterostructures of bi-layer selenene and monolayer WSe₂ domains obtained via the CVT method are characterized by optical microscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The Se/WSe₂ heterostructure exhibit improvements in the HER activity as evidenced by the overpotential which is dramatically decreased from 163 mV to 121 mV for a current density of 10 mA cm⁻² and the Tafel slope also reduces from 109 mV dec⁻¹ to 75 mV dec⁻¹ upon shining the light. The method could be extended to synthesize different 2D elemental and TMD heterostructures.

5:00 PM EL05.08.13 Complementary 2D Tunnel FETs with Extremely Asymmetric Dual-Band Heterostructures Hanbin Cho, Seonguk Yang, Donggyu Park and Joonki Suh; UINIST, Korea (the Republic of) ([1,2])

Conventional metal oxide semiconductor field-effect transistor (MOSFET) technology currently suffers from the scaling of supply voltage owing to the required power per computed bit of information tightly bound to the subthreshold swing (SS) of 60 mV/dec at room temperature. Tunneling field-effect transistor (TFET) is a promising building block for low-power and steep-slope switching applications in that the lower limit of MOSFET SS, inherently caused by thermionic emission, can be overcome by utilizing band-to-band tunneling. In this presentation, we propose the TFETs using band-offset engineering via 2D van der Waals (vdW) hetero- and multi-junctions. Indeed, 2D materials are ideally suited since they are free from non-ideal tunneling tendencies originating from lattice mismatch as seen in bulk hetero-junctions and their atom-thick body is under the complete electrostatic control. In the fabricated 2D heterostructured TFETs, SnSe₅ and SnSe not only function as the electron and hole reservoirs but provide a highly asymmetric band offset alignment to the intrinsic channel where MoS₂ and WSe₂ are employed for nTFET and pTFET, respectively. The van der Waals coupled TFETs show the promising device characteristics of low-power switching operations in terms of SS and off-current compared to MOSFETs using the same kinds of channels. In addition, complementary 2D TFETs, implemented in both n-type and p-type, expand the breadth of logic configurations. We expect to be able to leverage this naturally biased 2D material platform to implement low-power circuits.

5:00 PM EL05.08.14 Synthesis and Atomic-Scale Investigation of Phosphorus-Doped Graphene on Copper Oscar Chavez, Jerome Brown, Owen Hudak and Li Gao; California State University, Northridge, United States

Phosphorus doped graphene has potential applications in supercapacitors, lithium ion batteries, fuel cells, and sensors. A phosphorus-containing sole precursor has been used for the synthesis of phosphorus-doped graphene on the Cu(111) surface. The surface morphology, electronic structure of phosphorus dopants, and doping-induced variation of local work function of graphene have been studied on the atomic scale by using scanning tunneling microscopy, dI/dV spectroscopy and d2I/dV² spectroscopy. Bias-dependent atomic-resolution STM images of the predominant type of phosphorus dopants have been obtained. dI/dV spectra show the effect of phosphorus doping on the electronic structure of the graphene surface. d2I/dV² spectra show that the local work function decreases at the phosphorus dopant site, leading to a downward energy shift of field emission resonances. X-ray photoelectron spectroscopy measurements are also performed to characterize the overall phosphorus doping properties on the sample surface. This work provides atomic-scale experimental insights into the phosphorus dopants in graphene for the first time.

5:00 PM EL05.08.15 Synthesis, Structure and Magnetic Properties of a New Spin-1 Honeycomb Lattice KNiAsO₄ with a Zig-Zag Magnetic Structure Domindu Sinjewedi; University of Missouri–Columbia, United States

Identifying and characterizing new honeycomb magnetic systems are the key ingredients to explore new candidate materials for the Kitaev model as the model realizes the exact quantum spin
We demonstrate an approach to depositing MoS2 flakes on SiO2/Si substrates with a predefined pattern shape, utilizing localized electron irradiation on the effect transistors, thanks to their tunable band structures, reduced leakage current, and high carrier mobility. The patterning of 2D-TMDs is critical in device fabrication, traditionally requiring a complex lithography process. We demonstrate an approach to depositing MoS2 flakes on SiO2/Si substrates with a predefined pattern shape, utilizing localized electron irradiation on the surface of SiO2/Si wafers. Within the regions exposed to low-dose electron irradiation, we successfully achieve area-selective growth of MoS2 during chemical vapor deposition (CVD) process with selectivity of ~0.7. In contrast, negative selectivity with suppressed growth is achieved in heavily irradiated areas of the substrate.

We have investigated the modification of surface potential on SiO2/Si substrates due to localized electron irradiation using Kelvin probe force microscopy (KPFM) and demonstrated that selective growth takes advantage of the local surface potential difference. The variation of the surface potential is predictable by an analytical model. Raman spectroscopy analysis reveals the adsorption of carbon species due to irradiation, acting as a blocking layer that inhibits MoS2 growth and contributes to the observed negative selectivity. We will discuss the role of CVD parameters (e.g., precursor flux), surface potential, adsorption of carbon species, and surface topography change observed by atomic force microscopy (AFM) in achieving the desired selectivity in CVD growth of MoS2. Our findings pave the way for a controllable lithography-free patterned synthesis of 2D-TMD materials, eliminating the need for complex lithography processes and minimizing contamination. This study presents a promising approach to implementing a bottom-up fabrication process for the next-generation TMD-based device fabrication and its further scaling.

The introduction of 2D materials as an active or enabling component is of significant interest in the field of electrochemical energy storage because it provides properties such as mechanical stability, large surface area and at the same time low material requirements. Furthermore, graphene-like 2D structures show strong electrical conductivity and electrochemical stability. While each individual 2D material has unique advantages, the deliberate assembly of heterostructures made up of different flakes in configurations such as 2D/2D or particle-flake (OD/2D) emerges as an important advanced approach. Such finely built heterostructures not only improve functioning but also have potential to push the performance of energy storage devices to levels that were not previously possible. A simple, competitive and scalable strategy to produce heterostructures by combining OD nanoparticles and 2D graphene in the gas phase is reported in this research work. Gas-phase synthesis of graphene is known for more than a decade which is now further developed to give production rates of few hundred mg/h of few-layer graphene (FLG). By combining two independent gas phase reactors, this two-layer graphene is controllably mixed with other functional materials in the gas phase to obtain heterostructures without the use of structure directing agents. The reactor system was involving a microwave plasma and a hot wall reactor. Silicon nanoparticles were synthesized in the hot wall reactor, meanwhile graphene was produced in the MW plasma reactor. Both reactors were connected in such a way that the nanoparticles and graphene get in contact with each other directly in the gas phase after their inception. In this way the self-assembled heterostructures of graphene and nanoparticles are produced with the production rate reaching almost 800 mg/h. The materials were characterized with TEM, Raman spectroscopy, XPS and XRD to investigate the morphology, composition and structure. TEM images indicate silicon is present as almost spherical nanoparticles that form small aggregates. These particles are interconnected by graphene. EDX mapping shows silicon nanoparticles having graphene surrounding them. It is present between the aggregates of nanoparticles as well as connector flakes to each other. Raman as well as XRD spectra confirmed the presence of silicon and graphene in heterostructures with extraordinary purity. The presence of silicon in crystalline as well as amorphous form was also confirmed from Raman spectra. It will be shown that the successful formation of OD/2D silicon/graphene heterostructures used as anode material for lithium-ion batteries has illustrated some significant improvements. Compared to pure silicon, their combination results in excellent long-term stability of the anode while also increasing its Coulombic efficiency. Thus, the formation of these heterostructures in the gas phase offers the possibility to exploit the potential of silicon to significantly increase the anode storage capacity.

Chemical vapor deposition (CVD) with sulfur gas is the most popular method for synthesizing large-scale 2D materials with high quality. Various MoS2 can be obtained from this method using various precursors with different properties, process temperatures, and substrate materials. Solution process methods show advantages for preparing films with large size, high throughput, low cost, thickness control, and an environmentally friendly process. Even though there is sulfur in the precursors of the solution-process synthesis methods, supplementing the sulfur that is lost during the CVD process is unavoidable. In this study, two precursors of ammonium tetraethimolybdate and ammonium molybdate were used in different solvent formulations to make MoS2 crystalline by using simple thermal annealing and bottom-up thermolysis methods. These methods were relatively easy to handle, safe, and environmentally friendly processes. Importantly, these MoS2 atomic layers were completed without additional sulfurization using CVD, but just with a single step of annealing because of sulfur-rich formulations. The 2D atomic layers were controlled to 2 to 7 layers with precursor concentrations with both formulations, which were confirmed by STEM-FIB. Thin-film transistors (TFTs) were prepared from the solution-processed MoS2 on Al2O3 and SiO2 dielectric with thermal evaporated Al source and drain electrodes. The results show improved mobilities of 9 to 48 cm2 V-1s-1 and reasonable on-off ratios of around 1.0×104 with solid output saturations. These new methodologies can be applied to multifarious devices and have the potential for scalability in 2D MoS2 materials.

In this study, we report the fabrication of molybdenum disulfide (MoS2) thin films–based electronic devices. Nanostructured molybdenum disulfide (MoS2) thin films are grown as the active

5:00 PM EL05.08.17 Photoelectric Properties of Funnel Devices Based on Asymmetrically Strained Two-Dimensional Materials Kyung-Hwa Yoo; Yonsei University, Korea (the Republic of)

5:00 PM EL05.08.18 Lithography-Free Patterned Growth of Few-Layer MoS2 Assisted by Electron Irradiation Haobo Li; Edward K. Nalando and Silvija Gradecek; National University of Singapore, Singapore

5:00 PM EL05.08.19 Formation of Silicon/Graphene Heterostructures through Co-Gas-Phase Synthesis Muhammad Ali1,2; Hartmut Wiggers1 and Michael Pope2; 1University of Duisburg-Essen, Germany; 2University of Waterloo, Canada

5:00 PM EL05.08.20 Wafer-Scale Synthesis of MoS2 Atomic Layers with Different Mo Precursor Solutions and Application to Thin-Film Transistors Woon-Soon Choi; Hoseo University, Korea (the Republic of)

5:00 PM EL05.08.23 Fabrication of Nanostructured Molybdenum Disulfide (MoS2) Thin Film-Based Electronic Devices Kevin Qian, Ibrahim Giwa, Fabian Sanchez, Elton Mawire, Sherwood Dong, Eric Smith, Qunying Yuan and Zhiqiang Xiao; Alabama A&M University, United States

In this study, we report the fabrication of molybdenum disulfide (MoS2) thin films–based electronic devices. Nanostructured molybdenum disulfide (MoS2) thin films are grown as the active
semiconducting channel material for the fabrication of MoS₂-based field-effect transistors using plasma-enhanced atomic layer deposition (ALD). MoS₂-based electronic devices such as MoS₂ field-effect transistors, inverters, and ring-oscillators are fabricated with the ALD-grown MoS₂ film using the clean room-based micro- and nano-fabrication techniques. Hydrogen sulfide (H₂S) gas is used as the S source in the growth of molybdenum disulfide (MoS₂) while molybdenum (V) chloride (MoCl₅) powder is used as the Mo source. The MoS₂ film will be analyzed by the high-resolution tunnel electron micrograph (HTREM), scanning electron micrograph (SEM), X-ray photoelectron spectroscopy (XPS) analysis and Raman spectrum analysis. The fabricated MoS₂ device wafer will be annealed at high-temperatures (800 – 900 °C), and the electrical property of the MoS₂-based electronic devices will be measured before and after the high-temperature annealing and will be compared. The characterization results of the nanostructured molybdenum disulfide (MoS₂) thin films and the measurement results on the fabricated MoS₂-based electronic devices will be reported in the 2024 MRS Spring Meeting. Acknowledgments: The research is supported by National Science Foundation under Grant No. ECCS-2100748.

5:00 PM *EL05.08.24
High Performance GQD/Graphene Heterostructure Field Effect Phototransistor with Efficient Photoinduced Effects Muhammad Shehzad Sultan¹, Ernesto Espada Nazario¹, Bianca S Umpierre Ramos¹, Daniela D Negron Negrón¹, Amanda M. Gracia Mercado¹, Wojciech Jadwisienczak², Brad Weiner¹ and Gerardo Morell¹; ¹University of Puerto Rico - Rio Piedras, United States; ²Ohio University, United States

Graphene and highly luminescent graphene quantum dots (GQDs) have been widely used in optoelectronic devices as a photovoltaic material. Graphene Quantum Dots (GQDs) have been widely used for various optoelectronic devices as a photovoltaic material due to their high absorption coefficient and tunable bandgap. However, the low mobility of GQD films results in poor charge collection and device performance. By combining GQDs with graphene into hybrid GQDs/Graphene field effect transistors, photocarriers from GQDs are transferred to graphene, improving charge collection and transport, drastically increasing the photoresponsivity. In this study, we report the preparation of a GQDs/Graphene heterostructure in order to investigate the effect of GQDs on photovoltaic response of graphene. Using UV-vis absorption and photoluminescence (PL) spectra, the optical properties of graphene and the GQDs/Graphene heterostructure were measured and compared. Moreover, to investigate their electronic and charge transfer properties, we fabricated field-effect phototransistors (FEPT) on pristine graphene and GQDs/Graphene heterostructure thin films and investigated their photoactive electrical properties. Under illumination, both pristine and GQDs/Graphene FEPT show an increase in current and carrier mobility. The increased current and carrier mobility of GQDs/Graphene FEPT is due to the presence of a large number of photoexcited charge carriers. The current and carrier mobility in the GQDs/Graphene heterostructure FEPT were also lower than those in the pristine graphene FEPT. This is explained by GQDs n-type doping effect on graphene, which reduces the accumulation of holes in the active p-channel near the insulating layer and causes charge to be transferred from the GQDs to the graphene. As a result, we discovered a charge transfer effect in the GQDs/Graphene heterostructure, which could be used in optoelectronic devices.

8:30 AM *EL05.09.01
Neuromorphic Circuits and Devices Based on MoS₂ Andras Kis; Ecole Polytechnique Federale de Lausanne, Switzerland

Machine learning and signal processing on the edge are poised to influence our everyday lives with devices that will learn and infer from data generated by smart sensors and other devices for the Internet of Things. The next leap towards ubiquitous electronics requires increased energy-efficiency of processors for specialized data-driven applications. I will present here how we realised an in-memory processing device based on a two-dimensional materials platform that can potentially outperform its silicon counterparts in both standard and non-traditional Von Neumann architectures.

9:00 AM *EL05.09.02
Compute-in-Memory Hardware based on 2D Materials for Convolution Neural Networks Kah-Wee Ang; National University of Singapore, Singapore

The exponential growth of data storage and computational requirements has imposed severe power consumption challenges for digital computers built on traditional Von Neumann architecture. New computing systems using the compute-in-memory (CIM) concept could offer a potential solution to overcome the inherent energy consumption and latency issues. In particular, CIM based on analog memristors is promising to enable a low latency and energy-efficient approach for performing data-intensive tasks such as image processing by means of neural network training. Here, we demonstrate memristive crossbar arrays (CBA) using transition metal dichalcogenides for implementing convolution neural network (CNN) hardware. The memristor achieves a small switching voltage, low switching energy, and improved variability in addition to the ability to emulate synaptic weight plasticity. The CBA successfully implements both neuromorphic and matrix-heavy workloads in neural networks, including artificial-synapse-based ANN, multiply-and-accumulate (MAC) operations, and convolutional image processing with high recognition accuracy. Moreover, the column-by-column MAC operation manifests a highly parallelized computing ability, opening a route to enable hardware acceleration of machine learning algorithms for emerging artificial intelligence applications.

9:30 AM EL05.09.03
Transfer-Free Wafer-Scale Graphene Electronics on Sapphire Oliver Fenwick¹, Zhichao Weng¹, Sebastian Dixon², Lok Yi Lee³, Colin Humphreys¹,², Ivor Guiney¹, William Gillin¹, Robert Wallis², Bryan Wingfield², Paul Evans², Piotr Baginski³ and Joanna Baginska³; ¹Queen Mary University of London, United Kingdom; ²Paragraf Ltd., United Kingdom

The realisation of graphene solid-state electronic devices has been held back by challenges of processing high-quality monolayer graphene at scale. In this work, we used wafer-scale graphene as the electrode in selected electronic devices, notably OLEDs and memristors. The graphene was grown by Paragraf Ltd using their proprietary growth process to produce high quality, monolayer graphene grown directly onto 50 nm sapphire wafers in batches of up to 37 wafers in metal-organic chemical vapour deposition (MOCVD) reactors. All processes in device production are compatible with semiconductor production lines, and we find graphene to be remarkably robust to these processes.

Transfer-free wafer-scale graphene membranes will be reported in the 2024 MRS Spring Meeting.


9:45 AM EL05.09.04
Ultrathin ShTe₂/Ge₅Sh₂Te₆ Superlattices for Low-Power and High-Speed Phase Change Memory Xianqin Wu¹, Asir Intisar Khan¹, Huiruoz Zhang²,³, Heshan Yu⁴,⁵, Albert Davydov², Ichiro Takeuchi⁴, H.S. Philip Wong¹ and Eric Pop¹; ¹Stanford University, United States; ²National Institute of Standards and Technology, United States; ³Theiss Research, Inc., United States; ⁴University of Puerto Rico - Río Piedras, United States; ⁵Advanced Optical Materials, Advanced Optical Materials, 2101675 (2021). DOI: 10.1002/adom.202101675

Graphene is considered as a promising material for replacing ITO, which has long term supply issues due to its limited elemental abundance, but for this to become possible the as-grown graphene was patterned using photolithography and its conductivity was enhanced by doping with nitric acid prior to deposition of the OLED stack. The electrical and optical performances of the as-fabricated graphene-based OLEDs were identical to control devices with conventional ITO anodes [1].

Here, we present nanoscale PCM devices (~40 nm bottom electrode diameter) based on Sb$_2$Te$_3$/GST467 superlattices. Unlike traditional PCM materials, GST467 contains coherent SbTe nanoclusters within the Ge-Sb-Te matrix, enhancing crystallization and lowering the melting temperature. These nanoclusters act as precursors for crystallization, boosting the switching speed of GST467. By incorporating GST467 into our superlattice PCM devices, we achieved remarkable results, including a record-low switching power density of approximately 5 MW/cm$^2$, an ultra-low switching voltage of around 0.7 V, sub-1.5 pJ switching energy, rapid switching speed of about 40 ns, low resistance drift with 8 distinct resistance states, and high endurance of $~2 \times 10^6$ cycles.

The performance of our devices is attributed to strong heat confinement within the superlattice interfaces and their nanoscale dimensions. Additionally, the unique microstructural properties of GST467, coupled with its higher crystallization temperature, contribute to faster switching speeds and improved stability, surpassing some of the fundamental trade-offs observed in conventional PCM. Importantly, this study combines bottom-up natural interfaces in the nanocomposite with top-down superlattice interfaces in the same memory material, resulting in superior device performance.

4. A. I. Khan, E. Pop et al., IEEE EDL 43, 204-207 (2022)

Second, we have elucidated the factors controlling the crystallinity of graphene grown on Ge(110) using advanced dark-field low-energy electron microscopy (DF-LEEM) and micro-low-energy electron diffraction (µ-LEED). This insight is utilized to produce large-area graphene films with minimal rotational misalignment—a major step toward realizing state-of-the-art technologies harnessing the exceptional properties of graphene lacking defective grain boundaries. We have discovered a new phenomenon in which misoriented graphene domains nucleate from the edges of unidirectionally aligned graphene islands when the islands grow over Ge surface steps, increasing polycrystallinity throughout growth. Extensive synthesis studies provide strategies for suppressing this secondary nucleation of misoriented domains to achieve graphene films in which the predominant epitaxial orientation has high coverage > 99% and low rotational spread < 0.6°. These results clarify the varying crystallinity and irreproducibility of graphene grown on Ge(110) reported in the literature, demonstrate the importance of using techniques with high spatial and angular resolution when determining if 2D materials are single crystals, and provide a route towards the large-area synthesis of single-crystal graphene on commercially available and technologically useful substrates.


We validate this proposed method using current-voltage characteristics simulated by technology computer-aided design (TCAD). We find that this proposed method offers accurate mobility estimation for 2D semiconductor mobility, allowing us to properly account for contact gating in back-gated FETs without having to use complicated geometries to directly probe the channel.
Copper wires in the back-end-of-line (BEOL) interconnects typically require two layers surrounding them: a diffusion barrier preventing Cu from diffusing into the dielectrics, and a liner, ensuring cohesive Cu wires and smooth interfaces. The current industry standards for barrier and liner applications include TaN and Ta, respectively, which then form a bilayer with a typical thickness of ~4 nm. However, with the advent of the 3-nm technology nodes, interconnect half-pitches have reached the scales of 10 nm. Consequently, the barrier/liner bilayer would represent a significant fraction of the wire cross-section and increase the wire resistance and cause significant RC delays. The polycrystalline nature of the conventional TaN/Ta bilayer films prevents formation of a continuous and effective film in the ultrathin regime. Moreover, their performance as a function of the film thickness is poorly understood, especially in ultrathin films.

In recent years, this expected limitation of conventional barriers and liners led to intense efforts to replace them with 2D materials, as these can be continuous yet atomically thin. However, no approach reported thus far fulfills the requirements for BEOL integration, namely low temperature (~450 °C), uniform and scalable growth, thickness control and film conformity to the substrate. We have recently developed a novel approach to growing layered films of WS$_2$ that fulfills all of these requirements. Our WS$_2$ films function as bifunctional liners and Cu diffusion barriers. We demonstrate these functionalities through electrical measurements and modeling approaches toward evaluation of temperature-dependent diffusion barrier properties for standardized barrier evaluation in the ultrathin film limit.

This approach provides an ability to identify and study the thickness regime in which 2D-layer films are expected to outperform the standard TaN layers. We will also discuss measurements and modeling approaches toward evaluation of temperature-dependent diffusion barrier properties for standardized barrier evaluation in the ultrathin film limit.

**References:**

Ivaylo Hinkov1,2 and Mourad Cherif1,2; 1Université Sorbonne Paris Nord, France; 2Laboratoire des Sciences des Procédés et des Matériaux LSPM CNRS, France

Characterization of Hybrid Edge Results in Narrowed Bandgap of Bottom-Up Liquid-Phase Synthesis of Bent N=6/8 Armchair Graphene Nanoribbons Using Scanning Tunneling theoretically predicted. Additionally, we recently refined a Metal-assisted modified exfoliation protocol, allowing for the transfer of the exfoliated flakes onto various flat substrates. This enhances adhesion between monolayers and hydrophilic substrates, overcoming delamination issues associated with the Au-exfoliation method. We perform a comprehensive comparison between APTES-functionalized Au-exfoliated flakes and those obtained through conventional scotch tape exfoliation, evaluating process yield and monolayer quality. Characterization techniques, including ellipsometry, AFM, XPS, Raman spectroscopy, and photoluminescence spectroscopy, confirm the method's effectiveness and superior outcomes in terms of yield and crystal quality. Moreover, we propose a novel method to obtain GNRs, which we were able to characterize in terms of STS, as theoretically predicted. Additionally, we recently refined a Metal-assisted modified exfoliation protocol, allowing for the transfer of the exfoliated flakes onto various flat substrates. This demonstrates the feasibility of achieving extensive exfoliation on rigid substrates (Si, SiO2, ITO, Al2O3) as well as flexible substrates (PET, Kapton).

Two-dimensional (2D) materials have gained significant scientific interest owing to their exceptional properties and potential applications. Recently, Metal-assisted exfoliation technique has emerged as a valuable method for obtaining large and high-quality 2D monolayers. However, the process efficiency can be hampered by poor adhesion between the metal foil and the substrate. In this study, we address this issue by investigating surface functionalization of the target substrate using (3-Aminopropyl)triethoxysilane (APTES). The introduction of APTES significantly enhances adhesion between monolayers and hydrophilic substrates, overcoming delamination issues associated with the Au-exfoliation method. We report a comprehensive comparison between APTES-functionalized Au-exfoliated flakes and those obtained through conventional scotch tape exfoliation, evaluating process yield and monolayer quality. Characterization techniques, including ellipsometry, AFM, XPS, Raman spectroscopy, and photoluminescence spectroscopy, confirm the method's effectiveness and superior outcomes in terms of yield and crystal quality. Moreover, we propose a novel method to obtain GNRs, which we were able to characterize in terms of STS, as theoretically predicted. Additionally, we recently refined a Metal-assisted modified exfoliation protocol, allowing for the transfer of the exfoliated flakes onto various flat substrates. This demonstrates the feasibility of achieving extensive exfoliation on rigid substrates (Si, SiO2, ITO, Al2O3) as well as flexible substrates (PET, Kapton).

3:30 PM EL05.11.03 Characterization of Hybrid Edge Results in Narrowed Bandgap of Bent N=6/8 Armchair Graphene Nanoribbons Using Scanning Tunneling Microscopy and Scanning Tunneling Spectroscopy Hanfei Wang1, Gang Li2,3, Michael J. Loe3, Anshual Saxena4, Jianguang Yin5, Mامun Sarker3 and Shinyoung Choi2; 1University of Illinois at Urbana-Champaign, United States; 2The University of Chicago, United States; 3University of Nebraska–Lincoln, United States; 4The University of Texas at Austin, United States

Scalable fabrication of graphene nanoribbons with narrow band gaps has been a nontrivial challenge. A unique approach has been developed to access narrow band gaps by using hybrid edge structures. Bottom-up liquid-phase synthesis of bent N=6/8 armchair graphene nanoribbons (AGNRs) has been achieved in high efficiency through copolymerization between an ortho-terphenyl monomer and a naphthalene-based monomer, followed by Scholl oxidation. Through scanning tunneling microscopy (STM) characterization, an unexpected 1,2-aryl migration has been discovered, which is responsible for introducing 60 degrees kinked structures to the GNR backbones. Topographical STM scans consistently show asymmetric internal sturcures in agreement with the bent GNR structure resulted from unexpected competition between the allyl 1,2-migration on the naphthenate unit and the direct cyclodehydrogenation during Scholl oxidation. Through model study, we postulate that such 1,2-migration may not occur that frequently during liquid-phase synthesis due to the more rigid C-C bonds in a polymer backbone. Such defects of terminal structures should only take place occasionally, and the AGNRs should maintain close electronic properties to the proposed straight ribbons. The STM topography show, except for a few straight GNRs, most ribbons contain one or two kinks in their backbone. Scanning tunneling spectroscopy (STS) was employed to fully characterize the electronic structure of this GNR. A STS bandgap of 1.7 eV is found across and bent AGNRs deposited on hydrogen passivated silicon surface. The STS experimental result of AGNR bandgap is well in the range of 1 eV of the optical band gap and 2.2 eV of the calculated GW band gap. Application of bent N=6/8 AGNRs in efficient gas sensing shows its potential in broad applications of other innovative uses.

2:45 PM BREAK

3:15 PM EL05.11.04 Inductive Heating a Versatile Process for Large-Scale Single-Crystal Cu(111) and Graphene Synthesis : Experiments and Thermochemical Modeling Samir Farhat1,2, Wafa Alimi1,2, Ivaylo Hinkov1,2 and Mourad Cherif1,2; 1University Sorbonne Paris Nord, France; 2Laboratoire des Sciences des Procédés et des Matériaux LSPM CNRS, France

Inductive heating (IH) is proposed as a new concept to bring together centimeter-scale single crystal Cu(111) metal catalyst preparation and graphene growth in a combined process. Commercial polycrystalline metal catalyst is first heated by radio frequency (RF) magnetic fields. A nearly uniform magnetic field induced by Helmholtz-like coils penetrates the copper foil girding eddy currents. While the frequency of the current is being rapidly varied, the substrate temperature increases from room temperature to ~1030 °C in ~1 minute. Unlike Roll to Roll (R2R) methods where the copper is continuously passed in a hot furnace region [1], in our approach, the induction coils are moved at a constant speed generating a controlled thermal gradient. The rate of heating and cooling of the metal are hence much faster and gradient surface energy is better modulated. In addition, machine performance and maintenance costs could be reduced due to technological high-speed sealing and thermal constraints in the R2R process. In addition, for scale-up purposes, large oven are necessary to heat the metal foils. This becomes less energy efficient as system size is increased. In contrast, inductive heating only allows the heating of the thin metal films without heating the surrounding gas [2]. In our system, an edge of the Cu sheet was tapered into a tip shape, which ensured the nucleation of a single Cu(111) grain at the tip. The sliding of the coils across the copper foil caused the movement of the grain boundaries between the single crystal and polycrystalline regions and the grain of single crystal Cu(111) reached the width of the copper sheet as confirmed by XRD and EBSD. Consequently, graphene was synthesized using the same inductive heating reactor. From the optical microscopy image, all the hexagonal graphene domains are oriented in the same direction and the Raman spectrum shows the total absence of defects. We take the advantage of such system in order to better understand the mechanisms responsible for graphene growth in a chemical environment represented by a ternary C–H–Ar system. We specifically developed a thermochemical model with gas chemistry and surface reactions through Cu(111) site fraction and surface molar concentrations. The graphene growth rate is obtained by compiling the effects of gas and surface reactions via CHEMKIN software. The influence of the total pressure, substrate temperature and H2, CH4, Ar contents are obtained from the model and compared to the experiments. There was good agreement between experimental and the modeling results, providing an insight into optimizing CVD graphene growth.

References

3:30 PM EL05.11.05 Thin-Film Nanocarbonimetry Study of The Melting Transitions in 2D Phase-Change Superlattices Jie Zhao1, Aris Intisar Khan2, Mikhail Efremov3, Zichao Ye4, Xiaojing Wu5, H.S. Philip Wong2, Eric Pop2,6 and Leslie H. Allen1; 1University of Illinois at Urbana-Champaign, United States; 2Stanford University, United States; 3University of Wisconsin—Madison, United States

Today's nanoelectronics are reaching the limits of energy and latency for numerous data-intensive applications, including the Internet of Things (IoT) and artificial intelligence (AI). Improving the energy efficiency and speed of data storage remains at the core of tackling this grand challenge. Phase-change memory (PCM) is a storage technology combining the high speed of dynamic random-access memory and the non-volatility of flash memory. By simply stacking ~2 nm SnTe or Ge2Sb2Te5 together, superlattice (SL) phase change memory devices demonstrated an 8 times reduction in power consumption, compared to conventional PCM devices [1]. The unexpected device-level success lies in the unique thermodynamic properties of such two-dimensional (2D) heterostructures, which, unfortunately, are inaccessible to conventional characterization methods with limited sensitivity and speed. Thus, the underlying science responsible for success has remained a mystery.
Rapid Detection of Defects in Monolayer 2D Semiconductors by Polarized Raman Spectroscopy by Crystal A. Nattoo, Tara Pena, Koosha N. Nazif, Amalya C. Johnson, Fang Liu and Eric Pop; Stanford University, United States

An outstanding challenge in integrating two-dimensional (2D) transition metal dichalcogenides (TMDs) into future optoelectronics is optimizing high-quality and large-scale growths of these atomically thin materials. Several methods exist for wafer- and chip-scale growths of 2D-TMDs, such as chemical vapor deposition (CVD) and atomic layer deposition (ALD). Still, we see a large degree of variability from growth to growth due to intrinsic and extrinsic factors like defects and humidity [1]. Optimizing the rapid characterization methods used to discern material quality before fabrication is essential to improve the yield of devices produced during research and development, saving time and money.

Raman spectroscopy is a non-destructive and standard characterization technique, to examine various material features such as thickness [2], doping [3], strain [4], and disorder [5, 6]. However, the effect of doping and disorder on the Raman signatures still remains to be examined in some TMD systems (e.g., WSe2). In this work, we propose using cross-polarized Raman spectra to isolate the in-plane E’ mode from the out-of-plane A1’ mode with a 532 nm laser to properly examine defect-induced Raman features in two monolayer TMD materials of broad interest. Based on the dispersion curves, we focus on MoS2 and WSe2, because they have the most prominent optical phonon energy and dispersion for this method.

The isolation of the E’ mode by cross-polarization is especially effective in the case of WSe2, which shows a strong degeneracy of the E’ and A1’ modes around 250 cm⁻¹, making analysis a unique challenge. Due to the nature of defects interrupting the vibration of atoms in-plane, the transverse and longitudinal modes are most sensitive to changes in defect density. For this reason, we study the amplitude changes of the in-plane E’ mode in relation to the second order M point phonon modes that appear with increasing disorder.

After the data are collected, the spectra are fit with a Gaussian and Lorentzian spectral blend to extract the peak height, position, and full width at half-maximum (FWHM). The ratio between the left shoulder second-order phonon modes and the first-order E’ mode is used as a figure of merit to estimate the expected defect density and the majority carrier mobility in the 2D material. Our approach can estimate defect densities down to the order of 10¹¹ cm⁻² using TMD samples procured by different synthesis methods. To compare the method’s validity, the same samples are also characterized by conductive atomic force microscopy (c-AFM) and electrical measurements of mobility.

This rapid, non-destructive Raman characterization method can be integrated into commercial growth systems to accelerate TMD research and development for practical applications. Future work is also planned to expand these efforts to other TMDs. The work was supported by an NSF Graduate Fellowship (C.A.N.), an NSFAscend Fellowship (T.P.), by the SRC SUPREME Center and the Stanford SystemX Alliance.


SESSION EL05.12: Optoelectronics
Session Chairs: Sean Li and Muhammed Juvaid Mangattuchali
Friday Morning, April 26, 2024
Room 344, Level 3, Summit

8:45 AM *EL05.12.01
Towards Large-Area Black Phosphorous Midwave-IR Optoelectronics by Ali Javey1,2, 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

High-efficiency mid-wavelength infrared (mid-IR, 3–5 μm) optoelectronics, including light emitting diodes (LEDs) and photodetectors, are of high demand for emerging applications in spectroscopy, imaging, and gas sensing. Black phosphorus (bP) has emerged as a unique optoelectronic material for mid-IR applications with performances surpassing those of conventional III-V and II-VI semiconductors of similar bandgap. In this talk, I will present recent advancements on understanding and controlling the radiative and non-radiative recombination rates as a function of bP thickness. We observe higher photoluminescence quantum yields in bP as compared to conventional III-V and II-VI semiconductors of similar bandgap. In this talk, I will present recent advancements on controlling the radiative and non-radiative recombination rates as a function of bP thickness. We observe higher photoluminescence quantum yields in bP as compared to conventional III-V and II-VI semiconductors of similar bandgaps due to the smaller Auger recombination rate. As a result, bP mid-IR LEDs with external quantum efficiency of ~4% are reported, outperforming the state-of-the-art in this wavelength range. Furthermore, device encapsulation and packaging technologies are explored with extrapolated half lifetime of ~15,000 hours based on accelerated lifetime experiments. I will present strategies for large-area device fabrication and processing.

9:15 AM EL05.12.02
Photo-Gating through Unidirectional Charge Carrier Funneling in 2D TMDC / 2D Perovskite Heterostructure-Photodetectors by Leon Spee1, Julius Konietzka1, Annika Grundmann2, Martin A. Schroer1, Markus Wintener1, Holger Kalisch3, Michael Heuken3,4, Andrei Vescan5, Gerd Bacher1 and Franziska E. Muckel1; 1University Duisburg-Essen, Germany; 2RWTH Aachen University, Germany; 3AIXTRON SE, Germany

Two-dimensional (2D) van der Waals (vdW) semiconductors, such as transition-metal dichalcogenides (TMDs), have garnered increasing attention as promising materials for photosensing applications. Their appeal lies in their high oscillator strength, significant electronic mobility, and remarkable mechanical flexibility, promising novel application scenarios for optical sensing in healthcare, optical communication or different lifestyle applications. However, due to their intrinsically limited light absorption, high sensitivities and sensitivities are hard to achieve. To enhance photosensing, TMDs are frequently integrated into functional heterostructures with other vdW semiconductors like 2D Ruddlesden-Popper Perovskites to introduce a gain mechanism. However, the processes of energy and charge carrier transfer between TMDs and 2D Ruddlesden-Popper materials remain subjects of debate, making it challenging to elucidate the fundamental mechanism of device operation.

In this study, we present lateral heterostructure photodetectors composed of MOCVD-grown molybdenum disulphide (MoS2) and solution processed butylammonium lead iodide (BA₂PbI₄) that exhibit significantly enhanced responsivities, reduced dark current, and increased detectivity when compared to devices using MoS2 or BA₂PbI₄ alone. We provide compelling evidence that this improvement is linked to a gain mechanism facilitated by photo-gating within the MoS2 channel. This photo-gating results from a unidirectional transfer of holes from MoS2 to BA₂PbI₄ and the blocking of electrons by butylammonium ions. Our devices exhibit responsivities up to 10 A/W, which corresponds to a gain of 145. This research sheds light on the intriguing performance of heterostructure photodetectors based on 2D materials and their potential for practical device integration.
In anticipation of their promising applications in the deep-ultraviolet (UVC) spectral range, e.g., for disinfection, AlGaN-based UVC-Light Emitting Diodes (UVC-LEDs) have experienced a lot of attention over the last decade. However, these LEDs still face low performance regarding Wall Plug Efficiency (WPE) and External Quantum Efficiency (EQE) than blue-lighting LEDs [1,2]. One reason is the low electrical conductivity of the p-AlGaN cladding layer, which limits both, current injection in flip-chip geometry, and lateral current spreading for devices in standard geometry.

Graphene combines high electrical conductivity and high optical transparency in the UVC spectral range and has thus the potential to act as low absorbent contact layer in UVC-LEDs. Here we report on a transfer-free low-temperature approach for integrating graphene directly into AlGaN-based UVC-LEDs at temperatures far below 1000°C. We demonstrate functional UVC-LEDs in standard as well as in flip-chip geometry.

Based on our previous work [3,4] we used a plasma-enhanced CVD graphene process to directly grow graphene on the p-AlGaN layer of a UVC-LED at 670°C. The graphene has an optical transparency above 90% in the UVC region and an electrical sheet resistance of about 5 kΩ/sq. Using the directly grown graphene as a transparent contact layer, we were able to improve the EQE of UVC-LEDs emitting at 275 nm in standard as well as in flip-chip geometry to over 5%. With these proof-of-principle experiments, we have paved the way to a large-scale integration-friendly process of graphene-enhanced UVC-LEDs.


9:45 AM EL05.12.04

Bridging Macroscopic and Microscopic Nonlinear Optics with Layered Semiconductors

Chiara Trovatello1, Xinyi Xu1, Fabian Mooshammer1, D. Basov1, Giulio Nicola Felicce Rullo2 and P. James Schuck1; 1Columbia University, United States; 2Politecnico di Milano, Italy

Nonlinear frequency conversion provides essential tools for light generation, photon entanglement, and manipulation. Conventional nonlinear optical crystals display moderate second-order nonlinear susceptibilities and perform well in benchtop setups with discrete optical components. However, such crystals do not easily lend themselves to miniaturization and on-chip integration. Transition metal dichalcogenides (TMDs) possess 10-100x stronger nonlinear susceptibilities and, thanks to their deeply sub-wavelength thickness, offer a unique platform for on-chip nonlinear frequency conversion and light amplification. Recently, such giant nonlinearity has been exploited to demonstrate nonlinear light amplification at the ultimate thickness limit [1]; however, optical gain was still limited by the sub-nm propagation length.

The nonlinear conversion efficiency could be scaled by increasing the propagation length through the active medium. This is attainable by increasing the number of layers in the TMD sample. However, the nonlinear optical properties of semiconducting TMDs critically depend on their crystallographic symmetry. 2H-TMDs are naturally centrosymmetric, giving an opposite dipole orientation among consecutive layers. This results in a vanishing nonlinear susceptibility ($\chi^{(2)} = 0$) for crystals with even number of layers and precludes efficient conversion in multilayers. In contrast, 3R-TMDs naturally combine broken inversion symmetry ($\chi^{(2)} \neq 0$) and aligned layering, representing ideal candidates to boost the nonlinear optical gain with minimal footprint.

The nonlinear optical response of 3R-MoS2 has been explored in some recent pioneering studies [2,3], so far focusing on thinner crystals, reporting the quadratic enhancement with the layer number at the 2D limit, and showing a maximum SHG enhancement of $\approx 100$ occurring at specific thickness windows. Pushing towards general application, however, requires higher nonlinear enhancements and thus larger layer number, which in turn leads to more intricate interferences and interactions within the crystal.

Here we measure SHG from multilayer 3R-MoS2 crystals with variable thickness. We report the first measurement of the coherence length thickness will be $\approx 10^{-6}$. Further enhancement can then be achieved by regularly engineering larger crystals or waveguides with a periodicity on this length scale, or by exploiting birefringence.

Our results highlight the potential of 3R-stacked TMDs for integrated photonics, providing critical parameters for designing highly efficient on-chip nonlinear optical devices. By virtue of the exceptional nonlinear properties and the possibility of integration and phase matching in waveguide geometries, we foresee ultra-compact devices with extremely high nonlinear conversion efficiency — even exceeding multi-pass state-of-the-art photonic resonators of aluminum nitride — opening new frontiers for engineering on-chip integrated nonlinear optical devices including photonic resonators and optical quantum circuits.


10:00 AM BREAK

SESSION EL05.13 Optoelectronics and Magnetism I

Session Chairs: Ali Javey and Iuliana Radu
Friday Morning, April 26, 2024
Room 344, Level 3, Summit

10:30 AM EL05.13.01

New Form of High-k Dielectrics for 2D Field-Effect Transistors

Sean Li1, Junjie Shi1, Ji Zhang1 and Jing-Kai Huang2; 1University of New South Wales, Australia; 2City University of Hong Kong, Hong Kong

The integration of ultrathin insulators stands as a pivotal factor for the advancement of 2D Field-Effect Transistors (FETs) in cutting-edge technology. Presently, 2D semiconductor devices are yet to realize their complete theoretical potential, primarily due to the unavailability of suitable insulators. These insulators must strike a balance between maintaining minimal leakage currents and enabling a high gate capacitance to achieve superior gate coupling at sub-1nm Equivalent Oxide Thickness (EOT) scales. Furthermore, they must establish well-defined interfaces with the channel, exhibit minimal defect densities, and possess exceptional dielectric stability. This study showcases the power of dielectric engineering in elevating the performance of 2D FETs, offering viable avenues to develop 2D FETs characterized by remarkably low leakage currents, shorter channel lengths, and outstanding power efficiency.

11:00 AM EL05.13.03

Simultaneous Strain and Gate Tunability of Moiré Heterostructure Devices

Jordan Fonseca1, John Cenker1,2, Mai Nguyen1, Chaowei Hu1, Wang Xi1, George Rickey1, Takashi Taniguchi3, Kenji Watanabe3, Jian-Haw Chu1 and Xiaodong Xu1; 1University of Washington, United States; 2City University of Hong Kong, United States; 3National Institute for Materials Science, Japan

Moiré heterostructures of 2D materials have served as a platform for studying and engineering a wide variety of correlated phenomena and many-body physics. The atomic thickness of two-dimensional materials and the large effective lattice constant of moiré superlattices make electrostatic gating a particularly effective way to tune carrier density and thereby explore a rich phase
diagram of correlated effects. Independently, two dimensional materials exhibit unusually high elasticity and can sustain significant uniaxial strain before yielding. Uniaxial strain breaks rotational symmetry and changes interatomic spacing, altering many material properties in the process. An outstanding challenge, however, is simultaneously and independently tuning uniaxial strain and electrostatic gating in situ at cryogenic temperatures. In this talk, I will discuss our work to leverage novel approaches for efficient strain transfer to the moiré heterostructure in gateable van der Waals devices. I will show how the ability to traverse the strain-gating phase space for a high-quality transition metal dichalcogenide moiré heterostructure enables exploration of novel features in the photoluminescence spectra and discuss their origin in the underlying optoelectronic properties of this rich material system.

11:15 AM EL05.13.04
Electronic Properties of Quasi-1D Materials, TiS₃ and In₄Se₃
Alexander Sinitiski
University of Nebraska -Lincoln, United States

Two-dimensional (2D) layered materials have received much interest in recent years due to their ease of miniaturization by exfoliation techniques and very diverse physical properties. Quasi-one-dimensional (quasi-1D) materials, while seeing considerably less interest, can express many of the same desirable properties as conventional layered materials, with an added dimension of anisotropy. A representative example of quasi-1D materials is titanium trisulfide (TiS₃), a layered n-type semiconductor composed of chains of trigonal sulfur prisms with Ti⁴⁺ centers. Because of its moderate bandgap of about 1 eV, which is comparable to that of silicon, and theoretically predicted electron mobilities of up to 10,000 cm² V⁻¹ s⁻¹, TiS₃ is a promising material for electronic applications.

We demonstrate the ease of mechanical exfoliation of bulk TiS₃ crystals accompanied with theoretical calculations and show that these materials exfoliate into few-atomic-layer nanoribbons with very smooth edges. Their characterization by Raman spectroscopy shows a reliable, internally standardized shift of a few cm⁻¹ from monolayer to bulk demonstrating tunability typical of conventional layered materials. The TiS₃ field-effect transistors showed an n-type electronic transport with characteristics comparable to those of MoS₂, a popular 2D semiconductor. Their room-temperature mobilities of about 30 cm² V⁻¹ s⁻¹ were two orders of magnitude smaller than predicted theoretically, which we quantitatively explain by polar-optical phonon scattering in TiS₃. We demonstrate that TiS₃ is compatible with the conventional atomic layer deposition procedure for Al₂O₃, and the encapsulation of TiS₃ with alumina resulted in the mobility increase up to 43 cm² V⁻¹ s⁻¹. The quasi-1D TiS₃ chains exhibit an anisotropic photocurrent response to polarized light as well as a gate-tunable metal-insulator transition (MIT) and an access to the charge density wave (CDW) physics.

Many of the conclusions drawn for TiS₃ can be extended to other quasi-1D materials, such as In₄Se₃. In₄Se₃ has a different crystal structure, but it also features covalently bonded quasi-1D chains as its basic building blocks. We successfully exfoliated bulk In₄Se₃ crystals into few-nm-thick flakes with visible signatures of quasi-1D chains, similar to the exfoliated TiS₃ flakes. The In₄Se₃ flakes exfoliated on Si/SiO₂ have anisotropic electronic properties and exhibit field-effect electron mobilities of about 50 cm² V⁻¹ s⁻¹ at room temperature, as well as a polarization dependent photoresponse on the order of less than 30 ms. These two examples, TiS₃ and In₄Se₃, demonstrate the promise of quasi-1D materials for emerging electronic applications.

References:

1:30 PM EL05.14.01
Tailoring The Rashba-Induced Spin-To-Charge Conversion in 2D Transition Metal Dichalcogenides Interfaced with Oxide Ferroelectrics
Oliver Paull¹,², Khasan Abdakayumov², Sylvain Massabau¹, Céline Vergnaud², Luis M. Vicente-Arche¹, Alain Martz², Luca Iglesias¹, Matthieu Jamet² and Manuel Bibes¹; ¹Université Mixte de Physique, CNRS/Thales, France; ²Commissariat à l’énergie atomique et aux énergies alternatives, France

The direct and inverse Rashba-Edelstein effect in condensed matter is a viable source of charge-to-spin interconversion, towards the realisation of next-generation spintronic devices. One promising way of creating Rashba spin-orbit coupling (SOC) in an otherwise centrosymmetric material system is to interface it with a ferroelectric crystal, breaking inversion symmetry with the local electric field at the interface.

Two-dimensional (2D) crystals have emerged as a new class of materials that can exhibit a large range of quantum phenomena such as superconductivity, 2D magnetism, and non-trivial topological phases [1], [2]. Of these quantum phenomena, the Rashba effect has gained popularity recently as a result of its applicability to create charge-to-spin interconversion for next-generation spintronics devices. Highly stable PtSe₂, is one such 2D material which has a centrosymmetric crystal unit cell and a bandstructure that evolves drastically as a function of the number of monolayers deposited, evolving from a high band-gap semiconductor to a semi-metal [3]. Interfacing a 2D material with a ferroelectric (FE) crystal applies a strong local electric field at the interface which breaks the inversion symmetry and triggers the interfacial Rashba effect in the 2D layer. Importantly, the sign of the Rashba spin-orbit coupling depends on the direction of the FE polarisation, such that the spin texture chirality should reverse upon a change in direction of the FE polarisation [4]. This forms the basis of the functionality of a low-power FerroElectric Spin-Orbit (FESO) device.

In this work, we grow 2D materials such as PtSe₂ using molecular beam epitaxy and use a wet transfer process to interface them with a variety of ferroelectric surfaces such as LiNbO₃ substrates and BiFeO₃ thin films. The spin-to-charge conversion properties are then examined using a variety of experimental techniques and compared between samples with different ferroelectric polarisation directions and assessed in the context of a spin-to-charge conversion FESO device.

References:

1:45 PM EL05.14.02
Charge Carrier Balance in Scalable TMDC-Based Light Emitting Devices
Tobiloba G. Fabunmi¹, Henrik Myja¹, Annika Grundmann², Kalisch Holger², Andrei Vescan³, Michael Heuken³, Tillmar Kümmell⁴ and Gerd Bacher¹; ¹University of Duisburg-Essen, Germany; ²RWTH Aachen University, Germany; ³AIXTRON SE, Germany

2-dimensional transition metal dichalcogenides (TMDCs) such as WS₂ are ultrathin materials with huge oscillator strength, strong in-plane bonds, and in the case of monolayers a direct bandgap. These outstanding properties have stimulated the development of various concepts for light emitting devices [1], often based on micrometer-sized flakes. Recently, a scalable device architecture has been suggested, where wafer-scale TMDCs grown by metal-organic chemical vapor deposition (MOCVD) have been embedded between electron and hole supporting layers to form a vertical p-i-n architecture [2-4].

However, the luminance of TMDC-based LEDs in cw operation at room temperature is still limited to 50 cd/m² for microscale LEDs based on mechanically exfoliated WS₂ [5] and to about 1 cd/m² for scalable, 6 mm² large devices [2], respectively. One key requirement for optimizing the luminance is a balanced electron and hole injection into the active TMDC layer. In this work, we address the electron-hole balance in scalable WS₂-based LEDs by systematically varying the architecture of electron injection layers (EIL). We fabricated three different LED architectures: type 1 includes a ZnO EIL, type 2 contains Mg-doped ZnO as an EIL, and type 3 is a reference device without an EIL. At 5V forward bias, we observed a reduction of the current density by a factor of 10 in type 2 devices as compared to type 1. Simultaneously, the EQE was found to increase by an order of magnitude in the type 2 device compared to type 1, and a luminance of up to 3 cd/m² was obtained for type 2 devices. We attribute this to an improved electron-hole balance in type 2 devices, caused by a reduced efficiency of electron injection. Our interpretation is supported by device simulations using NextNano, which emphasizes the impact of a balanced electron and hole injection for efficient LEDs based on scalable 2D TMDCs.

References:
Towards CMOS-Integrated Graphene Hall Sensor Arrays with Individually Tunable Elements for High Sensitivity and Enhanced Uniformity

Salim El Kazzi, Sergej Pasko, Jan Mischke, Simonas Krotkus, Emre Yengel, Apostolia Manasi and Alexander Henning; Aixtron, Germany

To reach the silicon IC-industry, 2D materials need to pass the strict requirements of the semiconductor foundries and manufacturers. At the current stage of 2D materials research, it is critical for the community to develop work on the wafer-scale integration, yield, and reproducibility instead of selecting the best-performing ‘champion’ device produced on smaller scale. From a growth perspective, layer uniformity and repeatability are critical factors that need to be proven for any materials system considered in the CMOS technology.

Here, we report on the scaling up of 2D materials synthesis to 300 mm substrates. We focus on the different 2D integration schemes, which rely on the growth of 2D materials on amorphous or epitaxial substrates at different temperatures. We then highlight the importance of wafer scale uniformity and run-to-run repeatability for which we try to define for the community the metrology standard of 2D wafer-scale synthesis. Finally, we will address two other aspects related to cross-contamination and tool cleaning that are being solved to facilitate the entry of these materials into the Si-industry.

References:
complete and continuous membrane. The transferred quasi-2D amorphous carbon was firstly suspended as freestanding nanomembranes on TEM grid for imaging. The uniform contrast throughout in the low-magnification ADF-STEM image confirms that the film is macroscopically homogenous, and the SAED patterns show a characteristic diffuse halo, which verifies its amorphous nature.

Their mechanical properties were characterized by AFM nanoindentation performed on atomically thin nanomembranes suspended over 1.2 μm wide and 3 μm deep circular holes, giving an extracted high Young’s modulus of 400±100 GPa, which is comparable to that of crystalline graphene and h-BN, further verifies the homogeneity and continuity of the ultra-thin quasi-2D amorphous carbon prepared from the assembly and coalescence of carbon dots with strong lateral connections, which are very likely of covalent nature.

The achieved macroscopic uniformity, atomic-level thickness control, and processability allow our quasi-2D amorphous carbon films as dielectric in nanoelectronics devices, where their unique structure and properties were exploited to enable improved device performances. When utilized as gate dielectrics in graphene and 2D metal chalcogenides transistors, compared to amorphous bulk metal oxides, the ultrathin amorphous carbon films with predominant sp² carbon content can form clean interfaces with graphene and 2D metal chalcogenides, which leads to enhanced carrier transport mobility and minimum hysteresis. Compared to polycrystalline 2D h-BN, they have better processability and their amorphous atomic structures lead to drastically lower leakage current density (<10⁻⁴ A/cm² with thickness down to three atomic layers of 1.6 nm) with higher dielectric strength (breakdown field above 20 MV/cm) for substantially reduced power consumption and improved device reliability.

The atomic-level thickness and the presence of large-size carbon rings inside the atomic structure of quasi-2D amorphous carbon also make its multilayered assemblies attractive for insulating ion-transport media in memristors. Their intrinsic ultrathinness and distinctive atomic structures composed of heterogeneous carbon rings offer predefined filament formation pathways across atomically thin films, leading to drastically enhanced switching uniformity, reduced energy consumption (<20 fJ per operation), and faster operating speed (<20 ns) as the switching media for electrochemical memristor, without sacrificing endurance and retention.

Large Area Van der Waals MoS₂-WS₂ Heterostructures for Visible-Light Photocatalysis and Energy Conversion

- EL05.15.03
- SESSION EL05.15: Virtual Session: MOCVD and Device Technology of 2D —TMDC Layers and Heterostructures
- Session Chairs: Hippolyte Astier and Silvija Gradecak
- Tuesday Morning, May 7, 2024
- EL05-virtual

8:00 AM • EL05.15.01
Memristive Circuits based on Two-Dimensional Layered Hexagonal Boron Nitride for Radiofrequency Applications

Mario Lanza; King Abdullah University of Science and Technology, Saudi Arabia

Radiofrequency (RF) switches are essential components in modern communication devices, as they enable fast data transmission by driving or blocking electromagnetic signals of high frequencies (typically few/ten of gigahertz). The constant demand for higher data transmission rates requires RF switches capable of operating at higher frequencies, which represents a big challenge for commercial device developers. RF effect transistors and phase-change memristors (which are limited to ~60 GHz). In this talk I will present the fabrication of memristive RF switches, based on multilayer hexagonal boron nitride (h-BN), capable of operating reliably at frequencies up to 260 GHz. We build the first 2D-materials-based series-shunt device configuration and readily achieve outstanding insertion loss of 0.9 dB and isolation of 35 dB at 120 GHz. We accomplish consistent ambipolar switching with low resistances down to 9.3±3.7 Ω by introducing a low resistance tuning protocol, and achieve high endurance up to 2000 cycles (more than 60 times higher than previous reports on 2D-materials-based RF switches). These achievements represent a significant advancement towards next generation RF switches, as well as to the deployment of 2D materials in the semiconductors industry.

8:30 AM • EL05.15.02
Lytotropic Liquid Crystal Phases as Temples for Selective Interfacial Reactions to Asymmetric Functionalization of 2D Nanomaterials at Large Scale

Wei Wang; Aramco Americas: Aramco Research Center-Boston, United States

Anisotropic nanomaterials composed of two halves with different structure, chemistry, or polarity, known as Janus nanomaterials, have distinct properties when compared to symmetrically functionalized analogues. These materials have gained significant attention in many applications such as electronic thin films, drug delivery, sensors, optics, oil/water separation membranes, photocatalytically active micromotors, photocalysts, and interfacial modification. Two dimensional (2D) Janus nanosheets are especially intriguing considering their interfacial properties as well as their ability to assemble into higher order structures. In this research, we describe an approach to asymmetric functionalization of 2D nanosheets at large-scale through selective interfacial reactions using liquid crystal phases as templates. Several liquid crystal systems composed of surfactants, water and organic solvents were studied by birefringence imaging, cryo-TEM, small-angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) to optimize the microstructures and stability for using as “nanoreactor” templates, and the surfactants included cationic, anionic, non-ionic and zwitterionic types. In comparison to interfacial reaction in a conventional biphasic system, the efficiency of interfacial reaction within the liquid crystal templates can tremendously increase by more than million times (in >10⁴ order), enabling to scale up the synthesis of 2D Janus nanomaterials at industrial scale economically. Several samples of synthesized 2D Janus nanomaterials with different properties for different application have been demonstrated.

8:35 AM • EL05.15.03
Controlled Growth and Integration of 2D Semiconductors for High-Performance Electronics

Minsu Seol; Junyoung Kwon, Minseok Yoo, Changhyun Kim, Huije Ryu, Eun-Kyu Lee and Kyung-Eun Byun; SAIT, Samsung Electronics, Korea (the Republic of)

2D semiconductors have received much interest as next-generation channel materials. The ultrathin nature of 2D semiconductors affords notable advantages, including enhanced electrostatic gate control and continued transistor scaling, which are pivotal for advancing electronic devices. In this talk, I am going to present our recent progress related with growth, characterization, and integration of 2D semiconductors. We have successfully grown up to 8-inch wafer-scale MoS2 films on amorphous substrates through Metal-Organic Chemical Vapor Deposition (MOCVD). Furthermore, we have achieved the growth of single-crystalline MoS2 on selected areas. To assess film quality, we have employed non-destructive characterization methods. Through optimized integration processes, we have demonstrated the effective fabrication of field-effect transistors (FETs) on 8-inch wafers, resulting in exceptional uniformity in electrical performance, with a success rate exceeding 90%. Statistical analyses of high-performance 2D FETs, with variations in channel length, will be presented to provide insights into their performance characteristics. Additionally, this talk explores the persisting challenges associated with materials growth and device fabrication in this field, paving the way for future advancements in 2D semiconductor-based electronics.

9:05 AM *EL05.15.04
X-Ray Photoelectron Spectroscopy Study of 2D MoS2/Oxide Dielectric Interface Manish Chhowalla, University of Cambridge, United Kingdom

The interface between two-dimensional transition metal dichalcogenide (2D TMDs) semiconductors and dielectric has not been as widely studied as the metal/2D TMD junction. The dielectric for 2D TMD devices must be thermodynamically and mechanically stable as well as being chemically inert. The band offset between the conduction and valence bands of the dielectric and 2D semiconductor should be at least 1eV. The 2D TMD/dielectric interface should be clean and free of defects. In this presentation, we present detailed synchrotron XOS study of 2D TMD and oxide interface. Specifically, we have studied the band offsets between MoS2 and SiO2, HfO2, and ZrO2 using XPS. We find that the dielectrics strongly dope the 2D MoS2 with significant shift (>1eV) in the Fermi level. Our results provide insight into suitability of different dielectrics for 2D MoS2 FETs.

9:35 AM EL05.15.07
Use of Laser-Induced Graphene and Functionalized Magnetite Particles as Anchors in Electrochemical CA 15-3 Detection Devices Gabriela L. Araujo Bernal1, Ramón Gomez-Aguilar2 and Hugo Martinez-Gutierrez2, 1Escuela Nacional de Ciencias Biológicas-IPN, Mexico; 2Unidad Profesional Interdisciplinaria en Ingeniería y Tecnologías Avanzadas-IPN, Mexico; 3Centro de Nanociencias y Micro Nanotecnologías-IPN, Mexico

Iron oxide particles have been used in in vitro diagnostics and theranosis for nearly 40 years. Magnetite nanoparticles (MNPs) have become popular as supports for immobilizing biomacromolecules due to their magnetic properties, low toxicity, chemically modifiable surface, and high biomolecule loading capacity which promote constant ionic interaction. Coating magnetic nanoparticles with functional materials, such as silicon oxide (SiO2), has been shown to improve their stability and enable the addition of various functional groups to their surface without altering their properties. The SiO2 layer provides a chemically inert surface for the core nanoparticles in biological systems. An ISFET, or Ion-Sensitive Field-Effect Transistor, is a type of field-effect transistor that measures ion concentration in a solution. It can be used as an immunobiosensor when combined with techniques like antibody or antigen immobilization to detect specific biomolecules such as proteins or antigens. The concentration of target biomolecules in a sample is recorded by measuring the variation of the electrical potential at the gate of the ISFET. The changes in potential are analyzed to establish a correlation between the potential change and the presence and concentration of specific biomolecules. The CA 15-3 cancer-associated antigen has been found in the serum of over 70% of patients with advanced breast carcinoma and in a small percentage of patients with non-breast malignancies. Detecting circulating levels of the CA 15-3 antigen may aid in distinguishing breast carcinoma from other dysplasia.

The upper limit of normal (ULN) for circulating CA 15-3 was set at 40 U/mL, as this threshold most adequately distinguished healthy subjects and patients with metastatic breast cancer. The levels of the antigen CA 15-3 in the serum of 500 patients with non-breast cancer, whose age ranged from 2 to 84 years were studied. Among metallic particles, functional sable core-shell nanoparticles are promising candidates for electrochemical sensors as they can immobilize various materials of biological significance with proper chemical groups. Even if they show magnetic properties, they enable effective separation through external magnetic field induction. Magnetite, Fe3O4, is a prevalent iron oxide that can be converted into particles. They can be dispersed in proper solvents and have the potential to create atomic layers for example oxide surfaces (e.g., silicon or aluminum) with a suitable contact area, which can subsequently be functionalized by joining various bioactive molecules that hold high potential for use in various in vitro and in vivo applications. It is crucial to keep control over the synthesis conditions and surface functionalization of particles to achieve particles with specific dimensions, colloidal stability, and biological properties. Typically, the immobilization of peptides or proteins on particle surfaces is conducted through the activation of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide-N-hydroxysuccinimide hydrochloride (EDC-NHS).

This work proposes immobilizing the CA 15-3 ELISA kit antibody using functionalized nanoparticles with a magnetite core and silicon oxide shell (F-NPs) with amine groups that diffuse over the synthesis conditions and surface functionalization of particles to achieve particles with specific dimensions, colloidal stability, and biological properties. Typically, the immobilization of peptides or proteins on particle surfaces is conducted through the activation of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide-N-hydroxysuccinimide hydrochloride (EDC-NHS). Stable groups are created on the functionalized particles to immobilize proteins. A reactive surface is generated by inserting various concentrations of glucose, which gives rise to an immune neutralization reaction (antigen-antibody) producing ionized species. These species are detected through an ISFET that was built on a functionalization platform (PI) of LIG. Stable groups are created on the functionalized particles to immobilize proteins. A reactive surface is generated by inserting various concentrations of glucose, which gives rise to an immune neutralization reaction (antigen-antibody) producing ionized species. These species are detected through an ISFET that was built on a flexible substrate and subjected to electrical potentials whose are measured between the drain, source, and gate contacts characterizing them by IV saturation curves. This process obtains a proportional relationship between the decay of the current on the device and the added glucose concentration.

9:40 AM EL05.15.08
Investigating The Influence of Multivalent Transition Metal Dopants and Capping Ligands on The Lateral Growth of Photo-Optical Cu2MoS4 2D Nanostructures Using a Colloidal Method Sarika V. Chaudoo and Richard A. Taylor, University of the West Indies, Trinidad and Tobago

2D transition metal dichalcogenides (TMDs) is a class of emerging materials due to their unique and unconventional properties which allows them to have a host of applications such as for photovoltaics and photoelectrochemical conversion. Of these, ternary TMDs are underexplored and herein, for the first-time metal-doped layered tetragonal copper molybdenum sulfide (CMS) nanostructures using a facile, economically feasible and inexpensive colloidal hot injection method were grown at relatively low temperatures of 100 and 140°C and short time of 1 hour. The morphology, structure, and optical properties of the nanostructures were analyzed by powder X-ray diffraction, high resolution transmission electron microscopy with energy dispersive X-ray analysis, Raman spectroscopy, UV-VIS absorption, steady-state and time-resolved and photoluminescence spectroscopy. We demonstrate that colloidal cocrystallization processes, increase of oleic acid in combination with the main capping ligand oleylamine enable lateral growth of highly crystalline 2D CMS nanosheets with hexagonal shaped nanosheets and layered nanorods of approximate dimensions 17 nm and 69 nm respectively. In particular, metal doped nanostructures exhibit a correlation of metal ion fraction and particle morphology implicating impurity ions in lateral growth of high energy facets into larger domain 2D nanostructures. Overall, the data shows a correlation of structure, morphology, and stoichiometry on the optical properties such as the influence of point defects such as sulphur vacancies and dopant (Zn2+, Ni2+, Mn2+) substitutions and interstitials. Collectively, this study provides an avenue for the synthesis of ternary TMD 2D nanostructures primarily with shorter growth time and lower growth temperature and offer the opportunity to simply tailor the reaction conditions to afford materials with tunable properties for photovoltaic applications. Additional elements of the work entail examination of the dynamics of the growth of the 2D nanostructures using in situ X-ray characterization such as pair distribution function, small and wide-angle x-ray scattering and x-ray absorption spectroscopy to determine the influence of precursors, capping ligands and growth conditions on preferred edge facets. Such insights will be useful towards pinpointing specific growth factors for more targeted growth of these types of 2D nanostructures.

9:45 AM EL05.15.09
Longevity and Effectiveness of 2D-MoS2 in Two-Terminal Devices: A Systematic Investigation Shakir Bin Mujib, Sonjoy Dey, Gurpreet Singh and Paul Owiredu, Kansas State University, United States

Two-dimensional (2D) transition metal dichalcogenides (TMDs) are strong candidates for continued scaling of transistors to improve the current Si-based technology and facilitate next-generation nanoelectronic devices such as sensors and field-effect transistors (FETs) due to their band structures and properties. Although countless published studies report the electrical properties of TMDs, many are not attentive to the testing environment or the samples' age, which we have found significantly impacts results. Herein, we utilize 2D TMDs fabricated via different top-down and bottom-up approaches, fabricate two electrode devices, and systematically investigate their longevity and effectiveness. We characterized and compared devices using IV measurements in ambient and inert conditions and found the stability of three months for the device kept at later conditions. As expected, the observed atmospheric and aging effects have a more pronounced effect on thinner flakes. This work illustrates the importance of understanding the electrical testing environment and the impact of atmospheric aging on TMD materials.
Vanadium oxide (VO2) has aroused researchers' curiosity among the transition Metal Oxides (ZnO, TiO2, Ga2O3, V2O5, SnO2, CuO) because of its unique semiconductor-to-metal phase transition (SMT). VO2 is an n-type semiconductor having room temperature bandgap of 0.5-0.7 eV. It undergoes a structural transformation from semiconductor monoclinic phase (low temperature) to metallic rutile phase (high temperature) at transition temperature Tc ~ 340 K exhibiting ultra-fast, fully reversible, first-order phase transition accompanied by a notable change in electronic and optical properties. Transition Metal Dichalcogenides (TMDs) have also been considerably explored due to their distinctive electronic and mechanical properties. Nowadays, TMDs (such as MoS2, MoSe2, SnS2, InS2, etc) are proving to be extremely promising materials because of having tunable bandgaps depending on the number of layers of the material, high carrier mobilities, and strong exciton attributes. Vanadium oxide (VO2) has aroused researchers' curiosity among the transition Metal Oxides (ZnO, TiO2, Ga2O3, V2O5, SnO2, CuO) because of its unique semiconductor-to-metal phase transition (SMT). VO2 is an n-type semiconductor having room temperature bandgap of 0.5-0.7 eV. It undergoes a structural transformation from semiconductor monoclinic phase (low temperature) to metallic rutile phase (high temperature) at transition temperature Tc ~ 340 K exhibiting ultra-fast, fully reversible, first-order phase transition accompanied by a notable change in electronic and optical properties. Transition Metal Dichalcogenides (TMDs) have also been considerably explored due to their distinctive electronic and mechanical properties. Nowadays, TMDs (such as MoS2, MoSe2, SnS2, InS2, etc) are proving to be extremely promising materials because of having tunable bandgaps depending on the number of layers of the material, high carrier mobilities, and strong exciton attributes. Attributes to the outstanding properties of 2D layered materials and transition Metal Oxides, these materials are well known to give ultrafast, self-biased, and broadband photodetection. In this work, we deposited VO2 film on SiO2 substrates by using Pulsed Laser Deposition (PLD). MoS2 film was deposited on VO2 film using PLD form MoS2/VO2 heterostructure. For MoS2/VO2/SiO2 device, the responsivity was found to be 0.83 A/W as compared to 4.42 \times 10^{-4} A/W for VO2/SiO2 device at 595.83 mW/cm² power density using 1550 nm laser. Clearly, the MoS2/VO2/SiO2 device shows higher photodetection and hence gives better performance than VO2/SiO2 device.

8:15 AM EL03/EL06/MT01.01
Exploring The Application of Hybrid DFTB-Molecular Mechanics Approach to Computing Optical Properties Ruicheng Li, Gekko Budiutama, Keisuke Kameda, Sergei Manzhos and Manabu Ibara; Tokyo Institute of Technology, Japan
The Density Functional based Tight Binding (DFTB) method has seen a rise in adoption for materials modeling, as it permits electronic structure-level modeling of large molecules, interfaces, nanostructures, etc. with much smaller computational cost and similar accuracy when compared to Density Functional Theory (DFT) methods. The cost reduction in DFTB compared to DFT is achieved by the pre-parameterization of the elements of the Hamiltonian matrix as well as the repulsion potential between all pairs of atoms. However, parameterization for new systems with accuracies competitive with DFT in specific applications requires specialized manpower and large computational resources. This prevents the application of the DFTB method to systems for which it is not parameterized.

In our previous work (J. Chem. Theory Comput., 19, 5189-5198 (2023)), a DFTB-molecular mechanics (DFTB-MM) approach was introduced to expand the applicability of DFTB by modeling the interactions of the missing Slater-Koster parameters with an interatomic interaction potential fitted with machine learning. We have shown that when interactions between the atoms do not critically affect key mechanisms of interaction, we can obtain structures and partial densities of states with a similar accuracy to full DFTB. This in principle allows the use of DFTB in systems where not all pairs of atoms have been parameterized.

Here, we further explore the capability of the DFTB-MM method to the calculation of optical properties with Time-Dependent (TD-) DFTB for the modeling of systems whose optical properties are of interest. TD-DFTB permits calculations that include a large number of excitations, which is required for systems with high densities of states, and would not be feasible with TD-DFT. In particular, we investigate interfacial charge transfer in systems such as TCNQ (tetracyanoquinodimethane) on TiO2, whose spectra are sensitive to the computational approach. We show that key spectral features, in particular transitions that involve the interfacial charge transfer band, are similar in full DFTB and DFTB-MM, indicating that DFTB-MM is a viable approach also for optical properties.
nanoislands with minimum size of ~35 nm in diameter, suggesting the highest possible areal density could reach up to ~400 Gbit/in² [3]. Our work offers a simple and scalable method for creating morphotropic grain boundaries (GBs) in laterally interconnected cobaltite [1] and manganite [2] homostructures. Single-crystalline substrates and suspended ultrathin freestanding membranes provide independent templates for coherent epitaxy and constraint on the growth orientation, resulting in seamless and atomically sharp GBs. Electronic states and magnetic properties are difficult to predict directly from process settings: electroplating, physical vapor deposition, and additive manufacturing (laser powder bed fusion). Each of the three processes offers unique challenges and opportunities. Across these three exemplars, we are augmenting traditional process-structure-property investigations with an accelerated workflow to detect material structure/composition, prognose associated properties, and adapt the associated process to achieve improved product outcomes. This accelerated detect-prognose-adapt cycle is enabled by a deep fingerprint of material state, enabling unsupervised detection of high-dimensional clusters and cross-modal correlations. SNL is managed and operated by NTESS under DOE contract DE-NA0003525.

**SESSION EL06.01: Epitaxial Growth—Strain, Defects and Interfaces I**

**Tuesday Morning, April 23, 2024**

Room 343, Level 3, Summit

**10:00 AM *EL06.01.01 Synthesis of Electronic-Grade Quantum Heterostructures** Chang-Beom Eom and Jeun Kim: University of Wisconsin--Madison, United States

Modern quantum materials are inherently sensitive to point defects, and require a new synthesis route to produce epitaxial oxide thin films and interfaces clean enough to probe fundamental quantum phenomena. The recent discovery of robust superconductivity at KTaO₃ (111) and KTaO₃ (110) heterointerfaces on KTaO₃ bulk single crystals offers new insights into the role of incipient ferroelectricity and strong spin-orbit coupling. Electronic grade epitaxial thin film platforms will facilitate investigation and control of the interfacial superconductivity and understanding the fundamental mechanisms of the superconductivity in KTaO₃. The major challenge of research on KTaO₃ system is that it is difficult to grow high-quality KTaO₃ epitaxial
thin films due to potassium volatility. Recently, we have developed the hybrid PLD method for electronic grade KTaO₃ thin film growth, which successfully achieves this by taking advantage of the unique capabilities of PLD to instantly evaporate Ta₂O₅ in a controlled manner and evaporation of K₂O to maintain sufficient overpressure of volatile species. We successfully synthesized heteropitaxial KTaO₃ thin films on 111-oriented KTaO₃ bulk single crystal substrates with a SmSeO₃ hybrid template by hybrid PLD, followed by a LaAlO₃ overlayer. Electrical transport data show a superconducting transition temperature of ~1.35K. We anticipate that the ability to synthesize high-quality epitaxial complex oxides such as KTaO₃ that contain volatile elements will provide a new platform for exploring new physics and technological applications arising from unique characteristics such as large spin-orbit coupling.

This work has been done in collaboration with Jieun Kim, Jungho Lee, Muqiu Yu, Neil Campbell, Shun-Li Wang, Sangho Oh, Zi-Kui Liu, Mark S. Rzchowski, Jeremy Levy.

11:00 AM EL06.01.02 Unconventional Quantum Oscillations in EuO/KTaO₃ Heterointerface Km Rubi¹, Dumen Manish², Suvankar Chakraverty², Mun Chan¹ and Neil Harrison¹; ¹Los Alamos National Laboratory, United States; ²Institute of Nano Science and Technology, India

The coexistence of electric-field controlled superconductivity and spin-orbit interaction in two-dimensional electron gas (2DEG) based on complex oxides (e.g., SrTiO₃ and KTaO₃) hold great promise for advancement in spintronics and quantum computing. However, a comprehensive understanding of the electronic bands that give rise to the multifunctional character of these 2DEGs remains elusive. To address this, we recently investigated quantum oscillations in the magnetoresistance of a KTaO₃-2DEG in high magnetic fields (60 T), KTaO₃ is a 5d transition metal oxide, exhibiting a lighter effective mass of electrons and a stronger spin-orbit interaction at its conducting surface/interface than its counterpart SrTiO₃ [1-2]. A high-mobility spin-polarized 2DEG with the superconducting feature is discovered at the EuO/KTaO₃ interface [3]. In this talk, I will present novel insights into the electronic states of the EuO/KTaO₃ interface investigated through Shubnikov-de Haas (SdH) oscillations. Remarkably, we observed a progressive increase in cyclotron mass and oscillation frequency with the magnetic field, indicating the presence of non-trivial electronic bands [4]. Besides providing experimental evidence for topological-like electronic states in KTaO₃-2DEG, these results shed light on the recent predictions of topological states in the 2DEG based on similar perovskite transition metal oxides.

References

Acknowledgement: We acknowledge support from the National High Magnetic Field Laboratory, supported by the National Science Foundation through NSF/DMR-1644779 and the State of Florida, and the US Department of Energy “Science of 100 Tesla” BES program.

11:15 AM EL06.01.03 High-Mobility Two-Dimensional Electron Gases based on Strain Engineered Ferroelectric SrTiO₃ Thin Films Ruchi Tomar¹, Tatiana Kuznetsova², Srijani Mallik¹, Luis M. Vicente-Arche², Fernando Gallego¹, Maximilien Cazauxy³, Roman Engel-Herbert⁴ and Manuel Bubes³; ¹Unité Mixte de Physique, CNRS, Thales, Université Paris-Saclay, France; ²Pennsylvania State University, United States; ³Laboratoire Matériaux et Phénomènes Quantiques, Université de Paris, France; ⁴Paul Drude Institute for Solid State Electronics, Leibniz Institute within Forschungsverbund Berlin eV, Germany

Two-dimensional electron gases (2DEGs) based on the quantum paraelectric SrTiO₃ display fascinating properties such as large electron mobilities, superconductivity and efficient spin-charge interconversion owing to their Rashba spin-orbit coupling.¹ However, such 2DEGs have almost exclusively been generated in SrTiO₃ single crystals, with the few attempts to replace crystals by heteropitaxial SrTiO₃ thin films leading to low carrier mobility. This is limiting the potential to integrate SrTiO₃ 2DEGs in future devices as well as the possibility to introduce additional functionalities specific to SrTiO₃ thin films, such as strain-induced ferroelectricity. Here, we use oxide molecular beam epitaxy to grow high quality strain-engineered SrTiO₃ films that are ferroelectric up to 170 K. We then generate a 2DEG by sputtering a thin Al layer and demonstrate an increase in both the low and room temperature mobilities by up to factor of four compared to earlier literature. Furthermore, through Raman spectroscopy and magneto-transport measurements, we show that the ferroelectric character is retained after 2DEG formation. These results thus qualify our samples as ferroelectric 2DEGs up to temperatures well above previous results based on Ca-SrTiO₃ substrates (~30 K)⁴, opening the way towards ferroelectric 2DEGs operating at room temperature.

References:

11:30 AM EL06.01.04 Multifunctional Oxide-2DEGS for Spin-Charge Interconversion Annës Barthelemy; Unité Mixte de Physique CNRS/Thales, France

Spin-charge interconversion in systems with spin-orbit coupling offers a new path for the generation and detection of spin currents of great potential for application in spintronics. The Rashba-type spin-field coupling linked to the spatial inversion symmetry breaking appearing in the two-dimensional electron gases (2DEG) formed at the interface between LaAlO₃ and SrTiO₃ [1-2], or by deposition of Al, Ta or Y on SrTiO₃ [2, 3], Ca-SrTiO₃ [4] or KTaO₃ [5] allows for very efficient spin to charge interconversion [1, 2, 6]. Recently, possibilities to further enlarge or control the functionalities of oxide-2DEGS have emerged. One approach relies on making the 2DEG ferroelectric by exploiting the large electric-field- or Ca-doping-induced ferroelectric character in STO, while the other is by inducing spin polarization in the 2DEG by depositing a magnetic layer on top of the 2DEG. Combining both strategies, multifaceted 2DEGS have been realized, opening an avenue for ferroelectrically controllable chiral spin textures in 2DEGs and providing a new playground for non-volatile spin-orbitronics and non-reciprocal physics. We will review our efforts to obtain such multifunctional 2DEGS [7, 8, 9, 10].

References:
Interfacial polar discontinuities are a unique way to manipulate charge states at interfaces and to create novel two-dimensional electron states. One recent example for this phenomenon is the interface between AlN and GaN, where a discontinuity in the spontaneous polarization leads to the formation of two-dimensional electron (2DEG) or hole gas (2DHO). The polar-nonpolar interface between ABO3 perovskites offers new degrees of freedom to tune the interface states by the accessibility of mixed valence states. The accepted model explaining the formation of a 2DEG is based on the concept of charge transfer between the layers terminating the polar-nonpolar interface. To realize a 2DEG or a 2DHO of the interface is a prerequisite. When growing the heterostructures, it is a commonly assumed that the surface termination of the non-polar layer controls the interface properties. In this contribution we provide experimental evidence demonstrating that the compensation of the polar discontinuity can drive surface segregation and consequently, control the interface termination.

We study the interface formation between the cubic wide band gap semiconductor BaSnO3, and orthorhombic LaInO3, by combining analytical scanning transmission electron microscopy (STEM), photoelectron spectroscopy and density functional theory (DFT) calculations. The samples were grown by plasma-assisted molecular beam epitaxy on DyScO3 substrates at 835°C using a mixture of Sn and SnO3 as a SnO source. While TEM experiments of BaSnO3 bulk crystals and DFT agree that BaO is the most stable surface termination of BaSnO3, over wide range of chemical potentials, we find that the interface between BaSnO3 and LaInO3 is terminated by SnO2. This is consistent with the presence of a 2DEG, but also with our DFT calculations, which show this interface to be the most energetically favorable. STEM and PES show the presence of BaO on the surface of thin LaInO3 films indicating Ba surface segregation. Based on our DFT calculations we find that the driving force for Ba segregation is the compensation of the polar discontinuity at the interface. This compensation is an effect of the gradual reduction of the out-of-plane lattice spacing at the interface, which most efficiently compensates for the polar discontinuity. At the p-type BaO terminated interface it leads to non-polar distortions in the BaSnO3, while polar distortions remain mainly in the LaInO3, which compensate the polar discontinuity less efficiently. This shows that in perovskites in addition to surface energy and strain, the response of the system to compensate for the polar discontinuity must be considered as an additional driving force for segregation that can control the interface termination.

In a second part, we focus on the 1ML limit of superlattices, which can be considered as a new ordered ilmenite structure (R-3) and is predicted to be a ferromagnetic insulator by DFT methods. Furthermore, the capability to grow these corundum materials in a monolayer fashion unlocks a complete new set of ABO3 materials with a trigonal symmetry (R3, R-3, R3c) where the same holds for the growth of thin films of complex oxides by MBE, but the issue has been that it has not been possible to grow that many oxides in such a regime. In this talk I will describe the out-of-plane lattice spacing at the interface, which most efficiently compensates for the polar discontinuity. At the p-type BaO terminated interface it leads to non-polar distortions in the BaSnO3, while polar distortions remain mainly in the LaInO3, which compensate the polar discontinuity less efficiently. This shows that in perovskites in addition to surface energy and strain, the response of the system to compensate for the polar discontinuity must be considered as an additional driving force for segregation that can control the interface termination.

In this work, we study corundum Cr2O3 (V2O5-Cr2O3) superlattices with symmetric periodicities ranging from 1 to 14 monolayers (ML) grown by oxide molecular beam epitaxy (MBE). By means of transport and optical spectroscopy, it is shown how the strong electron correlations in V2O5 are suppressed by quantum confinement. While infrared and Raman spectroscopy prove that this is accompanied by the absence of the monoclinic ground state at low temperature. By combining density functional theory (DFT) and Raman spectroscopy, it is shown that this dimensional crossover can be largely explained by a change in the orbital states dictating the phase diagram of V2O5.

In a second part, we focus on the 1ML limit of superlattices, which can be considered as a new ordered ilmenite structure (R-3) and is predicted to be a ferromagnetic insulator by DFT methods. Furthermore, the capability to grow these corundum materials in a monolayer fashion unlocks a complete new set of ABO3 materials with a trigonal symmetry (R3, R-3, R3c) where both A and B are transition metals. Finally, we also propose a way to grow these materials in the polar ordered (R3c) structure where the existence of two magnetic sublattices promises new high-temperature multiferroicity, motivating the search for novel ordered trigonal materials.
conductivities cannot be changed substantially. Materials exhibiting a metal-insulator transition (MIT) above room temperature are quite rare, limiting their applicability in devices.

For the realization of the next generation of fast, energy-efficient nanoelectronics, there is a great need for new materials whose electrical and optical conductivities can be sensitively tuned between high (on) and low (off) states by altering a thermodynamic control parameter such as strain or temperature. Unfortunately, most materials are either metallic or insulating and their

Thermal laser epitaxy (TLE) is a novel technique for thin film deposition which employs continuous wave lasers to simultaneously heat both the substrate and elemental sources. This laser heating approach allows for evaporation or sublimation of nearly all elements from the periodic table, ultrahigh substrate temperatures exceeding 2000 °C, and broad compatibility with process gases at a wide range of pressures from UHV up to 1 Torr, among other benefits. As a result, TLE dramatically expands the parameter space available for thin film synthesis compared to existing epitaxy techniques. However, to date it has proven experimentally challenging to achieve simultaneous control of multiple laser based elemental sources with the flux stability and systematic fidelity necessary for the growth of ternary or multinary systems of interest such as complex oxides.

In order to establish the capabilities of TLE for the growth of such complex materials, we demonstrate here the successful epitaxial synthesis of several Ruddlesden-Popper phases of the Sr-Ru-O ternary oxide system via TLE. Near instant thermalization of both source elements and substrates from laser heating allows the process of thermodynamic phase control to be achieved rapidly during film deposition without the need for physical shuttering of sources. Additionally, we find that the “n=1” phase SrRuO$_3$ can be reliably synthesized at substrate temperatures in excess of 1200 °C and in a background environment of pure molecular oxygen, within an adsorption-controlled growth window that is inaccessible to conventional MBE approaches. We show that SrRuO$_3$ films grown under these conditions demonstrate extremely high structural, electronic, and chemical quality, as evidenced by the appearance of superconductivity at relatively high critical temperatures. In particular, the higher growth temperatures and elemental source fluxes afforded by laser heating allow us to achieve phase pure 214 without higher-N intergrowths typically observed in MBE-grown films, and growth rates more than 10 times faster than MBE. A detailed accounting of the experimental approach, growth thermodynamics and film characterization will be discussed.

This work not only demonstrates the feasibility of TLE for the synthesis of high-quality complex oxide thin films, but also suggests new routes to achieving thin film growth in other materials systems that remain as-yet inaccessible to conventional epitaxy techniques.

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**Fe Substitution Suppresses Oxygen Vacancy Formation and Stabilizes High-Valence Ni in Epitaxial La$_{0.5}$Sr$_{0.5}$Ni$_{1-x}$Fe$_x$O$_3$ Thin Films**


Recent discovery of superconductivity in Nd$_{0.7}$Sr$_{2}$Ni$_2$O$_{4.75}$ has inspired further exploration of nickelates to gain insights into the origins of high-temperature superconductivity. However, the synthesis of Sr- or Ca-doped nickelate thin films is challenging due to the instability of high-valence Ni and the competition between perovskite and Ruddlesden–Popper (RP) phases. Our recent study revealed that Sr doping in LnNiO$_3$ thin films significantly reduces the Ni valence from Ni$^{3+}$ to Ni$^{2+}$ and results in the formation of numerous RP phases as the Sr doping level increases from 0 to 100%. Further, DFT calculations on the La$_{1-2x}$Sr$_x$Ni$_2$O$_{4-δ}$ perovskite structure indicated a substantial increase in the oxygen vacancy formation energy from 2.96 to 1.85 eV as y varies from 0 to 0.5. In our current work, we synthesized a series of epitaxial La$_{1-2x}$Sr$_x$Ni$_2$O$_{4-δ}$ (LSNFO) thin films on LSAT(001) substrates using MBE oxide. We found that partial Fe substitution for Ni in La$_{1-2x}$Sr$_x$Ni$_2$O$_{4-δ}$ significantly enhances the structure quality and stabilizes the perovskite structure. Ni$_{1-x}$Fe$_x$O thin films grown under these conditions demonstrate extremely high structural, electronic, and chemical quality, as evidenced by the appearance of superconductivity at relatively high critical temperatures. In particular, the higher growth temperatures and elemental source fluxes afforded by laser heating allow us to achieve phase pure 214 without higher-N intergrowths typically observed in MBE-grown films, and growth rates more than 10 times faster than MBE. A detailed accounting of the experimental approach, growth thermodynamics and film characterization will be discussed.

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**Metal-Insulator Transition and Novel Ground States in Epitaxially Strained SmBaMnO$_3$ Thin Films**

Yorick Birkholzer, Anna S. Park, Noah Schnitzer, Evan Krysko, Jacob Steele, Hebatalla Elnoagar, Jelle Ruiter, Koen Draijer, Masoud Lazemi, Qijuan Che, Shigeaki Yamada, Taka-hisa Arima, Frank de Groot, David Muller, and Darrell G. Schlom.

Metal-insulator transitions (MITs) in d-block transition metal oxides can represent a potential route to the development of energy efficient electronic devices, as such systems may offer a lower operating voltage and lower power consumption than conventional electronic systems. A detailed understanding of the electronic and magnetic properties of these materials is therefore crucial. In the past, we have shown that epitaxial growth of SmBaMnO$_3$ (SBMO) thin films on SrTiO$_3$ (STO) substrates at low temperature allows for the observation of a MIT with a phase transition at room temperature. The MIT is accompanied by changes in the magnetic and optical properties of the film, which can be attributed to an increase in the metallic band filling and a decrease in the oxygen vacancy fraction.

In this study, we present a comprehensive investigation of the structural and spectroscopic properties of epitaxial SmBaMnO$_3$ thin films. The MIT is observed in the films grown on STO substrates, with a critical temperature of ~400 K. The MIT is accompanied by changes in the magnetic and optical properties of the film, which can be attributed to an increase in the metallic band filling and a decrease in the oxygen vacancy fraction. These results demonstrate the potential of epitaxial SmBaMnO$_3$ thin films as a platform for the development of energy efficient electronic devices.

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**Ongoing efforts entail the comprehensive investigation of the structural and spectroscopic properties of epitaxial SmBaMnO$_3$ thin films as a function of temperature and strain. To this end, we...**
In complex oxide materials the occurrence of ferroelectric, ferromagnetic or other properties are often determined by the detailed (oxygen) coordination of metal cations. More specifically, in the case of perovskite-type materials ABO3, where A and B are metal cations, by the B06 octahedral orientations and rotations. At interfaces in epitaxial oxide heterostructures, for example magnetic junctions or capacitive structures, this oxygen sub-lattice is found to be different from its bulk counterpart. I will briefly introduce the status of the often-used technique to fabricate epitaxial layers, ‘atomically controlled PLD’, as well as give a few examples of oxygen sub-lattice and interface engineering achieved by controlled thin film parameters such as, composition, digital thickness variation, polar discontinuous interfaces or the insertion of oxygen buffer layers that influence the perovskite-type BO6 sub-lattice or related structures. I will further elaborate on the effects of such thin film parameters on the structure and properties of various model systems that have been subsequently studied by in situ characterization techniques, high resolution scanning transmission electron microscopy. More practically, often-encountered problems due to dead-layer effects and interfacial issues when integrating oxides with technical platforms such as Si or GaN, will be discussed.

Lithium Incorporation in (111) NiO Epitaxial Layers Grown by Pulsed Laser Deposition Technique Ilhabani P. Sahu, Santosh K. Yadav, Simran Arora and Subhabrata Dhar; India Institute of Technology Bombay, India

Wide bandgap oxides such as ZnO, Ga2O3, and In2O3 have tremendous potential in UV-optoelectronics, yet the unintentional generation of certain donor type of defects in the film during growth make it challenging to achieve stable p-type doping in these materials. Nickel oxide (NiO) is a wide bandgap semiconductor of bandgap ranging from 3.6 - 4 eV. It is one of the few oxide semiconductors that exhibits stable p-type conductivity and antiferromagnetic properties with Neel temperature of 525K. The material also has high chemical and thermal stability. All these characteristics have made NiO a potential candidate for device applications such as exchange bias systems, field effect transistors, transparent hole conducting films, spintronics, UV-photodetectors and UV-LEDs. It has to be noted that stoichiometric NiO is an insulator, and p-type conduction in the film can be ascribed to the presence of nickel vacancies. However, controllable p-type doping with native defects is difficult to accomplish due to the formation of other unintentional compensating defects in the film. Intentional doping with monovalent atoms such as lithium will be interesting to explore. Keeping in mind that epitaxial films will give better device performance, there are efforts to grow epitaxial layers of NiO on different substrates such as sapphire, MgO and yttria-stabilised zirconia. In fact, the growth of NiO films with high epitaxial qualities have been reported by various techniques such as pulsed laser deposition (PLD), melt chemical vapour deposition, RF magnetron sputtering and molecular beam epitaxy.

Here, we study the incorporation of Li in (111) NiO epitaxial layers grown by PLD technique on c-sapphire substrates as a function of growth conditions. The structural, morphological, electrical and optical properties of the films have been systematically investigated. It has been found that the crystalline quality of these films deteriorates as the growth temperature is lowered. Surface morphology of the films, studied by atomic force microscopy (AFM) and field emission gun secondary electron microscopy (FEGSEM) shows smooth and continuous nature of the films with surface roughness lying between 0.4 - 1.4 nm. It has been found that the conductivity of the layers increases as the growth temperature is decreased. The enhancement of conductivity has been ascribed to the increase in density of nickel vacancy with the reduction of temperature. The investigation further suggests that there is a miscibility limit of Li in NiO. Li-clusters are observed in the films beyond a critical concentration of lithium. Further, it has been found that lithium inclusion results in hydrostatic tensile strain in the NiO lattice leading to the reduction of the bandgap. The study also shows that Li incorporation, which has also been verified by secondary ion mass spectroscopy (SIMS) and x-ray photoelectron spectroscopy (XPS), improves the electrical conductivity of the layers.

Potentiometric Detection of Serum Creatinine Utilizing Lead Dioxide and Carbon Nanotubes in a Single-Enzyme Reaction Sung Min Jeon, Dayeong Choi, Han Been Lee and Gi Hun Seong; Hanyang University, Korea (the Republic of)

Creatinine (CRE) serves as the end product of creatine, responsible for energy release in skeletal muscle. The baseline concentration of serum creatinine (Scr) typically ranges from 45 μM to 90 μM in females and 60 μM to 110 μM in males. Elevated Scr levels are commonly utilized in diagnosing acute kidney injury. Ongoing research focuses on developing reliable techniques for estimating Scr due to its critical role as a biomarker of significance. The Jaffe reaction, a colorimetric method utilizing picric acid, has traditionally been employed for clinical analysis of creatinine (CRE). However, this method presents several drawbacks, including the need for pH adjustment, interference issues, and, notably, the toxicity and explosiveness of picric acid. A prominent trend in CRE detection involves electrochemical enzyme sensors, offering enhanced sensitivity and selectivity. The inclusion of creatinine deiminase (CD) in the enzymatic approach addresses the aforementioned challenges, thereby improving sensor performance and selectivity. In this enzymatic method, CD reacts with CRE to produce NH3, subsequently converted to NH4+ and OH- in an aqueous solution. The NH4+ ion selective sensor and pH sensor then measure the concentration of CRE.

Single-walled carbon nanotubes (SWCNTs) are widely acknowledged for their outstanding electrical properties, characterized by high carrier mobility and current-carrying capacity, coupled with impressive chemical, thermal, and mechanical attributes. Surface modification techniques can be applied to introduce diverse functional groups on the SWCNT surface, enhancing their suitability for various applications. The incorporation of metal oxide deposits can impart electrical, electrochemical, and biocompatible properties, making them valuable in sensor manufacturing. Among the diverse applications, electrochemical pH sensors stand out, and metal oxide modification presents several advantages. These include notable sensitivity, rapid response times, prolonged operational lifespan, minimal interference with other ions, cost-effectiveness, ease of maintenance, and adaptability for miniaturization in flexible systems. While various metal oxide pH sensors such as titania (TiO2), zirconia (ZrO2), tungsten oxide (WO3) and SnO2 have been reported in recent years, their production often involves intricate and high-temperature processes. Lead dioxide (PbO2) emerges as a noteworthy choice for pH sensors due to its excellent electrochemical properties and straightforward fabrication method. However, PbO2-based pH sensors may exhibit deficiencies in oxygen or an excess of lead within the PbO2, potentially impacting electrochemical reactions.

In this investigation, we produced a thin film of lead dioxide deposited on carbon nanotubes (PbO2-CNT) and developed a PbO2-CNT ion-selective electrode (PbO2-CNT/ISE). These sensors served as highly sensitive potentiometric biosensors for CRE, capitalizing on the one-step selective conversion of creatinine by creatinine deiminase. We conducted the detection of OH- and NH4+ in an aqueous solution, generated through an enzymatic reaction, utilizing PbO2-CNT as a pH sensor and PbO2-CNT/ISE as an NH4+ selective electrode. The obtained results reveal a remarkable sensitivity of -75.56 mV log[CRE]-1 and 64.62 mV log[CRE] -1, with a calculated limit of detection of 0.06 μM and 0.13 μM, respectively, within the range of 10 to 400 μM. A selectivity test demonstrated robust discrimination against interfering materials in human serum, and the repeatability and long-term stability of our sensors were confirmed, indicating their high-level robustness. Furthermore, recovery tests for CRE concentrations (10, 25, 50, 70 μM) in spiked human serum yielded results of 104%, 98%, 103%, and 96% for PbO2-CNT, and 104%, 92%, 110%, and 97% for PbO2-CNT/ISE. These findings underscore the reliability and reproducibility of our sensors in detecting CRE for clinical applications.

High Performance of Ferroelectric Synaptic Device in Hf0.7Zr0.3O2 (HZO)/La0.7Sr0.3MnO3 (LSMO)/SrTiO3 (STO) Heterostructure by Optimizing Defect-Mediated Ferroelectric Switching Dynamics Hoon Jin Lee1, Joongbong Lee1, Hyunseok Kim2, Kyungwoo Choi3, You Seung Rim1 and Taeikby Choi1; 1Sejong University, Korea (the Republic of); 2Korea Institute of
High-performance artificial synaptic devices with linear synaptic weight and high precision are in high demand for hardware neural network (HNN) implementation. HF-based ferroelectric memristor has robust stable non-volatile analog resistive switching driven by its gradual polarization reversal. However, the high linearity and precision of the synaptic weight update are required to improve the accuracy of the neuromorphic chip application. Here, we demonstrate the high performance of ferroelectric synaptic devices in HfO2-ZrO2 (HZO)/La0.5Sr0.5MoO3 (LSMO)/SrTiO3 (STO) heterostructure, showing the high linearity (≈0.5), effective multiple conductance states (> 40), and low cycle-to-cycle variation (2.06%). The synaptic characteristics of the device are dominantly attributed to the inhomogeneous domain nucleation, ultimately affecting the precision and linear weight update achievable in continuous polarization switching. As an artificial synapse, experimental results with electrical pulse modulation closely mimic the neuro-inspired signal process dependent on spike timing and spike rate. These results supposed that oxygen vacancy engineering in ferroelectric synaptic devices is a powerful approach to improving effective precision and overcoming the limitations nonlinear synaptic behavior for the implementation of HNN. In addition, when applied to a hardware neural network with a crossbar array (20X20), the recognition accuracy of MNIST handwriting data was recorded as 94.8%.

Acknowledgments This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government(MSIT) (NRF; Grant No. NRF- 2021R1A2C2010781).

5:00 PM EL06.03.05 Effects of Temperature on Ruthenium Oxide Thin Films Using Pulsed Laser Deposition Tyffani Royal; North Carolina Agricultural and Technical State University, United States

Within this report, experiments were conducted to determine what effects temperature has on thin film composition, crystalline orientation, and roughness. Ruthenium Oxide (RuO2) thin films were grown using pulsed laser deposition on substrates at different temperatures (100°C, 200°C, 300°C). The properties of the thin films were observed using X-Ray diffraction, scanning electron microscopy, and atomic force microscopy measurements. It has been observed that the increase in temperature results in an increase in density, and roughness. The RuO2 thin films made at 500°C are able to form on a substrate with strong crystalline orientation. This orientation can become vital in how thin films are made for their intended purpose.

5:00 PM EL06.03.08 Topochemical Synthesis and Optical Properties of Epitaxially Strained SrCo(O2)3+δ Thin Films Tessa D. Tucker, Zongmin Yang, David Bugallo and Steven J. May; Drexel University, United States

Transition metal oxides (TMOs) are attractive in materials science for their structural versatility and property tunability. This tunability can be further expanded by incorporating a second anion, such as F or O, to alter the metal-anion bond ionicity or the metal charge density. In this work, we report on vapor-based fluorination of epitaxial SrCoO2.5 films. The films are grown by oxygen-assisted molecular beam epitaxy (MBE) under conditions that result in the brownmillerite structure. Topochemical fluorination was conducted on the as-grown films at 200°C using a quartz tube furnace under Ar gas flow with poly(vinylidene fluoride) (PVDF) as the fluorine source. Fluorination reactions were performed on SrCoO2.5 films synthesized on STO, LAO, LSAT and GSO substrates to understand the impact of substrate-induced strain on fluorine incorporation. Fluorine incorporation was confirmed via depth-dependent elemental analysis performed with X-ray photoelectron spectroscopy (XPS). Fluorine incorporation results in an expansion of the c-axis parameter as determined by X-ray diffraction. Optical absorption spectra, obtained through spectroscopic ellipsometry, reveals a blue-shift of the low-energy absorption edge by 0.1 – 0.3 eV depending on the substrate. This result is attributed to a widening of the band gap due to the increased ionicity of the Co-anion bonds.

This work was supported by the National Science Foundation under grant CMMI-2001888.

5:00 PM EL06.03.09 High-Throughput Combinatorial Approach to The Synthesis of a Lead-Free Relaxor Ferroelectrics System Di Zhang1, Katherine Harmon2, Michael Zachman2, Ping Lu3, Doyun Kim4, Qing Tu1 and Aiping Chen1; 1Los Alamos National Laboratory, United States; 2Argonne National Laboratory, United States; 3Oak Ridge National Laboratory, United States; 4Sandaia National Laboratories, United States; 5Texas A&M University, United States

Developing novel lead-free nontoxic ferroelectric materials is crucial for the next-generation microelectronic technologies in regard to clean energy and environmental sustainability. However, discoveries in material science and properties optimization have usually been a frustratingly slow process due to the limited throughput in traditional synthesis methods. In this work, using a high-throughput combinatorial synthesis approach, we fabricated lead-free ferroelectric superlattices and solid solutions of (Ba0.5Ca0.5)TiO3 (BCT) and (Ba0.5Sr0.5)TiO3 (BST) phases with compositional gradients. The high-resolution X-ray diffraction and scanning transmission electron microscopy (STEM) revealed the good film quality and well-controlled compositional gradient throughout the samples. Ferroelectric and dielectric properties identified the “optimal property point” achieved at the morphotropic phase boundary (MPB) with the composition of BST–52BST. The displacement vector maps revealed the tunable ferroelectric domain sizes by varying the single layer thickness of the [BCT/BZT]1 superlattices. This high-throughput synthesis approach can be applied to many other materials systems to expedite novel materials discovery and property investigations.

5:00 PM EL06.03.10 Tailoring Dielectric Permittivity in Gd2Co2O7.5 Films by Ionic Defects Alessandro Palliotti, Nini Pryds and Daesung Park; Danmarks Tekniske Universitet, Denmark

Fluorite-based crystalline materials have the general chemical formula AX2 (A = Ca, Hf, Zn, Zr, Ce), while X = F, O) and find wide application in fuel cells, electroceramics, oxygen sensors and exhaust reduction systems. Despite their rather simple and prototypical crystallographic structure, “fluorites” remain the subject of much academic research and unexpected scientific discoveries [1], such as ferroelectricity in HfO2-based thin films or large electromechanical coupling in polycrystalline Gd-doped CeO2-

5:00 PM EL06.03.11 Enhancement of Alkaline Hydrogen Evolution in BaRuO3 Thin Film via Surface Self-Reconstruction Do Hyun Kim, Jegon Lee and Woo Seok Choi; Sungkyunkwan University, Korea (the Republic of)

Hydrogen production through water splitting presents a promising avenue for carbon-free energy generation. Transition metal oxides (TMOs) are pivotal electrocatalysts known for their remarkable activity and tunability. Among TMOs, perovskite Ruthenates stand out due to their significant electrocatalytic potential in driving the hydrogen evolution reaction (HER). However, the precise influence of the surface chemistry of Ruthenates in alkaline solutions on their catalytic performance in HER remains a subject of ongoing exploration. In this investigation, we concentrate on the dynamic chemical and structural transformations occurring on the surface of cubic perovskite BaRuO3 (3C BRO) during the HER cycle and their direct impact on HER activity. To facilitate our analysis, we utilized epitaxial thin films, meticulously crafting atomically precise crystalline surfaces. This approach allowed us to elucidate the fundamental role of the surface in catalytic activity.

Remarkably, the HER activity of the 3C BRO epitaxial thin film experiences a substantial boost through cycling in an alkaline environment. Specifically, after the initial cycle, the HER overpotential decreased from 210 to 60 mV, reflecting an impressive ~70% improvement. With continued cycling, the initially high HER activity gradually wanes, ultimately reaching a saturation overpotential similar to that of RuO2 catalysts after approximately 50 cycles.
We have optimized the growth and stability of epitaxial thin films of SrFeO$_3$ grown by pulsed laser deposition. Then, using resonant soft x-ray scattering, we study how these complex magnetic phase separation in manganites leads to unique magnetic and electronic properties. 50% Ca-doped LaMnO$_3$ (LCMO), at the boundary of ferromagnetic (FM) and antiferromagnetic (AFM) magnetic, and magnetoresistance (MR) properties of LCMO. The MR, and colossal magnetoresistance (CMR), observed in LCMO/SIO bilayers were two orders and an order of magnitude (in %) larger, respectively than that in the single-layer film. We found the coexistence of FM and AFM/CO phases was responsible for the CMR and MR enhancement in the LCMO/SIO bilayer, pointing towards the importance of the phase separation and competition of both the individual materials in enhancing their magnetic and electronic properties.

8:45 AM *EL06.04.01
Richness of Spiral Magnetic States in Strontium Ferrite Thin Films Jennifer Fowlie; Stanford University, United States

Perovskite strontium ferrite, SrFeO$_3$, hosts a variety of spiral magnetic phases at low temperature including multi-q states of different proper screw and/or cycloid ordering [1]. Among them is a phase believed to support topologically-protected magnetic structures and may explain an observed finite-field anomaly in Hall effect [2]. SrFeO$_3$ is a fascinating material because, unusually, these effects exist despite the centrosymmetry of the crystal structure. Instead of a Dzyaloshinskii-Moriya interaction, the helimagnetism has been suggested to arise due to an interplay of electronic interactions [3]. We have optimized the growth and stability of epitaxial thin films of SrFeO$_3$ grown by pulsed laser deposition. Then, using resonant soft x-ray scattering, we study how these complex magnetic orderings depend on the biaxial strain state, which potentially influences the electronic structure.


9:15 AM EL06.04.02
Properties of Barium Bismuthate Layers on Si: Molecular Beam Epitaxy Study Islam Ahmad$^{1,2}$, Maxim Korytov$^1$, Olivier Richard$^1$, Patrick Carolan$^1$, Stefanie Sergeant$^1$, Thomas Nuyten$^1$, Thierry Conard$^1$, Stefan De Gendt$^{1,2}$ and Clement Merckling$^{1,2}$; 1IMEC, Belgium; 2KU Leuven, Belgium

With slowing down of Moore’s law, related to scaling of integrated circuits, alternative technologies such as quantum computing require research efforts for pushing the limits of new generation of electronics. A promising approach to achieve fault-tolerant quantum computers is to build qubits that are intrinsically protected against quantum errors thanks to the topological nature of the used materials. Such computations are realized when Majorana fermions are detected and manipulated. Topological superconductors are the perfect solid state material system for hosting Majorana bound states. Equivalently, an interface between a superconducting and a topological insulating layer is also expected to host such states, based on the proximity effect. Barium bismuthate (BBO) is a relevant material system because when hole-doped with potassium, it is a superconductor with a critical temperature of 29.8 K. In addition, with the spin-orbit coupling of bismuth considered, fluorine-doped BBO is predicted to be a topological insulator according to density functional theory (DFT) studies. The work presented is related to material development and characterization of the parent compound utilizing oxide molecular beam epitaxy (MBE) process. In our work, we integrate BaBiO$_x$ on Si(001) substrate, using an epitaxially grown strontium titanate SrTiO$_3$ single-crystalline buffer layer. It is demonstrated that the epitaxy of BaBiO$_x$ is only achieved in excess of oxygen plasma because of the volatile nature of bismuth molecules reaching the substrate. Due to the high vacuum environment in the oxide chamber of the MBE machine that can reach below 10$^{-8}$ torr as base pressure, ordered oxygen vacancies are created within the perovskite layers, forming a mixture of brownmillerite and perovskite phases. The mixed phase is demonstrated based on transmission electron microscopy (TEM) images. A method, in function of oxide MBE process parameters, to retrieve fully perovskite phase (with no ordered oxygen vacancies) is presented. Due to the breathing distortion within its lattice, barium bismuthate is a Peierls insulator with an optical band gap of 1.96 eV. Optical conductivity is measured using spectroscopic ellipsometry, showing a peak centred around 2 eV. The Raman response of BBO observed at 570 cm$^{-1}$ is attributed to the breathing distortion of BiO$_6$ octahedra, which is in resonance with a laser wavelength of 633 nm. In our studies, thickness dependence of the breathing distortion is studied. In the upcoming study, a light will be shed on the band structure of fluorine-doped by measuring it using angle-resolved photoemission spectroscopy (ARPES) to detect the existence of topological states.

9:30 AM EL06.04.03
Effect of Stoichiometry on The Atomic Microstructure of Thin Film BaTiO$_3$ Ashley Cavanagh; Larissa Little, Charles M. Brooks, Julia Mundy and Robert Westervelt; Harvard University, United States

Synthesis and characterization of thin film barium titanate is of great interest due to its promise for use in electro-optic modulators [1]. These devices require a thin film with a high electro-optic coefficient that can operate at low voltages and integrate into photonic circuits, so barium titanate’s strong linearity makes it an attractive candidate material. Barium titanate’s ferroelectricity means that it is also of interest for applications in nonvolatile ferroelectric memories. For use in photonic devices, we must understand how variations in film stoichiometry affect the electro-optic properties, local atomic structure, and ferroelectric structure of thin film barium titanate. We use molecular beam epitaxy (MBE) to grow high quality thin films of barium titanate with a high degree of stoichiometry control. In this talk, we use high-resolution scanning transmission electron microscopy (STEM) to compare the atomic microstructure of barium titanate films of varying stoichiometries grown on strontium titanate. High-resolution electron microscopy imaging allows us to evaluate atomic-level variations in crystal structure, local defects, and electrical polarization in thin films of barium titanate. By understanding the effect of stoichiometry on these variations, we can understand the degree of stoichiometry control needed to grow barium titanate thin films that are of sufficient quality for electro-optic device applications.
Yeongrok Jin and Jaekwang Lee

1:30 PM

emergence of metal-insulator transition in the electronic transport. In this study, we investigated the effect of Mo(4d)-doping with SrRuO3 (SRO) on 4d transition metal oxides (TMOs) because of its strong interplay among charge, spin, lattice, and orbital degrees of freedom. Their electronic structure is influenced not only by the on-site Coulomb interaction (U) and spin-orbit coupling (SOC) but also by Hund’s coupling (J_H). There have been several studies conducted to construct the correlated electronic phase diagram by varying the degree of those interaction parameters. One of the renowned 4d TMOs is the ferromagnetic SrRuO3 (SRO) with 4d^{2} configuration having abundant electronic states including non-Fermi liquid and Weyl semimetal states. The intrinsic SOC coupled with its ferromagnetism is important for the emergence of the Dzyaloshinskii–Moriya interaction beneficial for the observation of exotic quantum phenomena, such as the skyrmion formation and resultant topological Hall effect [1, 2]. On the other hand, SrMoO3 (SMO) with 4d^{4} configuration is the other reported metallic 4d TMO influenced by Hund’s coupling. However, its electronic transport mechanism is less understood compared to SRO despite its extremely small room-temperature resistivity with Fermi-liquid behavior [3]. Different from SRO, SMO is reported to have 4d-independent magnetic susceptibility exhibiting Pauli paramagnetic behavior. Previously, several attempts have been made to dope SRO thin films with 3d and 5d TM ions through Ru-site chemical substitution which results in the suppression of the ferromagnetism and emergence of metal-insulator transition in the electronic transport. In this study, we investigated the effect of Mo(4d^{2})-doping on SRO thin films by manipulating the degree of electronic and magnetic correlations through chemical substitution. We grew the epitaxially stabilized SrRu1-xMo_xO3 (SRMO, x = 0 - 0.5) thin films using pulsed laser deposition by alternately ablating two targets, SRO and SMO. The Mo concentration was selectively controlled by adjusting the laser pulse numbers according to the deposition rate of each target on (001) SrTiO3 substrates. The high quality of the resulting SRMO thin films has been confirmed by using x-ray diffraction accompanied by a systematic lattice compression per the increase in the Mo concentration. The modification of the complex 4d electronic structure by the 4d^{2}-doping is apparent in the hybridization between Ru 4d and O 2p orbitals, inducing systematic changes in the electric and magnetic properties of SRMO epitaxial thin film. Our results present further insights into understanding the systematic changes in the electronic properties of epitaxial SRMO thin films useful for spintronic device applications.

References:

10:00 AM BREAK
In this talk, I will discuss three main areas in the study of correlated electron materials:
1) Differentiating the influence of crystal structure and valence electrons in symmetry-breaking phase transitions, resolving a longstanding question in the field.
2) Using layered material structures as a lens to study electronic transitions at the nanoscale, backed by practical thin-film examples.
3) Harnessing machine learning throughout the quantum materials discovery process, from identification to synthesis.
I'll wrap up by highlighting how these advances impact the discovery and application of new quantum materials and may lead to novel applications.

2:30 PM BREAK

SESSION EL06.06: Epitaxial Growth—Microstructure and Functionalities
Session Chairs: Megan Holtz and Dongsheng Li
Wednesday Afternoon, April 24, 2024
Room 343, Level 3, Summit

3:30 PM *EL06.06.01
Quantifying 3D Chemical and Structural Order/Disorder in Thin Film Complex Oxides with Multislice Electron Ptychography
James M. LeBeau; Massachusetts Institute of Technology, United States

Determining chemical and structural order/disorder within functional oxides is often key to understanding the properties of these materials, for example, relaxor ferroelectrics. Conventional techniques such as X-ray, neutron, or electron diffraction are often used to study these features via diffuse scattering, but only offer insights into the global and average local structure of a sizable material volume. While recent advances in phase contrast imaging techniques in scanning transmission electron microscopy (STEM), such as iDPC, have helped to reveal connections between local polar and chemical order, these approaches are constrained by the ability to capture only a 2D projection of the structure within a thin TEM sample. Consequently, the origins of the exceptional piezoelectric properties of these materials continue to be a subject of debate.

In this presentation, I will explore how multislice electron ptychography can be leveraged to provide nanoscale structural, chemical, and polar variations in functional oxides in 3D. First, I will present the analysis of the reconstructed phase from the thin film paraelectric Pb2MgWO6. I will highlight how the approach provides access to the three-dimensional structure and chemistry of inclined anti-phase boundaries in this material. The comprehensive characterization offers deeper insights into their impact on local polarization, namely stabilizing antiferroelectric distortions at the boundaries. Second, I will discuss our study of the prototypical relaxor ferroelectric Pb(Mg1/3Nb2/3)O3-PbFeO3 (PMN-PT) using ptychography, where structural distortions of the cation and anion sublattices across slices are used to measure polar order in 3D. The results will be compared against conventional HAADF and dPC imaging from the same region to provide an understanding of the sampling volume of those techniques. Finally, I will discuss how multislice ptychography offers a pivotal tool to unravel the intricate relationships between defects, structure, and the influence of intrinsic and extrinsic factors on the behavior exhibited by functional oxides.

4:00 PM EL06.06.02
Unravelling The Effect of Nitrogen Doping on The Structure of LaFeO3 Epitaxial Thin Films
Krishna Prasad Koirala1, Shan Lin2, Le Wang3, Minju Choi4, Erjia Guo5, Peter V. Sushko6, Scott A. Chambers7, Chongmin N. Wang1 and Yingge Du1; 1Pacific Northwest National Laboratory, United States; 2Institute of Physics, Chinese Academy of Sciences, China

Heteroatom doping has proven to be an effective approach for fine-tuning the electronic and magnetic properties, as well as enhancing the electrocatalytic performance in ABO3-type perovskite oxides. Beyond the conventional cation doping at A or B-sites, partial replacement of oxygen anions in perovskite oxides by other elements, such as nitrogen (N), sulfur (S), and fluorine (F), has also been explored to modify their structure and properties. In this study, we aim to advance our understanding of how N doping in LaFeO3 films, influences their composition and structure, subsequently affecting their electronic and electrochemical properties. High-quality N-doped LaFeO3 (LFON) epitaxial thin films with different doping levels were grown on (001)-oriented Nb:SrTiO3 substrates using nitrogen-plasma-assisted pulsed laser deposition. Our X-ray diffraction and scanning transmission electron microscopy (STEM) measurements revealed that while the films are coherently strained in plane, with no observed distortions at the interface, there is a notable, up to 4% lattice expansion in the out-of-plane direction. By employing an integrated differential phase contrast (IDPC) imaging technique in STEM, we examined orthorhombic relaxation in both undoped and doped samples. We found no significant differences in octahedral tilting between them, while the doped LFON sample exhibited a higher prevalence of two orthogonal in-plane rotated structural domains. Moreover, atomically resolved electron energy loss spectroscopy (EELS) indicated that the Fe valence remains as Fe3+ after N doping, suggesting that the generation of oxygen vacancies serves as a compensatory mechanism for the charge difference between nitride and oxide ions. However, DFT calculations indicated that oxygen vacancies and substitutional N had little impact on the out-of-plane lattice parameter. Further experimental and theoretical investigations are necessary to uncover the underlying cause of the 4% lattice expansion in the out-of-plane direction. In summary, these findings provide a crucial guide for understanding how N doping affects the structure and properties of complex oxides, essential for designing novel electrocatalysts for water splitting.

4:15 PM EL06.06.03
Nearly Epitaxial ZrO2-Co Vertically Aligned Nanocomposites Thin Film with Tunable Magnetic and Optical Anisotropy
Yizhi Zhang1, Jiawei Song1, Ping Lu2, Julia Dietz2, Di Zhang3, Hongyi Dou4, Jianan Shen4, Zedong Hu4 and Haiyan Wang5; 1Purdue University, United States; 2Sandia National Laboratories, United States; 3Los Alamos National Laboratory, United States

Metamaterials have gained great research interest recently owing to their potential for property tunability, multifunctionality, and property coupling. As a new group of hybrid metamaterials, vertically aligned nanocomposite (VAN)-based thin films exhibit significant anisotropic physical properties and a broad range of property tailorability, such as optical anisotropy, magnetic anisotropy, and hyperbolic dispersion. In this work, self-assembled ZrO2-Co hybrid thin films, with high epitaxial quality and ultra-fine vertically aligned metallic Co nanopillars (with an average diameter of ~ 2 nm) embedded in a ZrO2 matrix, were successfully fabricated using a pulsed laser deposition (PLD) method. The Co pillar planar density can be effectively tuned, without changing the pillar size, by varying the Co concentration in the target, which results in tunable optical properties and magnetic properties. Specifically, a high saturation magnetization of 100 emu/cm3, strong out-of-plane magnetic anisotropy and tailorable magnetization properties were achieved. Coupled with hyperbolic optical dispersion from 950 nm to 1500 nm in wavelength, plasmonic Co metal nanopillars, and the unique dielectric ZrO2 matrix, this new nanoscale hybrid metamaterial shows great potential for future integrated optical and magnetic device designs.

4:30 PM *EL06.06.04
Epitaxial Memristors: Preparing for The New Generation Devices
Beatriz Noheda; University of Groningen, Netherlands

The search for devices that can emulate the behavior of neurons and synapses, in order to be used in brain-inspired, in-memory or on-edge computing, is extending among different research fields with an increasing number of materials scientists involved in the quest. However, the number of materials that have been considered as the key elements for these devices is restricted to the few that are compatible with CMOS integration. The need to process at low temperatures often produces polycrystalline or amorphous materials, limiting the control of the materials properties. Luckily, the emergent efforts towards epitaxial growth of complex oxides by ALD at low temperatures[1] allows us to dream of a future of epitaxial oxide microelectronics for which we want to be prepared. In this talk, we will show an example of epitaxial material that show interesting neuromorphic features, namely, self-oscillating behavior and generation of voltage spikes in epitaxial TbMnO3, a material that does not undergo a meta-insulator transition, and can be used as a compact neuristor[2].

With a rapidly growing family of vdW materials, the role of dielectric and metals have become more important than ever. In this talk, I will present challenges associated with the synthesis of atomically-precise three-dimensional (3D) perovskite nanomembranes followed by our group’s effort to address them. Using hybrid molecular beam epitaxy that employs a metal-organic precursor, titanium isopropoxide (TTIP), to supply both Ti and oxygen (without the need for additional oxygen), epitaxial SrTiO$_3$ (STO) films were grown directly on a graphene layer transferred on to bulk STO substrates. Films were then successively exfoliated and transferred onto other substrates. Using Raman spectroscopy and high-resolution X-ray diffraction, we show that the transferred STO membrane is single-crystaline and can be integrated with other vdW materials. I will also present sacrificial layer route to create oxide membranes resulting in room temperature dielectric constant of ~300. Finally, I will present several opportunities for materials physics and devices engineering using 3D nanomembranes.

9:15 AM EL06.07.02
Periodic Wrinkles in Freestanding Complex Oxide Membranes
Minvong Han, Tiffany C. Wang and Harold Y. Hwang; Stanford University, United States

A stiff film bonded to an elastic substrate shows a universal tendency to form periodic wrinkles upon application of compressive force [1]. This design principle has been employed to produce wafer-scale wrinkles in polycrystalline metal films on polydimethylsiloxane (PDMS) for applications in e.g. optical gratings or strain sensors [2]. When a single crystalline film is processed similarly in a nanoscale morphology, a spatially graded strain state with continuously varying lattice constant can be realized. In the regime of extreme bending, the strain gradient therein is known to generate significant modifications in mechanical and electromagnetic properties of the material [3,4]. The recent development of water-soluble oxide buffer layer enables viable lift-off of complex oxide membranes to be transferred onto an arbitrary elastic substrate [5]. In this study, we adopt this technique to prepare single crystalline oxide membranes on PDMS and fabricate a variety of periodic wrinkles in a fully programmable fashion using compression amplitude and membrane thickness as control parameters. Under large compressive force, the degree of bending extends to the limit where the membrane thickness is a few percent in size compared to the radius of curvature of wrinkles. In addition, we introduce our unique sample packaging methods to characterize electrical properties of wrinkled membranes while maximally preserving the overall sample geometry and the associated strain state.

References:

9:30 AM EL06.07.03
Maintaining The Structural Integrity of Wet-Transferred Graphene to Achieve Successful Exfoliation of BTO in Heterostructures Grown through Pulsed Laser Deposition (PLD)
Aaraful Husain, Suman K. Mandal, Shubham K. Parate and Shriniwas Raghavan; Indian Institute of Science, India

The epitaxial growth of functional oxides on graphene-coated substrates presents a promising avenue for producing self-standing epitaxial nanomembranes, thereby facilitating advanced scientific investigations, applications, and sustainable substrate reutilization. However, the conventional use of aggressive oxidizing conditions in the growth of epitaxial oxides can jeopardize the integrity of the graphene layer. This study introduces a systematic approach to safeguard graphene during the epitaxial growth of BaTiO$_3$ (BTO) on SrTiO$_3$ (STO) substrates coated with graphene. Our method involves an initial BTO growth phase using a laser source with a controlled aperture, thereby adjusting the growth rate to minimize damage to the underlying graphene layer. Additionally, a precisely regulated chemical vapor deposition (CVD) process is employed to grow graphene with larger grain sizes, thereby enhancing the crystalline quality of the remotely epitaxially grown BTO film. Gradual strain relaxation is observed in the resulting BTO films upon the incorporation of multiple graphene layers. The use of bilayer graphene facilitates the easy exfoliation and transfer of the BTO film to various substrates, including Si. These findings pave the way for the heterogeneous integration of different functional oxides, holding significant implications for the commercialization of perovskite oxides in flexible electronics.

9:45 AM BREAK
Nanoscale Control of The Ionic Evolution within Complex Oxides
Pu Yu

Over the last decades, ionic evolution emerges as a powerful tuning knob to manipulate the material functionalities of complex oxides. In this talk, we will present a few new strategies to explore ionic evolution at the nanoscale, including the scanning probe tip-induced ionic evolution and electron beam illumination induced chemical reduction. For the tip-induced hydrogen evolution, the Pt-coated scanning probe serves as an efficient hydrogen catalyst, leading to a hydrogen spillover across the nano junction between the probe and sample surface. Furthermore, the application of positively-biased voltage through the junction drives protons into the sample, while negative voltage extracts protons out, giving rise to reversible proton evolution. Due to the associated electron filling, this method can then offer an exciting opportunity to harvest advanced functionalities such as insulator-metal transition through the tip-induced proton evolution.

Furthermore, through the electron-beam illumination with a commercial scanning electron microscope, we also demonstrated locally controlled oxygen vacancy migration in the model system of VO₂, and achieved a nano-scale structural transformation into V₂O₅. In this approach, the electron beam induces both surface oxygen desorption through radiolytic process and positively charged background through secondary electrons, which contribute cooperatively to facilitate the vacancy migration from the surface toward the sample bulk, leading to nanoscale chemical reduction through oxygen vacancy formation. We envision that these two approaches can be readily applied for other material systems, providing a promising strategy to manipulate and design novel functionalities in oxide heterostructures on main-stream microelectronics.

This work was performed in collaboration with Dr. Dong Kyu Lee, Dr. Yunkyu Park, Sung Won Lee, Hyeji Sim, Dr. Younghak Kim, Dr. Gi-Yeop Kim and Prof. Si-Young Choi.

References
Future technologies are likely to exploit flexible heterostructures exhibiting multifunctional properties constructed from multiple materials. One example for the synthesis of such systems relies on remote epitaxy, which is a novel technique that allows for the fabrication of thin, freestanding single crystals and nanomembranes. It relies on a sacrificial layer (e.g., graphene) between a thin film and a single-crystalline substrate: during film deposition, the electronic interactions across the graphene are strong enough to enable epitaxial growth but weak enough to allow mechanical release of the film. Others have demonstrated methods for the fabrication of freestanding structures, but the procedures are often materials-specific in the interlayer permitting epitaxial growth. The remote epitaxy technique can be used to create single crystal heterostructures comprised of stacked epitaxial films, their properties optimized by minimizing incompatibilities between the different materials. Details regarding nucleation and growth via remote epitaxy remain unknown, however, due to the many difficulties in studying synthesis in the growth environment with atomic-scale resolution. This necessitates in situ studies sensitive to the atomic-level structure conducted in the growth environment. In situ measurements are particularly important for the synthesis of complex oxides such as perovskite oxides, where small changes to the degree of oxygen incorporation can impact the properties of the film/interface as well as degrade the graphene interlayer.

Here, in this talk, we will firstly demonstrate an in situ synchrotron X-ray investigation of perovskite oxide (e.g., SrTiO₃ and LaNiO₃) thin film growth by molecular beam epitaxy onto graphene few layer coated SrTiO₃ (001) substrates. X-ray phase retrieval methods were used to reconstruct the electron density profiles from X-ray crystal truncation rods measured under different growth conditions. Our in situ observations combined with post-growth spectroscopy provide a number of key insights regarding graphene in the synthesis environment and the resulting effects on the complex oxide/graphene heterostructure. Furthermore, we show that the graphene buffer layer could also enhance the physical properties of a functional oxide thin film grown by the remote epitaxy. We will present the study conducted on epitaxial VO₂ thin films to assess the effect of remote epitaxy on the metal–insulator transition (MIT). The epitaxial VO₂ heterostructures were synthesized on both bare Al₂O₃ (0001) substrates and Al₂O₃ substrates coated with a bilayer graphene. While both systems exhibit the MIT, the film grown by remote epitaxy on graphene demonstrates improved transport properties. Electrical transport measurements show that the on/off ratio is enhanced by a factor of ~7.5 and the MIT switching temperature window is narrower for VO₂ thin films grown on graphene. By characterizing the heterostructures with a suite of X-ray structural, chemical, and spectroscopic tools, we find that the graphene interlayer inhibits oxygen vacancy diffusion from Al₂O₃ (0001) during the VO₂ growth, resulting in improved electrical behaviors at the MIT.

3:45 PM EL06.08.06

Scanning Oscillator Piezoresponse Microscopy: New Tools to Explore Domain Wall Dynamics

Neus Domingo Marinon, Shivaranjan Raghuraman, Kyle Kelley and Stephen Jesse; Oak Ridge National Laboratory, United States

Dynamics of ferroelectric domain walls associated to domain wall switching are known to depend on bulk structure, being very sensitive to defects, chemical and structural pinning sites, as well as environmental conditions, modifying the electronic boundary conditions associated with screening dynamics. However, domain walls also show a sub-coercive field dynamics as a reversible motion, with vibrational states that strongly couple to local structure and composition of the domain wall. In this presentation, we will show a new microscopy mode based on a multipole approach which allows us to quantify domain wall oscillations under applied sub-coercive electric field, while simultaneously disentangle electrostatic from net electromechanical signals, which can introduce severe distortions on the net piezoelectric response around neutral domain walls. This technique allows quick visualization of domain wall displacement, their velocities and dependence on pre-existing domain configurations and defects. When applied to lead titanate, this technique shows significant oscillations of the 180° domain walls between the antiparallel c+/c- domains. Further, the displacement and velocities distinctly depend on existing a-c domain structures and relative orientations of domains. This technique can be readily applied to other heterostructures under a wide range of stimuli such as light, heat, force and bias.

4:00 PM EL06.08.07

Unprecedented Electromechanical Response in Antiferroelectric Thin Films

Lane W. Martin; Rice University, United States

Antiferroelectrics, long considered the somewhat less exciting cousin of ferroelectrics, are having their moment. These materials, which possess anti-polar order (i.e., antiparallel alignment of polarization at zero field), can be switched to polar (parallel) order by an external electric field thus producing a reversible antiferroelectric-to-ferroelectric phase transition and a characteristic double polarization-electric-field hysteresis loop. Such a unique field-induced antipolar-to-polar transition endows antiferroelectrics with properties that are of great interest for a range of applications including nonlinear dielectrics, capacitive-energy storage, electrothermal-energy conversion, and electromechanical actuation. While these materials have been known for many decades, they remain relatively less well studied and understood as compared to their ferroelectric relatives. To better understand the nature of such phase transitions in antiferroelectrics and to finely engineer the polarization properties for targeted applications requires that one can fabricate high-quality versions of antiferroelectric materials. In this spirit, recent years have seen a growth in efforts to study these materials, particularly as thin films. Epitaxial films offer researchers the opportunity to finely control and manipulate the structure, orientation, strain, and much more. In turn, we are offered unprecedented insights into the nature and evolution of these complex and, at times, poorly understood physical phenomena.

Here, we apply the lessons of thin-film epitaxy to the study of antiferroelectrics. This talk will provide an overview of our recent efforts to synthesize, control, and study antiferroelectric perovskite oxides. Our attention will focus on classic, prototypical antiferroelectric materials such as PbZrO₃ and PbHBO₃ and solid solutions and multilayers derived from these parent materials. In turn, we will demonstrate how epitaxy, strain, and buffer layers can allow us to finely control the orientation of the resulting orthorhombic films and, in turn, how this orientation control affects the manifestation of properties. In particular, we will explore how antiferroelectrics offer a pathway to overcome traditional limitations in the achievement of large electromechanical responses in thin-film materials. We will explore an unconventional coupling of the field-induced antiferroelectric-to-ferroelectric phase transition and the substrate constraints in these materials. A delimiting of the oxygen octahedra and lattice-volume expansion in all dimensions are observed commensurate with the phase transition, such that the in-plane clamping further enhances the out-of-plane expansion. In turn, an abnormal thickness scaling is realized wherein an ultrahigh electromechanical strain (1.7%) is produced from a model compound.

The unique field-induced polarization-electric-field hysteresis loop. Such a unique field-induced antipolar-to-polar transition endows antiferroelectrics with properties that are of great interest for a range of applications including nonlinear dielectrics, capacitive-energy storage, electrothermal-energy conversion, and electromechanical actuation. While these materials have been known for many decades, they remain relatively less well studied and understood as compared to their ferroelectric relatives. To better understand the nature of such phase transitions in antiferroelectrics and to finely engineer the polarization properties for targeted applications requires that one can fabricate high-quality versions of antiferroelectric materials. In this spirit, recent years have seen a growth in efforts to study these materials, particularly as thin films. Epitaxial films offer researchers the opportunity to finely control and manipulate the structure, orientation, strain, and much more. In turn, we are offered unprecedented insights into the nature and evolution of these complex and, at times, poorly understood physical phenomena.

4:30 PM EL06.08.08

Voltage-Gated Hybrid Ferroelectric-Supercative Quantum Devices

Maria Badamie; Mohammad Suleiman, Martin Sarott, Morgan Trassim and Yachin Ivy; 1Technion, Israel; 2ETH Zürich, Switzerland

The increasing demand for data storage and manipulation urges technological developements outside the silicon arena. Superconductors are promising for enabling low-power and quantum computing that addresses the data-access growth. A prominent advantage of these materials is the lack of dc electric resistance, which in turn allows zero-energy loss while transmitting electric currents. Nevertheless, following Ohm’s law, the resistance makes voltage biasing impossible. Thus, as opposed to voltage-gated semiconducting transistors, superconducting devices are operated with magnetic fields and RF signals, imposing large device footprint and hence hindering device miniaturization and high-density scaling. Here, we used a ferroelectric-supercative bilayer to demonstrate voltage-gated superconducting quantum devices. Films, wires and superconducting interference devices (SQUIDs) were fabricated and characterized. The ferroelectric polarization was used to produce controllable surface charge at the bilayer interface, which in turn induced changes in the quantum properties, including 54% change in the device switching current. Thus, non-volatile tuneable memory hybrid quantum devices were introduced.

SESSION EL06.09: Oxide Electronics—Devices and Computing

Session Chairs: Aiping Chen and Sundar Kunwar
Friday Morning, April 26, 2024
Room 343, Level 3, Summit

8:30 AM EL06.09.01

Dynamic Processes of Oxygen Ion Exchange in Strontium Cobaltite Bilayer Thin Films Driven by Oxidation and Reduction

Jill Wenderott; 1, 2, Eric M. Dufresne, Yan Li, Hui Cao, Qinteng Zhang, Narayanachari Kondapalli, D. Bruce Buchholz, Supratik Guha and Dillon D. Fong; 1Argonne National Laboratory, United States; 2Drexel University, United States; 3Northwestern University, United States; 4The University of Chicago, United States

Transition metal oxides (TMOs) possess various physical stoichiometry which can be the cause of distinct changes to physical and electronic properties. As an example, the well-studied TMO
behavior.

Stochastic self-oscillations. We utilized Scanning Transmission X-ray Microscopy to confirm a low to high electron-spin-state transition in the Co3+ ion during the insulator-metal-transition in SrCoO2.5 layer as compared to those near the heterointerface. Our results demonstrate a stable and reversible heterointerface, showcasing SrCoOx as a model system for study of ionotronic materials.

Photon correlation spectroscopy (XPCS) studies reveal strongly asymmetric behavior with slower dynamics appearing during reducing versus oxidizing conditions and similar dynamics in the SrCoOx strontium cobaltite (SrCoO3–δ – PV-SCO) – that reversibly transition via a topotactic pathway with the insertion or removal of oxygen. In the thin film form, this topotactic transition occurs while preserving high quality epitaxial films, making this system of interest for ionotronic devices. Here, BM-SCO/PV-SCO (001) (15 nm/15 nm) heterostructures on strontium titanate (STO) (001) and the interface of the systems are highly ordered. The dynamic nature of the spikes can be simulated in conventional semiconductors at the cost of energy efficiency, however a more attractive solution utilizes materials that natively produce such dynamic behavior.

Rare Earth Nickelates for Neuromorphic Computing Applications

As global information consumption grows, the energy required to support computations is consuming a significant portion of the global energy supply. Data centers alone consume 4.5% of all energy by 2025, with computing demands doubling every 3–4 years. Neuromorphic computing promises an energy-efficient solution based on the naturally efficient mechanisms that drive human thought and memory; it was recently calculated to outperform other technologies, including quantum computing, by at least 10,000x in terms of energy per operation. Spiking neural networks (SNNs) are extremely efficient, encoding information based on the time between voltage spikes defined by multiple local inputs. The dynamic nature of the spiking processes can be simulated in conventional semiconductors at the cost of energy efficiency, but however a more attractive solution utilizes materials that natively produce such dynamic behavior.

Materials with an insulator-metal transition (IMT) are ideal for accessing nonlinear transport properties that could be useful in SNNs. In addition, IMTs can be highly sensitive to structure, defects, and environmental factors. Coupling fundamental mechanisms to stimuli such as electric field, electrochemical gating, and optical stimuli is an attractive way of encoding adaptive behavior that is a function of multiple input variables. Recently, IMT materials such as VO2 and NbO2 have been used to replicate the Hodgkin-Huxley action potential in pull-up/pull-down neuistor circuitry. The IMT of NbO2 is at 1080 K, too high for energy-efficient use, while the IMT of VO2 is at 330 K (with doping up to 370 K), meaning active cooling is required for operation with silicon CMOS, which typically operate around 400 K. Meanwhile, RNOs have a tunable IMT from 100–600 K, with known sensitivity to many inputs. Therefore, it is attractive to improve our understanding of RNO synthesis, control the IMT, and leverage it for neuromorphic computing applications.

In this invited talk, I will overview our efforts to controllably synthesize RNO compounds (R = Gd, Eu, Sm, Nd, La) and leverage them for neuromorphic computing applications. I will first discuss synthesis of high-quality heteroepitaxial nickelate layers and bilayer stacks by RF magnetron sputtering, including successful stabilization of EuNiO3 by RF sputtering which we have not seen reported elsewhere. I will also focus on the connection between uncontrollable synthetic parameters such as target aging and resulting film properties. In addition to RF sputtering, I will discuss synthesis of heteroepitaxial layers and bilayer stacks by pulsed laser deposition (PLD) while connecting deposition parameters to measured properties. In particular, I will present EuNiO3/LaNiO3 bilayers with a residual resistivity ratio ~7 orders of magnitude. Finally, I will conclude with a discussion of our efforts to fabricate devices using nickelate bilayers, including a discussion of challenges and possible approaches to creating vertical devices for scalability. I will discuss our recent results of electrically-driven IMTs in NdNiO3 and NdNiO3/LaNiO3 bilayers which show strong negative differential resistance (NDR) – the key electrical characteristic leveraged in neuistor circuits.

The device concept of ferroelectric-gated semiconductor field effect transistors (FETs) has been intensively studied for the past three decades as a promising building block for developing energy-efficient nanoelectronics that can transcend the scaling limits of conventional semiconductor technology. The nearly metallic density of carriers within the Mott channel, however, imposes a major bottleneck for achieving substantial field effect modulation via a solid-state gate. In this study, we report a record high room temperature resistance switching in a rare earth nickelate (R\(\text{NiO}_3\)) channel controlled by a ferroelectric PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) (PZT) gate. We have systematically studied the ferroelectric field effect in R\(\text{NiO}_3\) (R = Sm, Nd, La) to identify the optimal channel parameters that enable continuous multilevel resistive switching.

In our work, we explore a novel class of spiking oscillators termed “thermal neuristors”. These neuristors function and communicate exclusively through thermal processes, utilizing the insulator-to-metal transition in vanadium dioxide. We showcase a diverse range of reconfigurable electrical behaviors that closely resemble those of biological neurons, including phenomena like the all-or-nothing law, type-II neuronal rate coding law, spike-in and DC out effect, spike-in and spike-out effect, and stochastic leaky integrate-and-fire law. Remarkably, inhibitory behaviors are achieved using just a single oxide device, and the transmission of cascaded information occurs solely through thermal interactions without any intrinsic circuitry. This research serves as the groundbreaking computational and energy-efficient thermal neural networks, advancing the field of brain-inspired computing.

Harnessing The Competing Roles of Charge to Design Ferroelectric-Gated Mott Transistors

Yifei Hao\(^{1}\), Xuegang Chen\(^{1}\), Le Zhang\(^{1}\), Myung-Geun Han\(^{2}\), Wei Wang\(^{2}\), Yue-Wen Fang\(^{3}\), Hanghui Chen\(^{3}\), Yimei Zhu\(^{2}\) and Xia Hong\(^{1}\);\(^{1}\) University of Nebraska - Lincoln, United States; \(^{2}\) Brookhaven National Laboratory, United States; \(^{3}\) New York University Shanghai, China

References


Piezo-Strain-Controlled Phase Transition in Single-Crystalline Mott Crossovers for Threshold-Manipulated Leaky-Integrate-And-Fire Neurons

Dong Kyu Lee, Sungwon Lee, Yunkyu Park, Si-Young Choi and Junwoo Son; Pohang University of Science and Technology, Korea (the Republic of)
Perovskite metal oxides offer a wide range of functionalities owing to their rich rich compositional diversity. Experimental results have shown that much-enhanced physical properties could be achieved by forming multicomponent or high-entropy perovskite oxides. In this talk, we discuss our efforts in the design and synthesis of compositionally disordered epitaxial perovskite metal oxide films with quenched A-site cations. Using rare-earth aluminum perovskite oxide with an equimolar ratio \((La_{1-x}A_{x})_2O_3\) as the model system, we show that a high entropy oxide system with equimolar A-site cations allows for the achievement of desired optical luminescence observed in mixtures and/or doping of RE aluminates while maintaining a highly crystalline single-phase. The high crystallinity of these materials paves the way for exciting new research of high precision scintillating applications.

2:00 PM EL06.10.02
Vector Substrates: How to Grow Epitaxially Impossible Heterostructures Yu-June Wu¹, Varun Harbola¹, Felix Hensling¹, Hongguang Wang¹,², Peter A. van Aken¹,² and Jochen Mannhart¹; ¹Max Planck Institute for Solid State Research, Germany; ²Stuttgart Center for Electron Microscopy, Germany

Substrates play a crucial role in thin film deposition, but they do not always align with the specific requirements of a particular experiment or application. For instance, they might be expensive or unavailable with a desired crystal lattice structure. To address this, we introduce the novel concept of "vector substrates." In this approach, the template layer for growing thin films is both chemically and structurally independent from the main substrate. Vector substrates are fabricated by transferring a membrane, which serves as the template layer and is grown on a reusable parent substrate, onto a carrier substrate. The template and carrier layers can be independently chosen and optimized, which reduces material costs and offers more flexibility. We validate the feasibility of this technology by presenting sets of vector substrates for high-quality epitaxial film growth and by demonstrating a clean interface between the transferred membrane and the carrier substrate. The vector substrate concept is in its early stages of development but holds significant promise to supplement conventional substrates and drives future advancements in substrate technology and the deposition of films and heterostructures.

2:15 PM EL06.10.03
Heterogeneous Nucleation of YBCO Film Deposited by MOD: Experimental Verification of a Thermodynamic and Kinetic Model Valentina Pinto¹, Michele De Angelis²,¹, Achille Angrisani Armonio¹, Andrea Augieri¹, Giuseppe Celentano¹, Andrea Masì¹, Silvia Orlanducci¹, Alessandro Rufoloni¹ and Massimo Tomellini²; ENEA, Italy; ²For Vergata University, Italy

The deposition of superconducting YBaCu4O7-y (YBCO) thin film can be performed through physical and chemical methods, being the latter ones really advantageous in terms of cost-effectiveness, versatility, and simplicity. Therefore, within the last decade, the use of chemical solution deposition method, in particular the metal organic decomposition (MOD) approach, for producing epitaxial YBCO films has played an increasing role in the development of scalable processes. In recent years, the need for a quantitative model for the YBCO heterogeneous nucleation emerged in order to better control the parameters affecting the formation of epitaxial film deposited by fluorine based MOD process. In fact, despite the great number of articles on YBCO deposition, the nucleation has been scarcely studied in the literature and only at qualitative level. However, it is a crucial step because the best superconducting properties are exhibited by YBCO film with the c-axis orientation. Recently, a thermodynamic and kinetic study on the heterogeneous nucleation of YBCO film has been proposed in [1]. The model focused on fluorine based MOD deposition on SrTiO3 (STO) single crystal and was developed on the basis of the classical nucleation theory providing an estimate of c-axis grain fraction as a function of water partial pressure and temperature. This latter calculation could constitute a useful tool to define the proper experimental conditions for depositing highly epitaxial c-axis c-sapphire film or low crystallization temperature may be necessary. In the present work, the controlling the formation of different epitaxial film deposited by fluorine based MOD deposition on STO single crystal has been performed at different crystallization temperatures and water partial pressure values. The prepared samples have been fully characterized through the analysis of microstructure, morphology, and superconducting properties. The c-axis fraction has been derived by x-ray diffraction analysis and the experimental data have been described by the theoretical curves calculated from the model. The deposition on a different substrate, namely LaAlO3 (LAO), has been also carried out to study the effect of the substrate on YBCO nucleation kinetics. In fact, the expression for the free energy barriers includes the work of adhesion of the YBCO substrate interface. The preliminary results obtained for YBCO/LAO samples evidenced the critical importance of this quantity and its technological implications. In general, the present study shows that a deeper comprehension of the nucleation mechanism can lead to the improvement not only of the YBCO superconducting properties, but also of the process robustness and reproducibility.

References:

2:30 PM EL06.10.04
Bridging Thin Films Growth and Advanced Electron Microscopy to Uncover Structure-Property Correlations in Oxide Electronics Robert Winkler¹, Alexander Zintl², Oscar Recalde³, Despina Nasiou¹, Lambert Alf³ and Leopoldo Molina-Luna¹; ¹TU Darmstadt, Germany; ²University of Antwerp, Belgium

Reactive Molecular Beam Epitaxy (RMBE), among other Volatile Physical Vapor Deposition (PVD) techniques, can precisely fabricate high-quality semiconductor heterostructures necessary for complex oxide electronics [1]. Their composition and crystallinity can be engineered through careful selection of growth parameters [2], [3], however are subject to the underlying layer. Here, we investigate the nucleation and growth of YBCO heterostructures, an important feature to deposit high-quality superconducting films on STO single crystal. The nucleation and growth of YBCO heterostructures on STO single crystal has been performed at different crystallization temperatures and water partial pressure values. The prepared samples have been fully characterized through the analysis of microstructure, morphology, and superconducting properties. The c-axis fraction has been derived by x-ray diffraction analysis and the experimental data have been described by the theoretical curves calculated from the model. The deposition on a different substrate, namely LaAlO3 (LAO), has been also carried out to study the effect of the substrate on YBCO nucleation kinetics. In fact, the expression for the free energy barriers includes the work of adhesion of the YBCO substrate interface. The preliminary results obtained for YBCO/LAO samples evidenced the critical importance of this quantity and its technological implications. In general, the present study shows that a deeper comprehension of the nucleation mechanism can lead to the improvement not only of the YBCO superconducting properties, but also of the process robustness and reproducibility.

References:

2:45 PM EL06.10.05
Phase Change Material VO2/Iridium/Yttria-Stabilized Zirconia Heterostructures on Silicon Christina Bestele and Helmut Karl, University of Augsburg, Germany

External parameters like temperature, strain and electric fields can be employed to control the metal-insulator phase transition (MIT) of the strongly electron-correlated material vanadium dioxide (VO2). This MIT is accompanied by an enormous decrease in electrical resistivity and optical transmittance in the infrared spectral region and especially the telecom window. VO2 thin films on dielectric and metallic layers are of importance. In this work, we demonstrate epitaxial growth of VO2 on yttria-stabilized zirconia (YSZ) and a layer stack of iridium/YSZ epitaxially grown on (001)-silicon, where the iridium layer forms a backside metallization that is used as an anchor plate and areal contact to the VO2 layer on top. The heterostructures were fabricated in the following way: at first, a dielectric and electrically insulating YSZ template-layer was grown epitaxially on a (001)-silicon substrate [3], followed by the growth of the VO2 thin film, both deposited by pulsed laser deposition. Similarly, the VO2/YSZ heterostructure was grown, except that the iridium layer was grown ex-situ by e-beam evaporation [4]. The iridium layer provides a highly electrically conducting electrode and the optical and electrical properties of the heterostructure can be controlled by adjusting the composition of the layer stack.

References:
allowing building capacitor structures with VO₂ to control the MIT by electric fields and to build vertical electronic switching devices for very fast sensing applications and current control. The YSZ template-layer inhibits silicide formation by blocking diffusion of the cations to the YSZ/Si interface. Pole figures, reciprocal space maps and temperature dependent μ-Raman spectroscopy measurements reveal (010)-oriented VO₂ layers with 30° in-plane rotated crystallites and high symmetry grain boundaries on both the (001) iridium/YSZ double layer and YSZ template-layer.

Based on these multilayers metal/VO₂/iridium capacitor structures on silicon were fabricated and the effect of an electric field on the MIT were studied by μ-Raman spectroscopy and spectral reflectivity measurements.


The on-demand design of transition-metal oxides (TMO) with emerging properties is imparted by the multivalent nature of the transition-metal ions and the accessible complexity of lattice structures [1, 2]. One can access a wide range of electronic landscapes by varying the structure and constituent elements in TMO. The oxygen dynamics in the system determines the resulting structure, and thereby their electronics. The metal hydride based topochanical reduction is one of the oxygen (de-) intercalation methods and it has been employed to synthesize otherwise difficult systems such as the infinite-layer nickelates (IL-nickelates), which was found to be superconducting upon doping [3]. In this path, from topochanical reduction of a perovskite SmNiO₃ thin-film, we obtain a novel valence-ordered and tri-component coordinated niobate phase [4]. This new phase, with the chemical formula of Sm₉Ni₉O₂₂ (SmNiO₂.₄₄) is formed by intricate planes of (303)pc (subscript pc refers to pseudocubic) apical oxygen vacancies (Vo) from the parent perovskite as revealed by x-ray absorption spectroscopy measurements [1, 2]. Using two-dimensional electron gas (2DEG) as a probe for optical studies, we demonstrate that the Fermi level binding energy changes, as a function of temperature, is proposed. Furthermore, restoration of the original properties or phases of the thin films after undergoing a metal-to-insulator transition illustrates routes to regulate the surface metal-to-insulator transition, especially in the case of insulating NiCo₂O₄ thin film which can undergo reversible metal-to-insulator transition (MIT) as a function of temperature [8]. The shift in the core level binding energies ceased to decrease. This shows that the prepared CoFe₂O₄ thin film can be dielectric at room temperature but more metallic at elevated temperatures. The dielectric nature of the film was restored only when the film was annealed in sufficient oxygen, indicating that the oxygen vacancies play a role in the transition of the film from dielectric (or insulating) to conducting. In contrast, similar studies on NiCo₂O₄ thin film showed that annealing of NiCo₂O₄ thin film, which was observed to be conducting, could make NiCo₂O₄ thin film insulating, and the original more metallic character of the NiCo₂O₄, thin film could be restored only when the sample was annealed in sufficient oxygen. A model that governs the core level binding energy changes, as a function of temperature, is proposed. Furthermore, restoration of the original properties or phases of the thin films after undergoing a metal-to-insulator transition illustrates routes to regulate the surface metal-to-insulator transition, especially in the case of insulating NiCo₂O₄ thin film which can undergo reversible metal-to-insulator transition with temperature. This work provides a better fundamental understanding of defect mediated surface phases for thin film oxides and opens avenues for defect assisted and/or temperature dependent capacitor future beyond CMOS devices.

4:00 PM EL06.10.08

XANES Analysis of Mn-Alloyed TiO₂ Coatings Grown by Atomic Layer Deposition: Probing The Crystallization Behavior

Devan Solanki, Deyu Lu and Shu Hu

University of Nebraska–Lincoln, United States

TiO₂ is a nontoxic, wide bandgap semiconductor with many excellent physical properties such as high chemical stability in acids and bases and good optical transparency to visible light, making it an excellent candidate for photocatalysis. Atomic Layer Deposition (ALD) enables synthesis of conformal coatings on various substrates by its layer-by-layer, surface-growth mechanism. However, controlling the crystallinity of the films, which can modulate properties such as the band gap and band edge positions, remains a challenge as TiO₂ is often amorphous as deposited but can be annealed into multiple polymorphs such as anatase, rutile, and brookite. Despite progress in understanding the reaction mechanisms and intermediates associated with the deposition of binary materials via ALD, there are still many questions surrounding the structure-processing relationship of ternary materials. For example, the role that dopants or alloying agents play in determining key properties such as oxidation state and crystal structure remain open questions.

Methods:

The X-Ray Absorption Spectroscopy (XAS) and X-Ray Absorption Near Edge Structure (XANES) measurements were conducted at the Inner Shell Spectroscopy beamline of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Lab. The data was collected at room temperature with the energy calibrated using a Ti foil. The Athena software package was used to calibrate the energy and normalize the data using the recommended parameters. XAS was collected in fluorescence mode with μ(E) = If / I₀ where If is the fluorescence intensity and I₀ is the incident intensity. Each spectrum is flattened so that the overall spectrum has an asymptotic behavior approaching 1.

Results:

The pre-edge feature in the TiO₂ sample, centered at 4968 eV is due to the oxygen vacancies and resultant undercoordinated Ti. The absorption maximum of that pre-edge feature is...
Manipulating distortion of SnO₆ octahedron by diffusion kinetics of Ni metal during exsolution process. Remarkably, the density of Ni NPs increases from 47 particles um⁻² to 304 particles um⁻² (Ca₀.₉Sn₀.₉Ni₀.₁O₃-δ) to 304 particles um⁻² (Ca₀.₉Sn₀.₉Ni₀.₁O₃-δ) by decreasing the Goldschmidt tolerance factor of perovskite stannate epitaxial films. Quantitative analysis using ambient pressure X-ray photoemission spectroscopy (APXPS) during in-situ exsolution process experimentally confirmed that Ni diffusion is enhanced with decreasing the tolerance factor of perovskite stannate. Experimental characterization combined with theoretical calculation shows that Goldschmidt tolerance factor of perovskite stannate promote the Ni diffusion kinetics from the oxide matrix to surface by manipulating the A-O bonding strength. Motivated by the high density of Ni NPs on perovskite stannate support, in-situ CO oxidation was also performed using APXPS to identify the effect of the catalytic activity of perovskite stannate support with exsolved Ni NPs. This new strategy on the manipulation of tolerance factor for promoting exsolved metal diffusion kinetics can be exploited to enhance the density of populated metal nanoparticles for emerging catalytic applications.

References
Here, we demonstrate the synthesis of epitaxial, hexagonal LuGaO₃ via pulsed-laser deposition, which has not yet been reported. Extensive X-ray diffraction-based structural studies verify the computational models, making them more reliable for future materials predictions. Novel Hexagonal Ferroelectric LuGaO₃ Pb₁₋ₓSrₓTiO₃ layers exhibit strong elastic and dipolar coupling, leading to a coercivity enhancement of the trilayer stack upon decreasing the strontium content of the Pb₁₋ₓSrₓTiO₃. Phase-field simulations further explain the polarization arrangement in the trilayer and the system’s subsequent collective switching pathway of the two order parameters. Formation of such in-plane domains in the Pb₁₋ₓSrₓTiO₃ leads to the formation of a labyrinthine vortex arrangement, unlike the highly unidirectional vortices observed in Pb(0.995Sr0.005)O₃ superlattices. Further, we have explored the coupling between different epitaxial hexagonal ferroelectrics of the form Pb₁₋ₓSrₓTiO₃/Pb₁₋ₓSrₓTiO₃/Sr₂O₃/Pb₁₋ₓSrₓTiO₃. Therein, the thickness of the Sr₂O₃ layer separating the two vortex structures controls the strength of the elastic and electric fields that extend between layers, affecting the sequence in which each trilayer would switch and the number of switching events. The result is an ability to produce low-field multi-state, four-step switching with robust retention and fatigue performance. Finally, in (Pb₁₋ₓSrₓTiO₃)₃/Pb₁₋ₓSrₓTiO₃ superlattices we have explored the dielectric tunability and out-of-plane switching and find improved tunability as a function of the chemistry of the Pb₁₋ₓSrₓTiO₃ layer, antiferroelectric-like switching due to an unraveling of the vortex phase upon application of the electric field, and strong back switching on releasing the same leading to improvements in the low-field energy storage as compared to PbTeO₃/PbTeO₃.

11:00 AM EL07.01.04
Novel Hexagonal Ferroelectric LuGaO₃ Jesse Schimpf¹, Megha Acharya¹ and Lane W. Martin²,¹; ¹University of California, Berkeley, United States; ²Rice University, United States

The presence of simultaneous ferroelectric and magnetic order in hexagonal LuFeO₃ has made it a promising candidate for next-generation microelectronics. At the same time, the metastable nature of this phase makes it an interesting case study for the synthesis of novel epitaxial materials. Its utility, however, is limited by its low polarization (~10 μC/cm²) and often poor film quality. Recent first principles predictions have identified a new hexagonal ferroelectric, LuGaO₃, which is isostructural to LuFeO₃ but is predicted to be thermodynamically stable and exhibit a higher polarization than LuFeO₃. While nonmagnetic, the enhanced polarization in LuGaO₃ could make it a more suitable ferroelectric, and alloying it with LuFeO₃ may serve to enhance the magnetic character while retaining more robust ferroelectricity. Overall, understanding the synthesis of newly predicted materials provides an important opportunity to verify and correct computational models, making them more reliable for future materials predictions.

Here, we demonstrate the synthesis of epitaxial, hexagonal LuGaO₃ via pulsed-laser deposition, which has not yet been reported. Extensive X-ray diffraction-based structural studies verify the hexagonal nature of this phase, while piezoresistive force microscopy studies show indications of stable, ferroelectric switching. While first principles calculations predict this phase to be thermodynamically stable (energy above 0.1 eV) in the bulk, the material separates into Lu₂O₃ and Lu₂GaO₄ phases. Film synthesis is even more complex and highly sensitive to growth conditions and epitaxial constraints. While (111)-oriented ytrria-stabilized zirconia is the preferred substrate for hexagonal ferroelectrics like LuGaO₃, it is also closely lattice matched with Lu₂O₃, which forms epitaxially with surprisingly high quality under a wide range of conditions, with excess gallium being segregated to large precipitates on the surface of the film. Energy dispersive X-ray spectroscopy shows a large gallium deficiency (as much as 30% off from the target stoichiometry) in these phase-separated films, likely reducing the stability of the perovskite structure. Deposition of the films at room temperature and subsequently annealing them circumvents the gallium loss enough to stabilize the hexagonal phase in extremely thin (~5 nm) films, while depositing in abnormally high oxygen partial pressures (1 Torr or more) has the same effect for thicker films, enabling more extensive structural and dielectric characterization which confirms the presence of a hexagonal, ferroelectric phase. We further examine the structure and dielectric properties as a function of synthesis conditions as the material transforms from predominately nonpolar Lu₂O₃ to ferroelectric hexagonal LuGaO₃. We then compare this to LuFeO₃, which does not exhibit the same phase separation and largely maintains the hexagonal phase regardless of the synthesis conditions. Finally, we examine the influence of alloying and multilayering of both materials to understand their stability and produce a more robust multiferroic. Interestingly, providing a thin (as little as 1.2 nm) buffer layer of LuFeO₃ is enough to stabilize hexagonal LuGaO₃ where it would otherwise phase separate on a bare substrate, further demonstrating the importance of epitaxy in phase selection. Extending this to a multilayer or solid solution has a similar effect. While such mixtures maintain robust ferroelectricity, a small degree of phase separation still persists and will likely require further tuning of the gallium chemistry to fully correct. Nevertheless, this work represents an important step toward finding a more robust hexagonal perovskite multiferroic and offers valuable insight on metastable materials synthesis.

11:15 AM EL07.01.05
Van der Waals Growth of Ferroelectric GeTe Thin Films by Industrial Magnetron Sputtering for Large-Scale Integration Pierre Noé¹, Nicolas Bernier¹, Damien Térébene¹, Jules LaGrave¹, Alexandre Oysel-Mestre¹, Jean-Baptiste Dory¹, Théo Frottier², Salvatore Teresi², Jean-Philippe Attane², Laurent Vila² and Françoise Hippert³; ¹Univ. Grenoble Alpes, CEA, LETI, France; ²Univ. Grenoble Alpes, CNRS, CEA, SPINTEC, France; ³Univ. Grenoble Alpes, Grenoble INP, LMGFP, France

Chalcogenide materials have attracted a lot of attention over the years due to their wide range of applications. Among them, some compounds such as Ge-Sb-Te based alloys exhibit a unique portfolio of properties, which has led to their wide use for non-volatile-phase-change memory applications [1,2]. In addition to memory applications, the GeTe phase-change alloy is also very promising for RF switches [3], for thermoelectrics [4,5], and offers numerous opportunities for optical applications[6] and photonic[7] as well as for the emerging field of spintronics [8]. GeTe has also been the subject of numerous studies, , due to the ferroelectric character of the stable rhombohedral α phase and the existence of a reversible structural transformation (around 430°C) between the rhombohedral α phase and the cubic paraelectric cubic β phase. The rhombohedral α-GeTe phase can be described as a deformed rocksalt structure that has undergone shearing along a cube diagonal ([111] or equivalent direction), with a relative displacement of the Ge and Te atoms along this direction, which is . responsible for the ferroelectric properties. In the α-GeTe phase a Ge atom is surrounded by six Te atoms forming a distorted octahedron with three short and three long Ge-Te bonds. This splitting is interpreted as resulting from a Peierls distortion. These properties have sparked interest in GeTe as a ferroelectric Rashba semiconductor, combining semiconductivity, strong spin-orbit coupling and non-volatility. In addition, GeTe has recently attracted renewed interest with the demonstration of non-ferroelectric control of spin-charge conversion in epitaxial germanium telluride films deposited by molecular beam epitaxy [8]. The sign of the charge current can be controlled by the orientation of the ferroelectric polarization, which can be switched by an electric gate despite the high intrinsic carrier density of GeT. In this context, the successful deposition of high-quality epitaxial ferroelectric GeTe films using a large-scale industrial deposition process could open up a new field of applications based on the non-volatile control of spin currents in semiconductor GeTe. In this presentation, we will show that the van der Waals growth of high structural quality ferroelectric GeTe thin films using industrial magnetron sputtering could be achieved, demonstrating that this material could be monolithically integrated on silicon for devices beyond CMOS such as reconfigurable spin-based and in-memory computing devices.

Key words: chalcogenide, GeTe, phase-change material, van der Waals epitaxy, ferroelectric

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SESSION EL07.02: Ferroelectrics II
Session Chairs: Yen-Lin Huang and Ruijuan Xu
Tuesday Afternoon, April 23, 2024
Room 342, Level 3, Summit

1:30 PM *EL07.02.01
Coexistence of Ferro- and Antiferroelectric Behavior
Dennis Meier; Norwegian University of Science and Technology, Norway

Ferroelectric domain walls are a rich source of emergent electronic properties and unusual polar order. For example, recent studies showed that the polarization configuration of ferroelectric walls can go well beyond the conventional Ising-type structure, exhibiting Néel-, Bloch-, and vortex-like polar patterns.

In my talk, I will present novel types of anti-polar domain walls and discuss their structure and unusual physical properties. In the first part of my talk, I will show that charged domain walls arise in $K_x[Nb_2O_5(BO_2)]$. The domain wall bound charges arise from a finite canted moment associated with the material’s antiferroelectric-like order, leading to distinct local piezoelectric and electrostatic responses. In the second part, I will talk about the emergence of anti-polar order at domain walls in Pb$_2$Ge$_3$O$_{11}$. The domain walls are highly mobile and exhibit an energetically costly antiparallel ordering of dipoles along the longitudinal direction, which we attribute to the hyperferroelectric nature of the system. The results provide new insight into the complex polar textures of domain walls, expanding previous studies towards anti-ferroelectric phenomena.

2:00 PM *EL07.02.02
Dynamic Mechanical Writing of Ferroelectric Bubbles
Chan-Ho Yang; KAIST, Korea (the Republic of)

Topological ferroelectric structures offering novel functionalities due to peculiar distributions of polarization and charge with long retention have been increasingly explored in a variety of dielectric systems, such as superlattices, strained films, and nanoscale islands. The polar structures, protected by topological constraints such as boundary conditions, appear as metastable states due to the interplay between strain, depolarization and gradient energies, but their precise control is still challenging. In this study, we demonstrate the observation of skyrmion-like centre-type polar bubble domains in supertetragonal BiFeO$_3$ thin films. These polar textures are mechanically generated by dynamic elastic force of vibrational tapping using scanning probe microscope tips. The formation of bubble domains is accomplished by emergence of strain-driven morphotropic phase boundaries wherein two competing structural phases coexist. The bubble domains can be accurately written, mechanically or electrically erased, and remain stable for longer than ~500 days. Vibrational tapping can bidirectionally switch out-of-plane polarization by exerting strong tapping force onto the elastically soft surface driven by the morphotropic phase transition, which may be attributed to non-linear flexoelectric effects in the large strain-gradient regime beyond the conventional flexoelectric concept. Our study presents insights into dynamic mechanical switching of polarization and provides a unique pathway into topological polar structures for next-generation energy-efficient electronic applications.

2:30 PM EL07.02.03
Real-Time Imaging of Nonequilibrium Domain Evolution into a Multiferroic Phase
Jan Gerrit Horstmann; Yannik Zemp1, Ehsan Hassanpour Yesaghi1, Thomas Lottermoser1, Mads Weber2 and Manfred Fiebig1; 1ETH Zurich, Switzerland; 2Le Mans Université, France

The properties and functionalities of multiferroic materials are governed by the microscopic domain structures of coexisting ferroic orders and their mutual coupling. Active control over multiferroic domains via external stimuli is desirable, with prominent examples in magnetoelectric inversion or transfer of domain patterns. These approaches typically harness electric or magnetic fields to affect the thermodynamically stable domain configuration within a multiferroic phase. Optical or thermal quenches through phase transitions can be used to transfer structural features between distinct phases, creating novel and potentially functional domain structures unattainable in thermal equilibrium. The impact of such transitions on multiferroic domain patterns and their dynamic evolution, however, remains a largely open subject.

In this work, we combine real-time Faraday imaging at kHz frame rates with fast optical excitations to investigate the evolution of domains across spin-reorientation transitions and into the multiferroic phase of Dy$_{0.7}$Bi$_{0.3}$FeO$_3$. We find that optically-induced thermal quenches of the system can be harnessed to imprint the characteristic bubble domain pattern of the weak ferromagnetic order at elevated temperatures onto the low-temperature multiferroic phase. We identify the quenching rate across the different spin reorientation transitions as the decisive parameter governing the domain memory and the formation of metastable domain states forbidden under equilibrium conditions. Our results highlight the potential of optical stimuli for the switching and control of multiferroic domain structures, enabling the creation of new functional states via nonequilibrium pathways.

2:45 PM DISCUSSION TIME

3:00 PM BREAK

3:00 PM EL07.02.05
Nanoscale Design of Polarization Using Lattice Chemistry Engineering in Layered Ferroelectrics
Ipek Efik1; Alexander Vogel2, Elzebta Gradauskaite1, William S. Huxter1,1, Christian Degen1,1, Marta D. Rossell2, Manfred Fiebig1 and Morgan Trassin1; 1ETH Zurich, Switzerland; 2Le Mans Université, France

Nanoscale electrostatic control of oxide surfaces enables physical phenomena and exotic functionalities beyond the realm of the bulk material, including superconductivity, multiferroicity, and topological properties promising for future nonvolatile memory applications. Here, by exploiting spontaneously forming charged interfaces in layered materials, we control the electrostatic boundary conditions in ferroelectric oxide heterostructures. We directly access the polarization dynamics of the layered ferroelectric model system Aurivillius Bi$_5$FeTi$_3$O$_{15}$ (BFTO) films during growth using in-situ optical second harmonic generation (ISHG). We identify the characteristic Aurivillius antipolar ordering of the dipoles along the growth direction, which leads to an oscillating intensity of the ISHG signal during the layer-by-layer deposition. In combination with reflection high-energy electron diffraction monitoring, we show how the polarization orientation of the films consistently changes from out-of-plane during the growth of perovskite blocks, to fully in-plane upon the completion of the unit cell with the fluorite-like (Bi$_2$O$_2$)$_2$ layers. Finally, we incorporate various functional perovskite units into the Aurivillius layered-crystal structure using the direct access to structure-dependent polarization dynamics during growth. Our work thus expands the limits of engineering the properties of layered oxide films to the sub-unit-cell-scale for the development of energy-efficient oxide electronics.

3:15 PM EL07.02.06
A Strain-Enabled Novel Multiferroic State in Barium Hexaferrite through Suppression of Quantum Paraelectricity
Zhiyen He1,2 and Guru Khalsa1; 1University of North Texas, United States; 2Cornell University, United States

Barium hexaferrite (BaFe$_2$O$_4$) is predicted to harbor a novel multiferroic phase within which frustrated antiferroelectricity and ferrimagnetism coexist. However, experimental studies have shown that in bulk barium hexaferrite, quantum fluctuations instead lead to a quantum paraelectric ground state at low temperature [1-2]. Strain is a popular method for tuning functional properties in epitaxial thin films and has previously been used to coax ferroelectric dipole order, for example in SrTiO$_3$ [3]. Similarly, recent theoretical exploration has suggested that strain may enhance antiferroelectricity in barium hexaferrite [4]. In this theoretical work, we combine first-principles calculations with quantum Monte Carlo simulations to explore the temperature- and strain-dependent properties of barium hexaferrite. We find good agreement between our model and available bulk experimental data. In the investigation of strained barium hexaferrite, we find that a modest compressive strain of approximately 1% enables the transition to a frustrated antiferroelectric phase with a critical temperature of greater than 10 K. Our results suggest that further investment in epitaxy and development of compressive substrates for hexaferrites may provide a promising route towards room temperature multiferroics.


3:30 PM EL07.02.07
Relaxor-Like Ferroelectric Behavior in Epitaxial NaNbO3 Films for Capacitive Energy Storage

Kevin J. Crust1, Arushi Khandelwal2, Ruijuan Xu2 and Harold Y. Hwang3
1Stanford University, United States; 2SLAC National Accelerator Laboratory, United States; 3North Carolina State University, United States

Electrostatic energy storage based on dielectric capacitors has garnered significant interest due to its fast charge-discharge speeds and high power density relative to electrochemical energy storage, but applications have been limited by large leakage currents, relatively low energy storage density, and the presence of lead in materials\textsuperscript{1,2}. NaNbO\textsubscript{3} is a lead-free alternative which has received much research attention in the last decade but work has primarily focused on its bulk form, with NaNbO\textsubscript{3}-based systems displaying both antiferroelectric and relaxor ferroelectric behaviors at room temperature with promising energy storage properties\textsuperscript{2,3}. Using pulsed laser deposition and selective etching, we have synthesized metal-insulator-metal heterostructures of La\textsubscript{0.6}Sr\textsubscript{0.4}MnO\textsubscript{3} and NaNbO\textsubscript{3} with high crystallinity and coherent epitaxial strain across a range of thicknesses. Both strain and thickness have previously been noted to greatly affect the properties of NaNbO\textsubscript{3} due to the close proximity of its antiferroelectric and ferroelectric ground states\textsuperscript{4,5}. Through careful optimization of the growth conditions, we achieve minimal leakage current even under large external electric fields and can observe relaxor-like ferroelectric behavior in both our thinnest samples (below 50 nm of NaNbO\textsubscript{3}) and our thickest samples (above 150 nm). This allows us to achieve improvements in both recoverable energy-storage density $W_{rec}$ and energy efficiency $\eta$ compared to previous NaNbO\textsubscript{3} thin films\textsuperscript{6,7}. This work demonstrates the potential of NaNbO\textsubscript{3} for dielectric energy storage and the advantages of epitaxial, single-crystal films for electrical characterization.

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3:45 PM EL07.02.08

\textbf{In Situ X-Ray Nano-Imaging of Heterogeneous Structural Response in a Relaxor Ferroelectric}

Aileen Loo1,2, Tony Chiang2, Tao Zhou3, Ziming Shao1, Yifei Sun1, Benjamin Gregory1, Martin V. Holt2, John T. Heron1 and Andrej Singer1, 1Cornell University, United States; 2Argonne National Laboratory, United States; 3University of Michigan--Ann Arbor, United States

Magmnetoelectric multiferroics transduce electrical and magnetic energy, which is critical for the development of new materials for sensors, motors, and computation devices. Composite heterostructures of a magnetostrictor coupled to a piezoelectric, such as the promising epitaxial FeGa on 0.7[PbMg\textsubscript{1/3}Nb\textsubscript{2/3}O\textsubscript{3}] - 0.3[PbTiO\textsubscript{3}] (PMN-P1), enable electric field control of magnetic polarization, while offering additional device utility compared to rare single-phase multiferroics. Such systems have been studied at the micron scale, but nanoscale strain distribution changes during switching are not well characterized. We use in situ hard x-ray nanodiffraction to simultaneously measure real and reciprocal space of devices under applied DC electric field, which allows us to attribute strain and lattice rotation information at the nanoscale. By applying non-linear least squares modeling of the phase coexistence across the morphotropic phase boundary in this heteroepitaxial system, we correlate the local strain behavior in the direction of the applied field and along the domain polarization axes. We analyze the phase distribution as a function of electrical bias and demonstrate the potential for real-time analysis in advanced microelectronics characterization.

4:00 PM EL07.02.09

\textbf{Understanding Fatigue and Wake-Up in Ultra-Thin Ferroelectric Hf\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2} Capacitors Using Cryogenic Measurements}

Balleen Saini1, Chanyoung Yoo2, John D. Baniecki2, Wilman Tsi1 and Paul C. McIntyre1,2, 1Stanford University, United States; 2SLAC National Accelerator Laboratory, United States

The need for logic and memory devices that are smaller, faster, and more energy-efficient is constantly growing. This has intensified the demand for innovative materials capable of scaling down and aligning with current CMOS processes. A next generation memory solution is non-volatile memories that are energy efficient and can enable new computing architectures. For high performance computing systems such as quantum computing, cryogenic embeddied memories are essential that would have an added benefit of eliminating thermally induced performance degradation mechanisms. One material that shows promise for nonvolatile memory applications is HfO\textsubscript{2}-based ferroelectric materials and research in this area has surged due to potential memory applications such as 1T1C ferroelectric random-access memory (FeRAM) and ferroelectric field-effect transistors (FeFET). The HfO\textsubscript{2}-based ferroelectric materials exhibit an increase (wake-up) or decrease (fatigue) of the remnant polarization with switching cycles which causes major reliability issues in device applications. Mechanisms such as field-induced phase evolution, domain depinning and defect redistribution with field cycling are reported to cause the observed polarization evolution with field cycling. The thermally activated nature of the above-mentioned mechanisms may produce a significant change in polarization endurance when the measurement temperature is varied. In our present work, we explore the effect of measurement temperature on the functional properties of ferroelectric Hf\textsubscript{0.6}Zr\textsubscript{0.4}O\textsubscript{2} (HZO) capacitors to further the understanding of mechanisms responsible for the observed endurance characteristics. Measurement are performed in a cryogenic probe station, which has the capability to reach extremely low temperatures as low as 10 Kelvin.

HZO capacitors of varying thickness (ranging from 4 nm to 10 nm) and with both Mo and TiN electrodes are examined. The HZO films have different crystalline phase fractions in the as-deposited (pristine) state. For HZO capacitors that exhibit electrical characteristics expected of films with majority ferroelectric orthorhombic phase (O-phase) in the pristine state, a decrease in remnant polarization and an increase in coercive voltage are observed as the measurement temperature is decreased from room temperature to 10 K. The polarization reduction is recovered by increasing the temperature back to room temperature, suggesting a strong effect of thermally activated domain wall motion at low temperatures. No fatigue during voltage cycling to switch the polarization is observed at low temperatures. On the other hand, pristine HZO capacitors with pinched polarization hysteresis (P-V) loops at room temperature and that, therefore, are expected to have very low remanent polarization at cryogenic temperatures. This suggests that modulating the phase fraction in HZO films can change the temperature dependence of polarization switching and field cycling endurance. The rate of wake-up for these samples is reduced at low temperatures.

5:00 PM EL07.03.02

\textbf{Combining Superlattices with Co-Doping -- Toward B6Ol Compatible Ferroelectric Materials with Improved Reliability at Bias and Temperature Stress}

David Lohning, Ayse Sainul, Shruthi Subramanian, Konrad Seidel and Maximilian Lederer; Fraunhofer IPMS, Germany

Interest in the concept of ferroelectric memory has been revived by the discovery of ferroelectricity in thin doped hafnium oxide films. Zirconium doped hafnium oxide (HZO) crystallizes at low temperatures (400°C and below), which makes it a compelling material for back-end of line (BeOL) implementation. Metal-ferroelectric-metal (MFM) capacitors are essential building blocks for realizing BeOL-compliant ferroelectric memory concepts. Placed in BeOL, these devices can be connected to the gate or drain contact of a standard logic device to achieve a one-transistor-one-capacitor (1T1C) ferroelectric field-effect transistor (FeFET) or a 1TC FeRAM, respectively.\textsuperscript{1}

Since the discovery ferroelectricity in hafnium oxide, scientists have been working to improve key properties of these materials, including remnant polarization, endurance, retention, imprint, and wake-up. Common methods of improvement include exploring different dopants, dopant concentrations, film thicknesses, and stacking options such as interface/electrode materials and superlattices\textsuperscript{2}.

Despite significant advancements, some reliability challenges persist, such as operation under high bias and temperature stress (BTS). Especially the automotive industry's strict demands for resilience and reliability under challenging BTS conditions exacerbate the issue. Currently, the Automotive Electronic Council's Quality requirements for Integrated Circuits (AEC-Q100) serve as the minimum standard for car manufacturers. Fulfilling the Grade 0 specifications, which demand stable performance within the temperature range of -40°C to 150°C, presents a major
challenge for ferroelectrics with a fluoride structure.

Recently, two methods have been reported that significantly improve the stability under BTS: (1) using ferroelectric [HfO2/ZrO2] superlattices with relatively thick sublayer thicknesses [3], and (2) co-doping, which introduces a small amount of an additional dopant [4].

Herein, we utilize both techniques to achieve optimal reliability properties. Analytical and electrical methods were used to characterize co-doped [HfO2/ZrO2] superlattices with various stacking options. To gain a deeper understanding of the structural properties, X-ray diffraction (XRD) and time-of-flight secondary-ion mass spectrometry (ToF-SIMS) were conducted.

Additionally, polarization versus electric field characteristics were measured to explore the electrical properties under various BTS conditions. Finally, endurance and retention characteristics under BTS conditions will be utilized to evaluate compatibility with the requirements specified by the automotive industry.


5:00 PM EL07.03.04
HoFeO3-BaTiO3 Nanofiber Heterostructure: Impressive Nanogenerator Performance Smita Chaturvedi1,2,1, Priyank Shyam3, Supriya Sahoo1, Mihir Iyer1, Shiv Shankar Jokare1, Avinash S. Kumbhar4, Boonshankarn Ramamorthy5 and Satishchandra Ogale2; 1Savitribai Phule Pune University, India; 2IISER Pune, India; 3Aarhus University, Denmark; 4IISER, India

HoFeO3-BaTiO3 (HFO-BTO) nanofiber multiferroic heterostructure showcase fascinating properties due to the coexistence of ferroelectric and ferromagnetic ordering. The nanofiber heterostructure is synthesized by combining the ferromagnetic component HoFeO3, and the ferroelectric component BaTiO3 via the electrospraying technique. The heterostructure exhibits phase fraction 3:7 of orthorhombic (Pbnm) HFO: tetragonal (P4mm) BTO. The heterostructure indicates the possibility of tunable magnetic and ferroelectric properties by tuning the phase fraction. Inclusion of HFO-BTO heterostructure into PDMS renders impressive nanogenerator performance. This trait in the heterostructure indicates that three main factors namely structure, morphology, and composition play crucial role in tuning the properties of the compound: (i) Structure: orthorhombic and tetragonal mixed phase contributes to the distortion of TiO6 octahedra in heterostructure: in-plane O–Ti–O angle sharply decreases as Ti atom shifts from inversion centre, giving rise to greater ferroelectric polarization. The increase in average Fe–O–Fe angle in heterostructure is 141° as compared to uncoupled HFO (139°), affects the Fe–O–Fe exchange coupling (ii) Morphology: the nanofiber heterostructure has (a) the interface induces strain field in heterostructure: in-plane O–Ti–O angle sharply decreases as Ti atom shifts from inversion centre, giving rise to greater ferroelectric polarization. The increase in average Fe–O–Fe angle in heterostructure is 141° as compared to uncoupled HFO (139°), affects the Fe–O–Fe exchange coupling (iii) Composition: The ferroelectric BTO and ferromagnetic HFO parent compounds are stabilised in heterostructure and exhibit enhanced magnetic and ferroelectric properties as compared to the individual parent compounds. Under the influence of electric as well as mechanical field, the response of HFO-BTO heterostructure based nanogenerator is superior in terms of polarization, output voltage, current density and power density.

5:00 PM EL07.03.05
Distortion of Inversion Symmetry in Biaxial Van der Waals Layered Oxide Leading to Negative Capacitance (NC) Effect and Intrinsic Ferroelectricity Rahul Mitra1,2,3, Unnikrishnan Manji2,3 and Yongxiang Li1; 1RMIT, Australia; 2CSIR-IMMT, India; 3AcSIR, India

Piezoelectric materials find applications in a diverse array of devices, such as sensors, resonators, motors, actuators, high-resolution ultrasound devices, and microscopic filters for cellular communications. The synthesis of single-phase α-MoO3 (MO) with a biaxial van der Waals (vdW) gap revealed orthorhombic Pmcn symmetry featuring a layered ABAB sequence with mirrored A and B layers. Applying a force magnitude of 0.5 N unveiled a force-driven dielectric constant of 12.5 in MO, showcasing distinctive dielectric saturation behavior. Ferroelectric investigations, conducted with a 10 kV/cm external electric field, demonstrated an efficiency peak of 46%, while the Berlincurve technique yielded a piezoelectric modulus (d33) of 30 pC/N. Negative capacitance (NC) effects, correlated with inductive reactance and ferroelectric-induced emf per Lenz's law, were observed. Combining these characteristics, a piezoelectric energy harvester (PEH) was engineered, achieving a peak voltage of 4 V under repeated finger tapping. When subjected to a resistive load of 100 MΩ, the PEH exhibited a power density of 7.32 x 10^1 µW/cm². These findings position a-MoO3 as an exceptional piezoelectric candidate in the realms of sensing and energy harvesting, contributing to the advancement of the Internet of Things (IoT) and Industry 4.0.

Session Chairs: Ipek Efe and Di Yi
Wednesday Morning, April 24, 2024
Room 342, Level 3, Summit

8:30 AM EL07.04.01
Sensing The Antiferromagnetic State of Multiferroics Using Spin Hall Measurements Ramamorthy Ramesh1 and Saaid Hussain2; 1 Rice University, United States; 2University of California, Berkeley, United States

Over the past decade the oxide community has been exploring the science of ferroic materials as crystals and in thin film form by creating epitaxial heterostructures and nanostructures. Among the large number of materials systems, there exists a small set of materials which exhibit multiple order parameters; these are known as multiferroics, particularly, the coexistence of ferroelectricity and some form of ordered magnetism (typically antiferromagnetism). The scientific community has been able to demonstrate electric field control of both antiferromagnetism and ferromagnetism at room temperature. There are some very intriguing new developments in SOT based manipulation of magnets. Particularly, the role of epitaxy and electronically perfect interfaces has been shown to significantly impact the spin-to-charge conversion (or vice versa). Current work is focused on ultralow energy (1 attouJoule/operation) electric field manipulation of magnetism with both voltage and current, as the backbone for the next generation of ultralow power electronics. We are exploring many pathways to get to this goal. In this talk, I will describe our progress to date on this exciting possibility.

9:00 AM EL07.04.02
Polar Magnetic Metals by Design Pu Yu; Tsinghua University, China

Polar metal with a combination of conflicting polarization and metallicity attracts great research interests recently with promising functionalities. Numerous searches have been carried out particularly in complex oxides with many exciting discoveries. Inspired by the promising magnetoelectric coupling in multiferroic systems with coupled polarity and magnetism, it is of fundamental interest to introduce magnetism (remove time-reversal symmetry) into polar metals to access exotic phases that might emerge through the coupled magnetic and polar orders. The difficulty in realizing a polar magnetic metal lies in circumventing the mutually exclusive requirements of polarity and metallicity, and at the same time incorporating suitable electron correlation effects to form magnetism. In this talk, I will present our recent effort to design and explore novel complex oxides with the breaking of both spatial-inversion and time-reversal symmetries, while maintaining magnetic ordering. We further demonstrate that the strong coupling between the polarity and magnetism of metallic system produces a collection of exotic properties, including the intrinsic magnetoelectric anisotropy with exotic magnetic field-free nonreciprocal electrical resistivity, and an emergent Hall effect. We envision that these materials and their derivatives will serve as a model family to probe the rich spectrum of emergent states in complex oxides.

9:30 AM EL07.04.03
Engineering Multiferroic Garnet-Peroxovskite and Spinel-Peroxovskite Nanocomposites Caroline A. Ross; Massachusetts Institute of Technology, United States

Nanocomposite oxide thin films consist of two phases that grow epitaxially on a substrate. Of particular interest are multiferroic nanocomposites consisting of pillars of a ferrimagnetic spinel such as CoFe2O4 (CFO) within a matrix of a ferroelectric perovskite such as BiFeO3 (BFO) grown on a perovskite substrate. CFO/BFO nanocomposites exhibit magnetoelectric coupling mediated by strain transfer at the vertical interfaces. We first discuss how patterning of substrates enables control of the locations and geometry of the self-assembled pillars. In particular, we describe the fabrication, microstructure and ferroic properties of ‘sideways multilayers’ consisting of parallel fins of CFO and BFO grown on (111) and (110)-oriented substrates patterned using a focused ion beam process, including the magnetic and ferroelectric domain structure. We then demonstrate nanocomposites made from perovskites and garnets. Iron garnets (IGs) are ferrimagnetic insulators of composition R3Fe5O12, where R is Y, Bi or a rare earth. They exhibit a range of useful magnetic properties including spin orbit torque switching, relativistic domain.
Multiferroics with coupled magnetic and electric orders, although rare, hold potential for low-energy-consumption materials for logic and memory capable of electric-field control of magnetism. Barium hexaferrite (BaFe$_{12}$O$_{19}$), the most common refrigerator magnet, is predicted to gain electric polarization order at room temperature in addition to its robust magnetism under in-plane, biaxial, compressive strain [1]. The recent realization of single-crystal substrates of Sr$_{1.03}$Ga$_{10.81}$Mg$_{0.58}$Zr$_{0.58}$O$_{19}$ (SGMZ) [2], an insulator that is isostructural to BaFe$_{12}$O$_{19}$, enables strain BaFe$_{12}$O$_{19}$ as SGMZ has a ~1.1% smaller in-plane lattice constant. In addition to strain, to induce the ferroelectric state, an epitaxial bottom electrode is needed to control the electric state for this hexaferrite multiferroic candidate. SrCo$_2$Ru$_{0.11}$ is a metallic ferromagnetic oxide [3], belongs to the same hexaferrite family as BaFe$_{12}$O$_{19}$, and has small (~0.3%) in-plane lattice mismatch to the SGMZ substrate. Consequently, a coherent SrCo$_2$Ru$_{0.11}$ epitaxial thin film on the SGMZ substrate would be ideal for straining BaFe$_{12}$O$_{19}$ and serving as the bottom electrode of a metal-insulator-metal structure to test for ferroelectricity in this predicted strain-induced multiferroic.

Here we show that a 1.1% in-plane biaxial compressive strain from SGMZ substrates can be imposed on up to 27.5 nm thick BaFe$_{12}$O$_{19}$ films. The full width at half maximum (FWHM) of the X-ray diffraction rocking curve of the 0020 peak in w ranges from 0.006° to 0.009°, the smallest ever reported. Scanning transmission electron microscopy (STEM) multislice ptychography results on a commensurately strain filed clearly show local electric polarization arising from the off-center displacement of Fe$^{3+}$ ions in the trigonal bipyramid sites, locally breaking the mirror-plane symmetry perpendicular to the c-axis of BaFe$_{12}$O$_{19}$. Second harmonic generation (SHG) proves the symmetry breaking on a larger scale from 6/mm (bulk paraelectric BaFe$_{12}$O$_{19}$) to 4mm (fully strained BaFe$_{12}$O$_{19}$). Commensurately strained BaFe$_{12}$O$_{19}$ containing 95% enriched Fe$^{57}$ has been synthesized. Mössbauer measurement will be made on this sample to quantify the splitting between the two sites of the iron cations in the trigonal bipyramidal sites.

Films of SrCo$_2$Ru$_{0.11}$ were grown by MBE on (0001) SGMZ substrates in an adsorption-controlled regime. With matching substrates and adsorption-controlled growth, we have grown epitaxial, fully strained SrCo$_2$Ru$_{0.11}$ thin films with even lower resistivity than SrCo$_2$Ru$_{0.11}$ single crystals [3]. Our next step is to grow a commensurately strained metal-insulator-metal BaFe$_{12}$O$_{19}$/SrCo$_2$Ru$_{0.11}$/SGMZ stack to test for ferroelectricity.


10:45 AM EL07.04.05
Manipulation of Isolated Spins in Ferroelectric Oxides from First Principles
Elizabeth Nowadnick1, Bradford Barker1, Nabaraj Pokhrel1, Md Kamal Hossain1, Katherine Inzan2,3 and Sinead M. Griffin1; 1University of California, Merced, United States; 2The University of Nottingham, United Kingdom; 3Lawrence Berkeley National Laboratory, United States

Electric field control of single spins can probe the fundamental atomic-scale limits of multiferroic behavior. One possible platform to explore this scenario is to form isolated spin centers in ferroelectric materials via inclusion of dilute concentrations of magnetic dopants. The preferred orientation of a spin is connected to its local crystallographic environment via the spin-orbit interaction, and is described by the magnetostrictive ansatzelectricity and anisotropy (MCAE). In a ferroelectric material, the local crystallographic environment can be modified by structural changes that occur during polarization switching under applied electric fields, which provides a path towards electric field control of the MCAE and a magnetic dopant’s spin directionality. Although the diverse properties and functionalities of ferroelectric complex oxides have been the subject of extensive research over the past decades, there is so far received limited attention as potential platforms for electric field-based single spin processing, which is of central interest to several modern technological applications. In this work, we combine group theoretical analysis with density functional theory calculations to explore two examples of tuning the spin orientation of isolated magnetic dopant atoms in ferroelectric oxide hosts. We first consider an isolated Fe$^{3+}$ dopant in the tetragonal, orthorhombic, and rhombohedral phases of the prototypical ferroelectric oxide BaTiO$_3$. We investigate how the MCAE and preferred Fe$^{3+}$ spin orientation evolves as the material traverses these structural phases of different crystalline symmetries. The different transformations that occur in different ferroelectric oxides offers a way of tuning those changes in orientation in the electronic structure. Second, we explore an isolated Fe$^{3+}$ dopant in the low-dimensional Aurivillius ferroelectric Bi$_2$WO$_6$, tracking how the MCAE and the preferred spin orientation evolve throughout ferroelectric switching. We find that the Fe$^{3+}$ spin aligns along a spin-easy axis in Bi$_2$WO$_6$ and that a 90° switch of the polarization direction leads to a 112° reorientation of this spin-easy axis. This work advances our understanding of electric field control of single spins, which has potential implications in the fields of spintronics and quantum computing.

11:00 AM EL07.04.07
Designed Magnetic Texture for Spin Transport in a Multiferroic Oxide
Peter Meisenheimer1, Maya Ramesh2, Sajid Husain3,1, Isaac Harris1,3, Shiyu Zhou4, Lucas M. Caretta4, David R. Schlom2, Paul Stevenson5, Zhi Yao3 and Ramamoorthy Ramesh6; 1University of California, Berkeley, United States; 2Cornell University, United States; 3Lawrence Berkeley National Laboratory, United States; 4Brown University, United States; 5Northeastern University, United States; 6Rice University, United States

Antiferromagnet-based spintronics are growing in popularity for potential applications in next-generation computational technologies due to their speeds and robustness to external fields. A key challenge in this area, however, is the control of antiferromagnetic order on the nanometer scales applicable to solid-state technologies. Bismuth ferrite (BiFeO$_3$) is a multiferroic material that exhibits both ferroelectric and antiferromagnetic properties at room temperature, making it a unique candidate in the development of electrically controllable magnetic devices. In BiFeO$_3$, the magnetic moments are arranged into a long-range spin cycloid, resulting in a unique set of magnetic properties that are intimately tied to the ferroelectric order. To date, however, understanding of this coupling between magnetism and ferroelectricity has generally relied on either average, mesoscale measurements to infer the magnetic structure and behavior.

Using high-resolution nitrogen vacancy (NV) diamond-based scanning probe microscopy, we show that this spin cycloid can be deterministically controlled with an electric field. The underlying energy landscape of the spin texture is shaped by both the ferroelectric degree of freedom and strain-induced anisotropy, where electric fields drive magnetoelectric switching in predictable ways that can be engineered. Through precise control of the crystal structure using thin film techniques, the magnetic structure of BiFeO$_3$ can be tuned to control magnon transport in the material, opening the door for efficient, electrically controllable magnetic devices.

11:30 AM EL07.04.08
From MagnetostRICTive Composites to Precise Magnetoelectric Field Sensing
Lukas Zimoch1, Stefan Schroeder, Eric Elzenheimer, Soeren Kaps, Thomas Strunskus, Franz Faupel, Michael Hoeft, Gerhard Schmidt and Rainer Adelung; University of Kiel, Germany

The demand for magnetic field sensors is rapidly increasing due to various factors, including the requirements for navigation, orientation, and motion tracking systems, as well as their growing utilization in the automotive sector and notably in biomedical applications. There are two magnetoelectric (ME) sensors discussed in this context. The first employs a magnetostrictive polymer composite (MPC) as its magnetosensitive material, which consists of ferromagnetic particles embedded within a soft polymer matrix. This capacitive sensor, featuring an electret [1], is specifically well suited for biomedical applications due to its low resonance frequency, typically around 100 Hz. To evaluate the sensor's performance, three measurements were conducted. Subsequently, a DC magnetic bias field measurement was carried out to identify the optimal operating point. In the final measurement, the sensor operated at its resonance frequency with the
optimal bias field. In each measurement, the amplitude of the resonance frequency was systematically reduced to determine the minimum field the sensor can reliably detect. The resonance frequency is in the range of 50-150 Hz, largely influenced by the MFC's geometry. The sensor requires a bias field of several mT. Furthermore, these measurements confirmed that no remagnetization occurs within the sensor during the bias sweep. Even without optimization, the sensor displayed linear behavior across four orders of magnitude. The magnetic characterization of the sensor revealed that it fundamentally operates as intended, with its magnetic properties remaining stable when exposed to magnetic fields. The sensor could provide valuable insights into the common challenge faced by all magnetic field sensors, which is noise. The mechanical characteristics of the sensor are derived from the polymer matrix, while the magnetic properties are predominantly determined by the components. Both parts can independently be adjusted or altered, allowing an investigation of the individual noise components. To understand all the mechanics of the sensor a second simplified approach was adopted.

The second sensor is the most elementary version of the first sensor, where only two macroscopic ferromagnets are used emulating two particles in the composite, to understand the underlying mechanisms of the MPC. One of these magnets is mounted to a silicon cantilever, while the other remains fixed beneath it. The magnets oppose each other. When an external magnetic field is applied, superposition takes place, and the cantilever starts to oscillate. On the top part of the cantilever a piezoelectric AlN thinfilm is placed between two electrode layers. The mechanical stress of the oscillation is transduced into an electrical voltage and generates a signal proportional to the applied magnetic field. In this composition magnetic noise amplitude densities as low as 47 pT/Hz have been measured \[2\]. It is possible to measure within the earth’s magnetic field without sacrificing any performance. The sensor shows a sensitivity of $2170 \text{ V/T}$ and doubles as an energy harvester. Without any optimization it was possible to generate 1.31 $\mu\text{W/cm}^2\text{Oe}$ with a magnetic AC field of 20 $\mu\text{T}$ in resonance.


The authors acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 286471992 – SFB 1261

11:45 AM Session EL07.04.09

Impressive Nanogenerator Application Using Nanoscale LuFeO$_3$: Role of Structure and Morphology

Smita Chaturvedi, Priyank Shyam, Sachin Kumar Singh, Avinash S. Kambar, Gopal Srinivasan, and Satishchandra Ogale

In the domain of multiferroicity, Lutetium orthoferrite (LuFeO$_3$) represents a potentially interesting material owing to the fact that it exhibits orthorhombic (o) and hexagonal (h) structures, which significantly differ in terms of lattice symmetry and the surroundings of the individual cations. This difference in structural symmetry contributes to unusual changes in physical properties. In o-LFO canting of Fe moments towards c direction gives rise to weak ferromagnetism below Neel Temperature (620 K), while, ferroelectricity is unexpected due to symmetry of lattice. On the other hand, weak ferromagnetism is not allowed in h-LFO unless the moments are along the 'a' axis. Present work is intended to realize the co-existence of o-LFO and h-LFO to achieve ferroelectricity and ferromagnetism simultaneously in a single nanostructure of two different morphologies i.e. nanoparticles and nanofibers. In multiferroic LuFeO$_3$ the hexagonal (h) phase is an intermediate metastable phase encountered during the amorphous to orthorhombic (o) transformation and is ferroelectric in nature. So far h-phase has only been stabilized in a substrate-supported layered ultrathin film form. Herein we show that the surface-induced strain field intrinsically present in nano-systems can self-stabilize this phase and the hexagonal to orthorhombic phase transition ratio depends on the shape of the nanomaterial. Thus, nanofibers (nanoparticles) strain-stabilize the o : h ratio of about 23 : 77 (75 : 25). The inclusion of nano-LuFeO$_3$ into PDMS renders impressive nanogenerator performance, consistent with the ferroelectric phase content. This trait in the biphase LuFeO$_3$, is attributed to: (i) Structure: Orthorhombic and hexagonal mixed phase: wherein the lattice dynamics change with temperature (both in case of nanoparticles and nanofibers), (ii) Morphology: (nanoparticles and nanofibers): wherein the dynamics of interparticle interactions would differ for nanoparticles and nanofibers.

| 1:30 PM | *EL07.05.01* | Strain Manipulation of Ferroelectricity and Flexoelectricity in Freestanding Membranes

Harold Y. Hwang, 1,2, Stanford University, United States; 2SLAC National Accelerator Laboratory, United States |

The ability to create and manipulate materials in two-dimensional (2D) form has repeatedly had transformative impact on science and technology. We have developed a general method to create freestanding complex oxide membranes and heterostructures using epitaxial water-soluble buffer layers, with millimeter-scale lateral dimensions and nanometer-scale thickness. This facilitates many new opportunities; here we will focus on the use of membrane dimensions, tensile strain, and strain gradients to control the ferroelectric and flexoelectric response of oxide membranes.

| 2:00 PM | *EL07.05.02* | Synthesis and Properties of Single Domain BiFeO$_3$ Thin Films and Free-Standing Membranes

Chang-Beom Eom and Pratap Pal, University of Wisconsin–Madison, United States |

BiFeO$_3$ (BFO) is positioned for success as a magnetoelectric material system, but its optimum usage in faster and more energy-efficient magneto-logic devices require advances. Most importantly, a ferroelastic and antiferromagnetic monodomain state with single-step deterministic switching is desirable for reliable low-power magnetoelectric devices with reproducibility and scaling using BiFeO$_3$. This would allow deterministic and robust control of both the internal magnetoelectric coupling in BiFeO$_3$ and the exchange coupling of its antiferromagnetic order to a ferromagnetic overlay.

We have fabricated epitaxial (001) and (111) BFO thin films with both ferroelectric and antiferromagnetic monodomain states. Additionally, we have fabricated freestanding membranes of ferroelastic and ferroelectric monodomain BiFeO$_3$ using an Sr$_2$CaAl$_2$O$_6$ (SCAO) sacrificial layer. The membranes exhibit deterministic switching over a hundred thousand electric field cycles with lower voltage and faster switching dynamics than their thin-film counterpart. This progress is promising toward energy-efficient magnetoelectric memory devices. We will discuss additional multifunctional applications of these BFO membranes.

This work has been done in collaboration with J. L. Schad, K. J. Lee, Y. Yao, A. M. Vihakar, R. D. Johnson, P. G. Radaelli M.S. Rzchowski and C.B. Eom.

CBE acknowledges support for this research through the Gordon and Betty Moore Foundation’s EPiQS Initiative, Grant GBMF0965 and a Vannevar Bush Faculty Fellowship (ONR N00014-20-1-2844). Magnetic and transport measurement at the University of Wisconsin–Madison was supported by the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), under award number DE-FG02-06ER46327.

2:30 PM BREAK
Anomalous Hall Effect and Topological Hall Effect in NiCo$_2$O$_4$ Thin Films and Free-Standing Manters Xia Hong: University of Nebraska-Lincoln, United States

The inverse spinel ferrimagnetic NiCo$_2$O$_4$ possesses high Curie temperature and high spin polarization, making it a promising material candidate for spintronic applications. The magnetic state of NiCo$_2$O$_4$ films depends sensitively on the strain and disorder effects, which can lead to unconventional spin transport. In this talk, I will discuss our recent studies of the magnetotransport anomalies in epitaxial NiCo$_2$O$_4$ thin films and free-standing NiCo$_2$O$_4$ membranes, including linear magnetoresistance, anomalous Hall effect (AHE), and topological Hall effect (THE). NiCo$_2$O$_4$ films deposited on (001) MgAl$_2$O$_4$ substrates exhibit strong perpendicular magnetic anisotropy down to 1.2 nm (1.5 unit cell) thickness, while the (110) films possess in-plane magnetic anisotropy. Films with high crystallinity show quasi-linear magnetoresistance in magnetic fields up to 17 T with weak temperature dependence. The AHE exhibits a nonmonotonic temperature dependence and sign reversal driven by both temperature and film thickness, revealing the intricate interplay between the impurity spin scattering, band intrinsic Berry curvature, and correlation effect. THE has been observed in (110) NiCo$_2$O$_4$ films and (001) NiCo$_2$O$_4$ membranes at low temperatures. The former has been correlated with magnetic bubble domain formation, as revealed via magnetic force microscopy, suggesting the emergence of bimeron spin textures. The latter can be sensitively tuned by magnetic field cooling. Our study provides effective material strategies for designing spin transport in NiCo$_2$O$_4$ via strain and disorder, paving the path for its technological implementation. This work was primarily supported by NSF through Grant No. DMR-1710461 and EPSCoR EQUATE Award No. OIA-2044049.

Atomic Scale imaging of Topotactic Phase Transitions in Free-standing Strontium Cobaltite Membranes Seung Sae Hong\textsuperscript{1}, Hudson Shih\textsuperscript{1}, Rohan Dhall\textsuperscript{2} and Yayoi Takamura\textsuperscript{1};\textsuperscript{1}\textsuperscript{1}University of California, Davis, United States; \textsuperscript{2}Lawrence Berkeley National Laboratory, United States

Topotactic phase transitions (TPTs) are structural phase changes that involve the significant loss or gain of oxygen atoms while preserving the crystalline framework of the lattice. In perovskite oxides, TPTs have recently emerged as innovative pathways for designing complex oxide materials. These transitions induce dramatic alterations in metal oxidation states and atomic coordination, enabling a wide range of electronic and magnetic states, from magnetic ordering to unconventional superconductivity. Moreover, the reversible nature of TPTs holds promising implications for practical applications such as neuromorphic computing devices, garnering significant attention in both fundamental physics and device applications.

Despite the growing research interest in TPTs in recent years, the microscopic details of these transitions, encompassing both structural changes and ionic transport, remain largely unexplored. This is partly due to the constraints imposed by the thin film heterostructure geometry, which limits our ability to directly visualize the transition through conventional means. In this report, we present recent advancements in free-standing oxide membranes that enable the local nature of TPTs to be visualized using electron microscopy. As a model system to comprehend the local structure of TPTs, we examined strontium cobaltite (SrCoO$_3$-δ), which can transition between a ferromagnetic metal (perovskite) and an antiferromagnetic insulator (brownmillerite). Transmission electron microscopy studies of SrCoO$_3$-δ membranes unveiled the formation of anisotropic domains in the midst of the transition. Furthermore, atomic-scale images revealed the intricate nature of strains and crystallographic symmetries that dictate the domain patterns. Free-standing oxide membranes offer an ideal platform for in-situ and in-operando studies of TPTs, providing insights into the predictable design of switching phenomena in oxide materials.

Intrinsic Properties of Ferroic Materials Independent of Substrate Effects Varun Harbola, Yu-Jung Wu, Felix Hensling, Hongguang Wang, Peter A. van Aken and Jochen Mannhart; Max Planck Institute for Solid State Research, Germany

Substrates are essential in thin-film deposition, yet they do not always meet the specific requirements of a given experiment or application and, in some cases, may even hinder in intrinsic measurements of epitaxial thin films. For example, SrTiO$_3$, one of the most widely used substrates, goes through an antiferrodistortive transition at 105 K which can lead to substrate artefacts extrinsic to the thin film properties grown atop the substrate. However, the bulk of the substrate in its single crystal form is not required to support epitaxy, as only the top few unit cells near the surface define the epitaxial template for thin film growth. We introduce the novel concept of "vector substrates" where the template layer for epitaxy can be chosen independently of the bulk of the substrate. Thus, by choosing the right composition of a bulk carrier substrate and the template layer, we can reduce, if not eliminate artefacts resulting from the behaviour of the bulk substrate. The fabrication of vector substrates leverages thin-film membrane technology by growing a template layer on a parent substrate and then transferring it onto a carrier substrate, thereby generating the vector substrate. By comparing the magnetisation of La$_{0.67}$Sr$_{0.33}$MnO$_3$ grown on a conventional SrTiO$_3$ substrate and a SrTiO$_3$ on-sapphire vector substrate, we show that we can indeed eliminate the extrinsic antiferrodistortive artefact on a vector substrate. Therefore, the concept of vector substrates can provide a platform to measure ferroic thin films and the characteristics independent of substrate effects.

References:

Fabrication of Hybrid Particles with Dual-Functionality for EMI Shielding and Heat Dissipation Yeonju Park, HyeRyeong Oh, Hyeongkeun Kim and MyongJae Yoo; Korea Electronics Technology Institute, Korea (the Republic of)

Semiconductor packaging technology and industry are developing toward higher performance, higher integration, thinner thickness, and miniaturization. Consequently, there is a problem in that the amount of heat generated from the device increases and electromagnetic interference (EMI) occurs inside the PIM semiconductor. Therefore, packaging requires both high heat dissipation and EMI shielding performance.

In this study, an insulating and heat dissipating thin film was deposited on the surface of the magnetic particles. The deposited thin film composition was analyzed through elemental analysis. The insulating properties of the fabricated particle were measured and it was confirmed that the resistance increased. Heat dissipation properties and EMI shielding properties of the fabricated particles were measured by manufacturing composite film. Our results achieved 13% increased thermal conductivity properties compared to films manufactured using pristine particles. EMI shielding characteristics were measured in the Ka band (26.5-30 GHz), and reflection and absorption performance were calculated and analyzed.

Magnetic Entropy Changes in Rare-Earth Tetraborides (RB$_4$, R = Dy, Ho, and Tm) Beomki Cho\textsuperscript{1} and Songhee Han\textsuperscript{2};\textsuperscript{1}IST, Korea (the Republic of); \textsuperscript{2}Mokpo National Maritime University, Korea (the Republic of)

The RB$_4$ (R = Gd, Tb, Dy, Ho, and Tm) compound presents an intriguing system with simultaneous magnetic ordering and geometrical frustration, leading to a strong interaction within the material. The interaction manifests in consecutive magnetic transitions at temperatures $T \approx T_{N1}$ and $T_{N2}$ (where $T_{N1} > T_{N2}$) and results in a highly anisotropic magnetic configuration when in an ordered state. In this study, we systematically investigate the anisotropic entropy change ($\Delta S_{AN}$) of single crystals of RB$_4$ (R = Dy, Ho, and Tm). Our findings reveal distinct behavior: the negative entropy change above $T_{N1}$ follows conventional field-dependence, while a positive entropy change below $T_{N2}$ follows anomalous field-dependence. Notably, ErB$_4$ ($T_{N1} = 15.5$ K) and TbB$_4$ ($T_{N1} = 11.7$ K) demonstrate $\Delta S_{AN}$ values of $11.6$ J/(K kg) and $10.2$ J/(K kg), respectively, at $T > T_{N2}$ and for $H = 50$ kOe, accompanied by relative cooling power (RCP) values of $237.1$ K/J/kg and $225.9$ K/J/kg. Interestingly, DyB$_4$ ($T_{N1} = 20.5$ K) exhibits a significant $\Delta S_{AN}$ value of $18.8$ J/(K kg) near $T = T_{N2} = 13.0$ K and an RCP value of $208.39$ J/kg for $H = 50$ kOe. These $\Delta S_{AN}$ and RCP values demonstrate the potential of these compounds for applications in refrigeration using rotational magnetocaloric effect (RMCE). Additionally, HoB$_4$, ErB$_4$ and TbB$_4$ exhibit also promising behavior for RMCE even at temperatures of $T < T_{N1}$, particularly during low-field cooling ($H < 50$ kOe). This work highlights the suitability of RB$_4$ compounds as effective materials for RMCE cooling, covering a broad temperature range above and below the antiferromagnetic Néel temperature. Specifically, the anisotropic entropy change...
observed in DyB near T\textsubscript{c} = T\textsubscript{N2} holds considerable potential for RMCE applications, such as hydrogen liquefaction due to its occurrence which a limited temperature range, accompanied by large ΔS\textsubscript{AS} and RCP values.

### 5:00 PM EL07.06.03

**Tuning of Orientation and Magnetic Properties of Ferromagnetic Aerogels produced through a Magnetic-Field Assisted Synthesis**

*Rosemary L. Calabro\textsuperscript{1,2}, Alexander D. Ciampa\textsuperscript{1}, Edward Tang\textsuperscript{1}, Kennedy V. Munz\textsuperscript{2}, Olivia S. Raykhman\textsuperscript{1}, Malina O. Hatton\textsuperscript{1}, Zachary T. Bone\textsuperscript{1}, Felita W. Zhang\textsuperscript{1}, Kelsey M. Healy\textsuperscript{1}, Peter H. Chapman\textsuperscript{1}, Stephen F. Bartolucci\textsuperscript{2}, Joshua A. Maurer\textsuperscript{2} and John Burpo\textsuperscript{1}, United States Military Academy, United States; \textsuperscript{2}U.S. Army DEVCOM Armaments Center, United States*

Ferromagnetic aerogels possess many desirable properties such as low densities, high porosities and surface areas, and interesting magnetic properties which allow opportunities in a wide range of applications including sensing, energy storage, switches, thermostats, catalysis, and many others. In a majority of these applications, the aerogels consist of some type of host material such as silica or a polymer that is doped with a ferromagnetic nanomaterial. However, ferromagnetic aerogels that consist only of the magnetic material without a host are highly desirable because they allow higher magnetizations per unit mass, better exposed surfaces, and simpler structures. We have prepared magnetic nanowire aerogels using a magnetic-field assisted synthesis which allows formation of magnetic nanowire aerogels in a fast, simple, and scalable manner. In a typical synthesis, a metal salt such as iron or cobalt chloride was placed inside a magnetic field, and sodium borohydride was added to the gel that could then be slowly dried into aerogels or conform into thin films, depending on the desired application. The applied magnetic field strength was varied from 0 mT to 150 mT and had impact on the nanowire aspect ratios and orientation, the magnetization and coercivities of the aerogels, the mechanical properties, and the observed surface areas and porosities. Typically, low applied field strengths showed low ordering and small aspect ratios while higher applied fields increased the orientation and aspect ratios of the nanowires. Bimetallic iron-nickel aerogels were also prepared and the influence of the metal counterion was studied. The counterion not only impacted the rate of the reaction, but also the shape of the nanostructures within the formed aerogels. The iron-to-nickel ratio also influenced the nanowire length and magnetic properties. The magnetic field assisted synthesis strategy allowed rapid formation of template free ferromagnetic aerogels and can be expanded to achieve a wide range of bimetallic materials.

### 5:00 PM EL07.06.04

**Engineering Reliability and Crystallization Orientation by Al Doping of Ferroelectric Hafnium-Zirconium Oxide**

*Ayse Sünbül\textsuperscript{1}, David Lehniger\textsuperscript{1}, Konrad Seidel\textsuperscript{1}, Lukas Eng\textsuperscript{2} and Maximilian Lederer\textsuperscript{1}, Fraunhofer IPMS, Germany; \textsuperscript{2}Institute of Applied Physics, Technical University Dresden, Germany*

Due to its scalability and CMOS compatibility, ferroelectric hafnium oxide (HfO\textsubscript{2}) has attracted attention since its discovery in 2011 [1, 2]. Many elements can be used as dopant [3, 4] to stabilize the ferroelectric (FE) orthorhombic phase of HfO\textsubscript{2}. Especially Zr doping of HfO\textsubscript{2} (HZO) has some advantages for back-end-of-line (BEoL) integration, due to its low crystallization temperature [5].

FE materials can be used in memories as ferroelectric field-effect transistors (FeFETs) that are non-volatile and applicable in low-power systems. Good endurance and retention, high remanent polarization, and high-temperature resilience are required for embedded FE memories and the automotive industry requires high-temperature operation (up to 150 °C specifications given by the Automotive Electronics Council) which is not fulfilled by current HZO devices. Al can be co-doped into HZO (HZAO) to overcome the reliability challenges of HZO such as high-temperature, high-bias operation, endurance, and imprint limitations [6]. In this study, different Al concentrations (up to 3 at. % Al) were doped into HZO and various crystallization annealing conditions (400 °C, 650 °C, and 800 °C) were investigated. Increasing Al concentration and increasing annealing temperature in HZO resulted in more antiferroelectric-like behavior. Additionally, endurance at high temperatures (up to 150 °C) and high-bias conditions (up to 5 MV/cm applied electric fields) were drastically improved in HZAO compared to HZO. A correlation between crystallographic phases and electrical results (coercive field E\textsubscript{C} and remanent polarization P\textsubscript{r}) was made. The ratio of (111)/(002) diffraction peak intensities increases with lower Al concentrations. Increase in P\textsubscript{r} and E\textsubscript{C} is observed with increasing ratio of (111)/(002) diffraction peak intensities. Consequently, this work will discuss the tuning of electrical properties (such as P\textsubscript{r}, E\textsubscript{C}, and endurance) depending on application requirements by controlling annealing conditions and Al doping concentration. It will investigate the impacts of Al concentration and anneal conditions on reliability aspects such as enhanced endurance, reduced leakage and high temperature resilience.


### 5:00 PM EL07.06.05

**Deep UV Photo Electron Microscopy to Spatially Probe Work Function in Oxygen Vacancy Reduced Hf\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2}**

*Fernando J. Vega Avamá1, Alex M. Boehm2, Andrew R. Kim2, Samantha Jaszezowski1, Jon F. Ihlefeld1, Taisuke Ohita1 and Thomas Beechem1, Purdue University, United States; 2Sandia National Laboratories, United States; 3University of Virginia, United States*

Oxygen vacancies are known to both stabilize the ferroelectric orthorhombic phase of Hf\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} (HZO) and promote leakage pathways limiting endurance of devices based on this material. For this reason, the energy states of oxygen vacancies were investigated using photoelectron emission microscopy (PEEM) as their concentration was varied via laser exposure. Following a controlled oxygen vacancy (V\textsubscript{O}) reduction via incremental and areal laser dosing on HZO, 213nm deep-ultraviolet (DUV) photoelectron emission microscopy (PEEM) was used to spatially probe the resulting modification in work function. Monotonically increased with laser-induced reduction in oxygen vacancy concentration culminating in a total increase near 70 meV. The change implies a Fermi-level shift toward the valence band as the total available charge states are reduced as oxygen vacancies are removed. A reduction in charge states is also supported by the observed reduction in photo emission yield after laser dosing. Beyond the quantitative change, the smooth monotonic change in work-function and photoemission yield suggest the presence of a “defect band” that forms in HZO due to the presence of vacancies rather than a single discrete state.

### 5:00 PM EL07.06.06

**La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} Perovskite: PVDF Based PENG with Enhanced β-phase Through Self-induced Polling for Green Energy Harvesting**

*S M Ayvert Allah Shohag, Luke Franco, Adhira Tippar, Ahmed Touhami, Swati Mohan and Jasim Uddin, The University of Texas Rio Grande Valley, United States*

Global demand of sustainable and efficient energy sources continues to rise of novel materials and their application in energy harvesting. Sr\textsuperscript{2+} doped Lanthanum Cobaltite (La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3}) perovskite stands out as a promising candidate due to its unique properties and versatility as piezoelectric material as well as in antimicrobial properties. Piezoelectric Nanogenerators (PENGs), which can produce electrical power from mechanical energy via ferroelectric effect, are one of the ambient sources of green energy. PENGs have gathered a huge attention due to cost-effectiveness, mechanical stability, and easy installation process. In this work, Lanthanum Cobaltite (La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3}) perovskite, a ferroelectric material, was synthesized by sol-gel- molten-salt process and then characterized by X-ray diffraction, and scanning electron microscopy ensures the uniform morphology of nanoparticles. Further poly (vinylidene difluoride) (PVDF), N,N-dimethylformamide and acetone solution were used to make a flexible composite film using La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} nanoparticles by spin coating, self-induced polling process and curing. Fourier transform infrared spectroscopy (FTIR) investigation ensures that self-induced polling process was effective to identify the structural β phase. PVDF/La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} composite film is then placed in between two copper sheets to fabricate the piezoelectric nanogenerator. The 7.5\% PENG demonstrates the open-circuit voltage of 2.5V. The peak-to-peak voltage and peak to peak current values were also reported for all different weights, frequencies, and doping range. Finally, the PENG was used as a smart weight sensor and motion sensor to operate low-power electronic devices. Beside this we also observed antimicrobial properties of La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} nanoparticles by the Kirby Bauer testing method, our synthesized La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} nanoparticles showed much better activity against *Escherichia coli* and two other Bacillus species as well. This work explores La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} nanoparticles potential as antimicrobial properties and piezoelectric nanogenerator for green energy harvesting, contributing to greener and more sustainable energy solutions.

SESSION EL07.07: Emerging Ferroics I
Ferroelectric random access memories, ferroelectric tunnel junctions, and ferroelectric diodes. It has been found that Al$_{0.93}$B$_{0.07}$N and Zn$_{1-x}$Mg$_x$O thin films often undergo a wake-up process where the margin still exceeded 200 μC/cm$^2$ in Al$_{0.93}$B$_{0.07}$N. The predicted OS retention is 82% after 10 years baking at 200°C. Zn$_{1-x}$Mg$_x$O is even more robust in opposite state retention. A key challenge is to increase the cycle lifetime by prevention of premature dielectric breakdown events.

8:45 AM EL07.07.01
Multilayered Thin Film Ferroelectric Wurtzites Robert J. Spurling$^1$, Chloe Skidmore$^1$, John Hayden$^1$, Josh Nordlander$^1$, Joseph Casamento$^{1,2}$, Kyle Kelley$^3$ and Jon-Paul Maria$^1$; $^1$The Pennsylvania State University, United States; $^2$Massachusetts Institute of Technology, United States; $^3$Oak Ridge National Laboratory, United States

We report on observations of ferroelectric switching in multilayered sputtered thin films based on wurtzite Al$_{1-x}$B$_x$N. Ferroelectric switching is achieved in thin film stacks containing ferroelectric and polar non-ferroelectric layers. Total polarizations indicate switching is achieved across the entire film stacks, suggesting propagation of ferroelectric domains across interfaces between layers. We investigate switching pathways and wake-up behavior in these films as characterized through an array of structural and property measurement techniques. We also discuss synthesis controls in Zn$_{1-x}$Mg$_x$O sputtered thin films, with an emphasis on connections between structure and electrical properties. We focus on the effect of oxygen chemical potential and temperature on film microstructure and resistivity.

9:00 AM EL07.07.03
Developing Phase Field Models for The Physical Vapor Deposition of Ferroelectric Doped AlN John Wellington-Johnson$^1$, Roxanne Ware$^1$, Remi Dingreville$^2$ and Lauren M. Gartel$^1$; $^1$Georgia Institute of Technology, United States; $^2$Center for Integrated Nanotechnologies, United States

While unique functionalities, such as ferroelectricity and ferromagnetism, have been observed in transition metal doped AlN thin films, the addition of these dopants can negatively impact the films crystalline quality. Avoiding phase segregation, surface faceting, or crystallite misorientation is critical to ensure that the full ferroelectric potential of these materials can be reached. Further insight into the microstructural evolution of AlN in the presence of transition metal dopants is necessary to understand the impact of these dopants on film growth and ferroelectricity. In this work, phase field models are developed for physical vapor deposition, microstructural development, and ferroelectric response of transition metal doped AlN thin films. These models are then compared to doped AlN thin films grown by pulsed laser deposition (PLD) and sputtering. Doped AlN thin films were deposited onto platinumized silicon substrates via ultra-high-vacuum PLD, RF or DC sputtering. The substrate growth temperatures ranged from 200 °C to 800 °C with an incident laser energy from 100 to 300 mJ and a laser repetition rate of 10 Hz for PLD growth. Increasing the growth temperature decreases the full width, half maximum of the predominant (002) X-ray diffraction peaks, indicating an increase in orientation which is corroborated by the model. Atomic force microscopy and scanning electron microscopy show the evolution of the surface morphology and microstructure with changing processing conditions. Increased surface faceting is observed with increased dopant concentration and segregation as determined by X-ray photoelectron spectroscopy (XPS). There is also a clear correlation between the deposition conditions and the ferroelectric response, with increased electrical breakdown for DC sputtered films compared to RF sputtering and pulsed laser deposition. Overall, these results illustrate that the ferroelectric properties highly sensitive to the growth conditions and resulting microstructure.

9:15 AM EL07.07.04
Impact of Electrodes and Interfaces in Ferroelectric Switching of Sub-100nm Al$_{1-x}$Sc$_x$N Vamshi Kiran Gogi$^1$, Christopher Chae$^2$, Jinwoo Hwang$^2$ and Rashmi Jha$^2$; $^1$University of Cincinnati, United States; $^2$The Ohio State University, United States

Ferroelectric materials have garnered huge research interest in the last 50+ years as these materials possess a variety of interactions between electrical, mechanical, and thermal properties that can enable multiple functionalities. The reports of ferroelectric behavior in Aluminum Scandium Nitride (Al$_{1-x}$Sc$_x$N) has widened the potential use of ferroelectric functionality in microelectronics beyond SiO$_2$ based ferroelectrics. Particularly, Ferroelectric Field Effect Transistor (FeFET) is a compelling application of these materials that can enable novel logic and memory devices. However, most studies have reported Ferroelectricity in thick AlScN films and more work is needed to understand their behaviour in sub-100 nanometer thickness regime. Additionally, role of electrodes and interfacial layers when AlScN is integrated in FeFETs is not well-known. This work reports the role of electrodes in Ferroelectric Switching of sub-100 nm Al$_{1-x}$Sc$_x$N (x≈22%) films. Sub-100nm Al$_{0.78}$Sc$_{0.22}$N has been deposited via reactive co-sputtering and impact of electrodes such as W, Ti/Ru and Sc has been studied in metal-insulator-metal and metal-insulator-si-on-p configurations. We demonstrate the effects of rapid thermal annealing and its impact on polarization in these thin films. Notably, RTA can alter the film properties and modifies the interface. On Silicon substrate, we also report the influence of oxygen mediated defect structures in ferroelectric switching of these III-V nitrides. True Ferroelectric switching has also been investigated through PUND (Positive Up and Negative Down) analysis accounting for leakage current induced effects on these AlScN thin films grown on different metals. The film microstructures have been investigated using TEM and EDS analysis that has been correlated with electrical test data on polarization. We believe this work is important for tailoring AlScN materials and interfaces to achieve the desired FeFETs performance.

9:30 AM EL07.07.05
Synthesis of New Nitride Material Manganese Cobalt Nitride by RF Co-Sputtering Sita Dugu$^1$, Rebecca Smaha$^1$, Shaun O'Donnell$^2$, Andrew Treglia$^2$, Stephen Lany$^1$ and Sage Bauers$^1$; $^1$National Renewable Energy Laboratory, United States; $^2$Colorado State University, United States

Transition metal (TM) nitrides have historically been used as cutting tools due to their outstanding properties such as high hardness and strength, excellent thermal conductivity, and unique electrochemical properties. In 2019, Sun et al. [1] constructed a stability map of inorganic ternary metal nitrides using high-throughput computational methods based on a data-mined structure prediction algorithm. While this work predicted hundreds of new ternary nitrides, only one new chemical space was predicted to contain a previously unknown compound comprising nitrogen and two TMs: MnCoN$_2$. In this study, a series of Mn-Co-N thin films are synthesized by RF magnetron sputtering and characterized for structural and magnetic properties. Combinatorial Mn-Co-N thin films are deposited using reactive co-sputtering at different temperatures ranging from 25 – 450°C and various process pressures. The phase of the as-grown material is checked by X-ray diffraction. Survey density function theory total energy calculations are performed in parallel on six prototype structures based on zincblende or rocksalt lattices. Comparing the calculated structures with experimental diffraction patterns, the synthesized films better match the rocksalt-derived structures, which also exhibit lower formation energy than the zincblende candidates. However, only the primary diffraction peaks are seen, suggesting a large amount of cation anti-site disorder. Manganese and cobalt concentrations are measured by X-ray fluorescence and nitrogen concentration by Rutherford backscattering spectroscopy, confirming nearly 1:1:2 concentrations of Mn-Co:N with some reduced N due to O impurities. Scanning electron microscopy and energy dispersive x-ray spectroscopy are also performed, which illustrated the presence of all elements at their respective energy levels. Magnetic properties for MnCoN$_2$ films have been studied by SQUID magnetometry, which demonstrates that the film possesses a weak moment of remanant magnetization 0.01 emu/g and coercive field of 0.5 T. The study of moment vs temperature shows a transition temperature at ~10 K and overall antiferromagnetic correlations. To better understand the origin of the magnetic moment in the compound and its correlation with structure and stoichiometry (both anion and cation), we perform X-ray Absorption Spectroscopy (both near edge and extended fine structure). Our experimental confirmation of this new TM$_2$-TM$_2$-N ternary nitride motivates renewed effort in new materials prediction and discovery in similar ternary spaces, which we are actively pursuing. For example, in our ongoing computational search, several more TM$_2$-TM$_2$-N have been predicted as new stable nitrides.

Hafnia ferroelectrics hold great promise for the development of nano-devices that may take advantage of their permanent and switchable electric polarization. Hence, their technological interest has made them a focus of attention. But that is not all: surprisingly, these materials are proving to constitute a ferroelectric class of their own, displaying many intrinsic behaviors that seem genuinely unprecedented and certainly lay outside the "standard model" of soft-mode ferroelectricity in perovskite oxides. In this talk I will present first-principles results to discuss and explain some of those intriguing behaviors. In particular, I will discuss the evidence for (im)proper ferroelectricity – and a possible soft-mode behavior – in these compounds. I will also address the question of whether hafnia should be consider a triaxial, biaxial or uniaxial ferroelectric, explaining how the last option may be sufficient (and convenient) to account for the behavior of many woken-up samples. I will then show that, within such a uniaxial picture, it is possible to identify a centrosymmetric reference phase that yields a straightforward description of all the known low-energy polymorphs of these materials, evidencing how they are structurally connected. Finally, I will discuss the piezoelectric response of hafnia ferroelectrics, emphasizing the various unique features it presents (e.g., sign tunability). Time permitting, I will summarize other recent results of my group, e.g., on hafnia-based superlattices.

Work done in collaboration with Hugo Aramberri, Sangita Dutta, Binaey Mukherjee and Natallya S. Fedorova (Luxembourg Institute of Science and Technology). Funded by the Luxembourg National Research Fund through Grant FERNW0/20/15079143/TRICOLOR.

11:00 AM EL07.08.02
Memristive Devices with Ferroelectric Materials
Beatrix Nobels, University of Groningen, Netherlands

The field of neuromorphic computing has recently broadened with the emergence of memristive devices as key elements that allow both processing and storage of information in the same unit. One of the materials classes that attract interest is ferroelectrics, as they offer non-volatile memory but also have been demonstrated to behave as memristive devices, allowing multiple resistance values and opening the possibility of their use as artificial synapses in hardware artificial neural networks, as well as in analogue information processing. I will present our work in this direction with different ferroelectric materials (HfO₂, BiFeO₃ an BaTiO₃) and their differnet synaptic characteristics.

11:30 AM EL07.08.03
The Impact of Crystallinity on Ferroelectric Properties of Epitaxial Rhombohedral Hf₀.₅Zr₀.₅O₂ Films
Soo Kim, Maximilian Becker, Nives Strkalj, Megan Hill, Ziyi Yuan and Judith MacManus-Driscoll, University of Cambridge, United Kingdom; Institute of Physics, Croatia; Lund University, Sweden

Ferroelectric hafnia oxide is of great interest in the semiconductor industry due to its complementary metal-oxide-semiconductor compatibility and scalability. It has potential to be used as actuator, sensors, transducers, memories, etc. Out of all the dopants studied, zirconium doped hafnium oxide, Hf₀.₅Zr₀.₅O₂ (HZO), has been the most promising and widely investigated composition with reported remanent polarization (P_r) of ~ 20 μC/cm² and coercive field (E_c) of ~ 1 MV/cm. However, there are limitations with ALD-grown ferroelectric HZO films in terms of wake-up effect, endurance and tuning of P_r and E_c for specific application such as ferroelectric random-access memory (FeRAM), ferroelectric field effect transistor (FeFET), negative capacitance field effect transistor (NCFET), and many more. In this work, model systems of HZO films were deposited by pulsed laser deposition (PLD) in which the epitaxial rhombohedral ferroelectric phase was stabilised. All the films show wake-up free ferroelectric behaviour with P_r > 7 μC/cm². With increase in laser fluence from 0.5 to 1.3 J/cm², EC increased from ~ 2.7 MV/cm to ~ 3.3 MV/cm. In order to understand the origin of such change in ferroelectric properties, we separate out individual influences of O content, strain and microstructure via x-ray photoelectron spectroscopy, x-ray diffraction, and scanning tunneling electron microscopy.

11:45 AM EL07.08.04
Polar Orthorhombic Phase Stabilization of Hf₀.₅Zr₀.₅O₂ by inserting Seed Layer of HfO₂ and ZrO₂
Yongchi Su and Yen-Lin Huang; National Yang Ming Chiao Tung University, Taiwan

Ferroelectric materials exhibit electrically switchable polarization states that can be utilized in non-volatile memory devices such as ferroelectric random access memory (FeRAM), ferroelectric field effect transistor (FeFET), and ferroelectric tunnel junctions (FTJs). Among various ferroelectric materials, Hf₀.₅Zr₀.₅O₂ (HZO) has attracted significant interest owing to its potential for thickness scalability and compatibility with CMOS technology. However, hafnia-based ferroelectric materials still have some difficulties needing to be overcome. For example, hafnia-based materials have many polymorphs, including monoclinic phase, tetragonal phase, and orthorhombic phase. Among all the phases, only the orthorhombic phase with space group (Pcm2₁) exhibits the ferroelectricity, yet it is a metastable phase for HZO.

Therefore, how to stabilize the orthorhombic phase formation at a limited thickness regime is the central issue for a large-scale application of HZO. Another issue is that hafnia-based materials often suffer from the wake-up effect, which may result from the defect accumulation or the transformation from non-polar phase into polar phase. This issue is also related to the orthorhombic phase stabilization and the quality of thin films. To address these drawbacks and improve the ferroelectric performance of HZO thin films this study proposes another approach by inserting an ultra-thin layer of HfO₂ or ZrO₂ serving as the polar phase stabilizer. This reduces the lattice mismatch between the bottom electrode (La₀.₇Sr₀.₃MnO₃) and the HZO layer. We found that by optimization of the insertion layer the pure polar phase is stabilized and the device exhibits the desired ferroelectric properties.

Our results offer new insights into the stabilization of HZO and the development of wake-up-free hafnia-based devices, with the hope of paving the way for next-generation non-volatile memory applications.

1:30 PM EL07.09.01
Hf₀.₅Zr₀.₅O₂-Based Ferroelectric Heterostructures for Non-Volatile Memories and Artificial Synaptic Devices
Yuewei Yin and Xiaoguang Li; University of Science and Technology of China, China

The rapid development of information technology requires memory devices with fast speed, low power consumption, high density, etc. HfO₂-based ferroelectric thin films are promising for the advanced information memory devices, especially due to the good silicon compatibility and intrinsic advantages of ferroelectricity. Recently, we used atomic layer deposition to construct high-
quality Hf$_x$Zr$_{1-x}$O$_2$ (HZO) ferroelectric thin film heterostructures and investigated corresponding prototype memory devices, including ferroelectric capacitors for FeRAM and ferroelectric tunnel junctions for neural network computing. The ferroelectric endurance properties of Ti/Ni/HzO/Ti/N capacitor were studied, and it was found that the ferroelectric fatigue is reduced by increasing pulse width. Accordingly, a recovery method by introducing wake-up effect was utilized to realize a weaker fatigue, a sufficient switched resistance. Ultimately, we showcase the high-quality Pt/YHO/La$_{0.7}$Sr$_{0.3}$MnO$_3$ devices and measure the resistance hysteresis loops. This innovative material holds significant potential for improving the performance and efficiency of ferroelectric tunnel junctions.

2:00 PM EL07.09.02

Ferroelectric Tunneling Junctions Based on Yttrium Doped Hafnium Dioxide

Wei Chen Hung1, Yen-Lin Huang1 and Chun-Wei Huang2; 1National Yang Ming Chiao Tung University, Taiwan; 2Feng Chia University, Taiwan

Hafnium dioxide (HfO$_2$)-based thin films are considered promising ferroelectric materials for modern semiconductor integration. Various methods have been explored to induce ferroelectricity in hafnium oxide-based thin films, including atomic layer deposition, chemical vapor deposition, and solid solution techniques. Among the diverse doping species, yttrium-doped hafnium dioxide (YHO) stands out as a novel candidate due to its robust ferroelectric polarization, reliability, and scalability.

In this study, we are going to utilize the high ferroelectric polarization value of HYO, approximately 50 μC/cm$^2$, to showcase ferroelectric polarization modulation of tunneling resistance. We also propose the device structure of ferroelectric tunneling junctions using YHO as the tunneling layer. We fabricate high quality epitaxial YHO thin films using pulsed laser deposition on single crystal SrTiO$_3$ (110)/(001) (STO) substrates. The crystal orientations of YHO were analyzed using X-ray diffraction, confirming the presence of the ferroelectric orthorhombic (Pca$_2_1$) phase with two structure domains. Ferroelectric tests were carried out on our YHO films using a ferroelectric tester and piezoresponse force microscopy and ferroelectric tester.

Subsequent to the ferroelectric measurement, we utilized conductive atomic force microscopy and piezoresponce force microscopy to measure variations in polarization direction and tunneling resistance. Ultimately, we showcase the high-quality Pt/YHO/La$_{0.7}$Sr$_{0.3}$MnO$_3$ devices and measure the resistance hysteresis loops. This innovative material holds significant potential for improving the performance and efficiency of ferroelectric tunnel junctions.

2:15 PM EL07.09.03

Influence of Stack Design On The Electrical Performance of HfZrO$_2$ Ferroelectric

Charlene Chen1, Ray Meck1, Jared McWilliams1, Navinndhi Upadhyay2, Mario Laudato2 and Nguyen Vu1; 1EMD Electronics, United States; 2Western Digital Corporation, United States

Hafnium-zirconium oxide (HZO) ferroelectrics have been attracting growing interest in different memory applications owing to their complementary metal oxide semiconductor (CMOS) compatibility and scalability capability [1]. Unlike their perovskite and wurtzite ferroelectric counterparts, HZO retains an excellent leakage and decent ferroelectric response at very low thicknesses [2]. This work highlights the role of bottom and top electrodes on the electrical performance of thin film HZO such as remnant polarization, endurance, and leakage. Crystalinity, thickness, and roughness of the electrodes are found to play critical roles in improving the film quality, reducing the thermal budget, and ultimately improving the electrical response of HZO films.

Wake-up free sub 100 Å thick HZO films with back-end-of-line compatible annealing conditions exhibiting high remnant polarization (2P$_r$ = 54 μC/cm$^2$) and low leakage ($10^{-5}$ A/cm$^2$ at 1 MV/cm) are achieved. The trade-off between polarization and the coercive field is also discussed for achieving the desired ferroelectric performance for different memory applications.

2:30 PM EL07.09.04

Integrated Ultrathin Ferroelectrics in Negative Capacitance Transistors towards Energy-Efficient High-Performance Computing

Nirmran Shanker3, Suraj Cheema1 and Sayeef Salahuddin2,1; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

With the exponentially increasing demand for high-performance computing, the energy efficiency of transistors must continue to improve [1]. In particular, negative capacitance (NC) [2] in ferroelectric materials has emerged as a route to increase the gate capacitance, i.e. lower equivalent oxide thickness (EOT), of a transistor which can reduce the operating voltage and therefore power. However, integration of NC gate oxides in advanced silicon transistors requires ferroelectric stabilization in the ultrathin (sub-2nm) regime on silicon, which is a significant materials challenge for conventional ferroelectrics. To overcome this, we stabilized ferroelectricity on silicon down to 1nm [3-4] and 0.5nm [5] in doped HfO$_2$ and undoped ZrO$_2$, respectively, which are the high-k dielectrics used in today’s advanced logic and memory devices. Notably, these ultrathin ferroelectrics demonstrate signatures of ultrathin-enhanced polarization [3-5], in strong contrast to conventional perovskite oxide-based ferroelectrics.

Next, we leveraged the competing atomic-scale anti-ferroelectric-ferroelectric orders to design NC in 1.8nm HfO$_2$/ZrO$_2$ superlattices [6-8] and 1nm ZrO$_2$ [9], the thicknesses used in today’s advanced transistors and future node transistors, respectively. In contrast to the conventional ferroelectric-dielectric picture for NC stabilization, the microscopic origin of NC in these gate oxides is mixed anti-ferroelectric-ferroelectric order, which broadens the materials space for NC realization. Furthermore, this work establishes the first demonstration of capacitance enhancement in the NC-based HfO$_2$/ZrO$_2$ system, in which elevated low EOT down to 5Å [6-9]. Accordingly, when these NC gate oxides were integrated into thin oxide transistors [3-9], the increase in gate capacitance without degradation in carrier velocity and reliability [6-7], record high ON current and transconductance was obtained at 90nm channel lengths [8-9]. Additionally, there are early indications of industrial adoption as the 1.8nm HfO$_2$/ZrO$_2$ superlattice gate stack has successfully been integrated within a US Defense CMOS R&D Foundry [8] and an advanced FinFET transistor process in an industrial semiconductor foundry [9]. Overall, the materials breakthroughs in this work—ultrathin ferroelectricity and negative capacitance—in the simple CMOS-compatible HfO$_2$/ZrO$_2$ material system provides a new route towards energy-efficient computing.


2:45 PM BREAK

3:15 PM EL07.09.05

300-nm Wafer-Scale Deposition of Ferroelectric HfZrO$_2$ for High Electrical Performance with Back-End-Of-Line Compatible Conditions

Jared McWilliams1, Charlene Chen1, Ray Meck1, Randall Higuichi1, Ruben Waldman2 and Nguyen Vu1; 1EMD Electronics, United States; 2Applied Materials, Inc., United States

Atomic layer deposition (ALD) of hafnium oxide and zirconium oxide has been extensively studied to replace SiO$_2$ as dielectrics in complementary metal oxide semiconductor (CMOS) technology [1]. Since the discovery of ferroelectricity in Hafnia-based oxides in 2011 [2], there has been growing interest in developing an ALD process to achieve good ferroelectrics within the required thermal budget for back-end-of-line CMOS. This work will discuss the advantages of using ALD precursors with wide ALD windows for achieving high-quality ferroelectric
Characterizing Negative Capacitance in Ultrathin Ferroelectric HfO$_2$-ZrO$_2$ Towards Energy-Efficient Advanced Transistors

Ohyun Xue$^1$, Nirmaan Shanker$^1$, Suraj Cheema$^1$ and Sayeef Salahuddin$^{1,2}$

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Negative capacitance (NC) [1] has emerged as a promising solution to overcome fundamental energy-efficiency limits in conventional electronics, in which internal ferroelectric order within the gate stack of a field-effect transistor can enable low-power operation. In particular, by swapping the conventional high-$\kappa$ dielectric with a negative-$\kappa$ ferroelectric gate stack, enhanced gate capacitance, i.e. lower equivalent oxide thickness (EOT), can be realized in advanced Si transistors, resulting in key performance benefits in transistors compared to established semiconductor foundry benchmarks [2-3]. We have previously stabilized NC in sub-2-nm HfO$_2$-ZrO$_2$ heterostructures [2-3], where we observe a capacitance enhancement, definitive proof of NC stabilization, over the SiO$_2$ interlayer [2-3] via small-signal capacitance measurements. However, the full internal polarization-electric field ($P$-$E_{FG}$) relation was not extracted for these NC gate oxides.

In this work, ultrafast pulsed $I$-$V$ measurements are used to map the ‘$S$’-shaped $P$-$E_{FG}$ relation in various ultrathin (sub-2-nm) HfO$_2$-ZrO$_2$ NC gate stacks towards realizing both EOT and physical thickness scaling for power- and dimension-scaling, respectively. The extracted $P$-$E_{FG}$ relation shows a negative $dP/dE_{FG}$ region, a clear signature of NC stabilization. Additionally, by integrating the $P$-$E_{FG}$ relation, the characteristic ferroelectric double-wall energy landscape was extracted and modelled with a Landau-Ginzburg-Devonshire framework. Both $P$-$E_{FG}$ and energy landscapes were then used to quantify the degree of NC stabilization across the various gate stacks. Overall, this work further confirms NC stabilization in ultrathin HfO$_2$-ZrO$_2$ heterostructures via large-signal pulsed $I$-$V$ measurements (as opposed to conventional measurements) and provides a methodology to quantify the degree of NC stabilization.

advantages of both materials to address the challenges associated with high switching voltages in HZO and the integration of perovskite ferroelectrics into the CMOS process. Our findings may pave the way for enhanced performance and efficiency in ferroelectric-based devices, such as Ferroelectric Field-Effect Transistors (FeFETs) and Ferroelectric Tunnel Junctions (FTJs).

4:30 PM EL07.09.10

Load Line Analysis of The Memory Window in Amorphous Indium-Gallium-Zinc Oxide-Based Ferroelectric Thin-Film Transistor

Jae Hoon Lee1,2, Yong Hee Lee1, Joon-Kyu Han1,3 and Cheol Seong Hwang1; 1Seoul National University, Korea (the Republic of); 2SK Hynix Semiconductor Inc., Korea (the Republic of); 3Sogang University, Korea (the Republic of)

Ferroelectric thin-film transistors (FeFETs) attract a great deal of interest for their potential to reduce operating voltage and enhance durability in non-volatile memories by minimizing the interfacial layer thickness through the use of amorphous oxide semiconductors (AOS) instead of silicon (Si). Especially, FeFETs with amorphous indium-gallium-zinc oxide (a-IGZO) channels offer high on-off ratios, fast operation speed, and compatibility with complementary metal-oxide-semiconductor (CMOS) technology. The Memory Window (MW) of FeFETs holds significant importance, particularly in applications such as multilevel cell non-volatile memory and neuromorphic systems. However, there have been limited reports on the MW achievable with n-type a-IGZO, primarily due to the scarcity of hole carriers necessary for polarization switching. This study investigates the attainable MW through load line analysis in FeFETs. Load line analysis is a widely used technique that enables a comprehensive graphical representation of the intricate operation of solid-state circuits with nonlinear charge-voltage or current-voltage responses. In contrast to ferroelectric field-effect transistors (FeFETs) based on Si, which can secure an MW at the twice coercive voltage (2V_c) level, the inherent characteristics of FeFETs based on AOS material result in an inevitably smaller MW due to the absence of an inversion mode.

Furthermore, the influence of various process conditions in FeFETs is explored, including the atomic layer deposition temperature of the aluminum-doped hafnium oxide (HAO) ferroelectric layer, rapid thermal annealing temperature for the HAO layer, and the thickness of the n-IGZO channel. Aluminum is selected as the impurity for hafnium oxide due to its thermal stability and compatibility with CMOS processes. The impact of these process variables on ferroelectric performance in metal-ferroelectric-semiconductor-metal capacitors and the FeFET structures is analyzed by evaluating polarization-voltage, capacitance-voltage, and current-voltage characteristics under various conditions. In addition, load line analysis is performed at each process condition based on these characteristics. These findings can potentially guide the development of high-performance FeFETs with optimized MW for various applications.

4:45 PM EL07.09.11

Large Electromechanical Coupling in Zr-Doped Ceria

Maxim Varenk1, Boyuan Xu2, Tali Pechersky-Savich1, Junying Li1, Ellen Wachtel1, David Ehre1, Prabлад Routh1, Sergey Khodorov1, Anatoly Frenkel1, Yue Qi6 and Igor Lubomirskiy1; 1Weizmann Institute of Science, Israel; 2Brown University, United States; 3Stony Brook University, United States

We have investigated the electrostriction (ES) effect in Zr-doped ceria (Zr_xCe_yO_8) ceramics. ES is a second order electromechanical response, i.e., strain, n, is proportional to M^2, where M is the applied electric field. The ES strain is a longitudinal electrostriction strain component. In this work, we have successfully determined ES strain sensitivities for ceria using oxygen vacancies (V_o) which provide charge compensation for aliovalent dopants or for cerium reduction (Ce^3+). The ES induced by V_o is restricted to frequency <1 Hz and low saturation strain (u_sat < 15 ppm).

Doping CeO_2 with Zr results in a large ES strain coefficient, reaching μM^2/V^2 for x=0.1. This effect persists to frequency 3 kHz and to a220 ppm, making ZrO_2-CeO_2 competitive with the best commercial electrostrictors (PMN-PT15), but with 100 times lower dielectric permittivity and three-fold higher elastic modulus. XAS data, DFT modelling and ab initio molecular dynamics (AIMD) calculations demonstrate that elastic dipoles formed by Zr-doping are dynamic. In the absence of an E-field, [ZrO_8]-local bonding units remain, on average, centered with respect to the second (cation) coordination shell. Due to bond anharmonicity displacement of Zr by an E-field requires less energy than displacement of the host cations, resulting in a large dynamic elastic dipole. This polarizable elastic dipole gives rise to large electrostrictive strain and constitutes the first example of non-classical electrostrictors (NCES) relying solely on substitutional point defects.

M^2 of Zr-doped ceria increases exponentially with Zr content for x=0.1, suggesting that the connection of Zr ions to electrostrictive strain may not be simply additive. Zr-doping also increases the relative dielectric permittivity, from 26 (x=0), to 220 (x=0.1) and lowers the elastic modulus from 227GPa (x=0) to 214GPa (x=0.1), even though the number of chemical bonds remains unchanged. AIMD calculations report that stiffness for moving [CeO_2]-local bonding units is essentially isotropic and is 2-2.4 times higher than for [ZrO_2]. Stiffness for moving [CeO_2] first nearest neighbor to Zr is only slightly decreased than in the bulk. These results can provide the theoretical basis for the reduction of the Young’s modulus and increase in the dielectric permittivity with Zr doping.

When the concentration of Ce^3+ is ≥ 100 ppm in Zr_xCe_yO_8, accompanied by the formation of oxygen vacancies (V_o) for charge compensation, ES is suppressed. In addition, by co-doping ZrO_2-CeO_2 with 0.5mol% of aliovalent dopants - Ca, Sc, Yb or La - we observed that the aliovalent dopants reduce the electrostriction strain coefficient by more than an order of magnitude and restores the values of Young’s modulus and dielectric permittivity close to values those of undoped ceria. Since all these co-dopants, irrespective of valence and ionic radius, lead to a similar result, we concluded that the species responsible for the suppression of electrostriction in Zr doped ceria must be the oxygen vacancies. This finding is supported by XAS measurements and AIMD calculations. Fourier transform of Zr K-edge EXAFS spectra reveal that, even though the molar ratio ZrCe/V_o = 40:1 in the co-doped compounds, oxygen vacancies nevertheless succeed in introducing enhanced disorder into the second coordination shell (cation) of Zr. DFT modelling predicts that a [ZrO_2-V_o], local bonding unit is stiff and asymmetrically distorts adjacent unit cells, leading to an elastic interaction length in the lattice between Zr-ions two-and-a-half-unit cells, which, in the absence of oxygen vacancies, can allow limited collective motion. However, such collective motion does not lead to a phase transition even at 123 K, implying that interaction between Zr-ions is neither sufficiently strong nor sufficiently long-range to produce freezing of the displacement, an effect that has been observed for perovskite relaxors.

SESSION EL07.10: Poster Session III
Session Chairs: Morgan Trassin, Ruijuan Xu and Di Yi

Thursday Afternoon, April 25, 2024
Flex Hall C, Level 2, Summit

5:00 PM EL07.10.01

Strain-Driven Solid—Solid Crystal Conversion in Chiral Hybrid Perovskites with Paramagnetic-To-Ferromagnetic Transition

Haining Zheng and Kian Ping Loh; National University of Singapore, Singapore

Hybrid organic–inorganic perovskites (HOIPs) are promising stimuli-responsive materials (SPMs) owing to their molecular softness and tailorable structural dimensionality. The design of mechanically responsive HOIPs requires an in-depth understanding of how lattice strain induces intramolecular rearrangement that impacts physical properties. While chirality transfer from an organic cation to an inorganic lattice is known to influence chiral-optical properties, its effect on strain-induced phase conversion has not been explored. As opposed to achiral or racemic organic cations, hybrid organic cations can potentially afford a new dimension in strain-responsive structural change. Herein, we demonstrate that mechanical strain induces a solid phase crystal conversion in chiral halide perovskite single crystals ([R55]-FeCl4) (FE = (4-Fluorophenyl)ethylamine) from a 0D isolated CuCl4 tetrahedral to 1D corner-sharing CuCl4 octahedral framework via the incorporation of Cu..F interaction and N-H...F hydrogen bonding. This strain-induced crystal-to-crystal conversion involves the connection of neighboring 0D CuCl4 tetrahedra via Cu2-...Cl-...Cu2 linkages as well as the incorporation of a F-terminated organic cation as one of the X atoms in Bx6 octahedra, leading to a reduced band gap and paramagnetic-to-ferromagnetic conversion. Control experiments using nonchiral or racemic perovskite analogs show the absence of such solid phase conversion. To demonstrate pressure-sensitive properties, the 0D phase is dispersed in water-soluble poly(vinyl alcohol) (PVA) polymer, which can be applied to a large-scale pressure-induced array display on fibrous Spandex substrates via a screen-printed method.

Reference:

5:00 PM EL07.10.02

Filterless Visible-Range Color Sensing and Wavelength-Selective Photodetection Using Bandgap Engineered Ferroelectric Ceramic

Vasilii Balanov1, Filip Temerov1, Vladimir Pankratov2, Wei Cao1 and Yang Bai1; 1University of Oulu, Finland; 2University of Latvia, Latvia

Photodetectors, photodetectors, or color sensors are key components for various optical and optoelectronic applications. Semiconductor-based photodetection has been a dominant area which is excellent at measuring the photon intensity of incident light. However, the wavelength of the incident light to be measured must be known beforehand and it mostly depends on auxiliary methods to filter unknown wavelengths. In this work, an alternative and simple mechanism that is using a monolithic, bandgap-engineered photoferroelectric ceramic to blindly determine the
wavelength and intensity of incident light at the same time is demonstrated. The photoferroelectric compound is Ba- and Ni-codoped (K,Na)NbO₃ exhibiting a direct band gap of ≈2 eV and a spontaneous polarization of ≈0.25 C/m². The band–band charge carrier transition is confirmed by multiple characterization methods of photoluminescence, photodielectric spectroscopy, and photoconductivity. The exsistent optoelectrical cumulative effect enabled by the simultaneous narrow bandgap and strong ferroelectricity allows to reliably distinguish the wavelengths of 405, 552, and 660 nm as well as the power density ranging from 0.1 to 10 W/cm², with the photosresponsivity of up to 60 µA/W.

5:00 PM EL07.10.03
First Principles Insights into Phase Transitions, Disorder and Electronic Properties of Lead-Free Ba-Based Tetragonal Tungsten Bronzes
Benjamin A. Williamson, Nora S. Lendal and Tor Grande; Norwegian University of Science and Technology, Norway

Tetragonal tungsten bronzes (TTBs), with the general formula A₂M₃Ir₄O₉ (BNN) are a family of ferroelectric materials, which, due to their broad compositional space and structural flexibility make them a suitable framework for tuneable lead-free oxide ferroelectrics.

The Ba-containing TTBs such as Ba₄Na₂Nb₂O₉ (BNN) with a Tc of ≈−560°C[1] is of particular interest in high temperature applications where there is a lack of suitable materials. Previous experimental work on substituting the A-site Na cation with larger alkali metals: K and Rb, show a systematic decrease in Tc in addition to uncovering the integral role that cation disorder plays on the structural parameters of these systems.[1]

However, there is little in terms of mechanistic understandings of these compositions using first principles characterisation techniques. In this work, density functional theory (DFT) calculations using both standard and hybrid functionals are performed on BNN-based compositions: Ba₄A₂M₃Ir₄O₉ (A = Na, K, Rb; M = Nb, Ta). In particular, we probe the origin of the high Tc as well as the thermodynamics of disorder. In particu

and the trends associated with the compositional engineering, as well as the thermodynamics of disorder and its effect on structural and electronic properties. The effects of this study are discussed in line with experimental work done in parallel as well as implications for the future direction of these materials.

5:00 PM EL07.10.04
Chlorine Substituted Organic Linker in Two-Dimensional Halide Double Perovskite Ferroelectric with Directional Dependence Properties
Shubham A. Raiput, Sudhadevi Antharjanam and Aravind Kumar Chandiran; Indian Institute of Technology Madras, India

Ferroelectric materials have garnered significant interest due to their unique electrical and structural properties, holding immense promise for diverse electronic applications. This study introduces a novel 2D layered halide double perovskite ferroelectric material denoted as Cl₁₋ₓBrₓPA₄AgInBr₈ (CPAIn). Through the strategic substitution of halogenated A-site organic linker 3-chloropyrrolidinammonium, CPAIn demonstrates exceptional non-centrosymmetric properties and remarkable ferroelectric behaviour, with a Curie temperature (Tc) of 197°C. One of the key findings of this research is CPAIn's anisotropic ferroelectric behaviour, characterized by a notably high spontaneous polarization (Ps) of 6.25 µC.cm⁻² along the perpendicular orientation to the octahedral layers.

This observation underscores its potential for applications requiring precise control over polarization direction. Notably, the material exhibits differential resistivity along distinct crystalllographic axes, with resistance measuring 9.71 MΩ.cm along the parallel direction and 18.81 MΩ.cm along the perpendicular direction. This variance is attributed to the role of organic cations as insulators, modulating charge transfer dynamics within the material. As demonstrated by CPAIn, the ferroelectric characteristics present intriguing opportunities for future development and construction of advanced electronic devices. This endeavour represents a noteworthy advancement in tapping into the complete capabilities of ferroelectric materials for a diverse array of technological uses. The distinctive qualities of CPAIn outlined in this investigation render it an attractive contender for further research and pragmatic integration into cutting-edge electronic devices.

5:00 PM EL07.10.05
Synthesis and Characterization of Tellurium Doped Tin Sulfide (SmSTe) Nanomaterials
Ramanathan K. Natarajan, Hui Cai1,2 and Matthew E. Metcalf1; 1University of California, United States; 2Lawrence Berkeley National Laboratory, United States

The presence of a spontaneous electric dipole even in the absence of an applied external electric field defines ferroelectric materials. By symmetric requirements, this is possible only in non-centrosymmetric structures where non-zero net polarization is possible. Bulk 2D Tin sulfide (SnS), an exciting member of the group IV-VI semiconductor materials with ferroelectric properties exhibits centrosymmetry which can be broken by doping. In this work, we successfully synthesized tellurium doped SnS, achieving different doping concentrations via the traditional chemical vapor deposition method. The samples were characterized using Optical microscopy, Raman spectroscopy, X-Ray Photoelectron spectroscopy and Atomic Force Microscopy. By tuning the growth parameters, we have been able to determine optimal growth parameters for these doped crystals, thus precise control has been achieved. Hence, this work would open fresh opportunities for bulk ferroelectric 2D SnS with future potential use in high quality, scalable, tunable, and high-performance technological applications.

5:00 PM EL07.10.06
Zwitterion-Based Organic High-k Dielectric Materials
Simone Jeffers, Rotee A. Kaur1, Renita M. D’Souza2, Timothy L. Kelly2, Vance E. Williams3 and Loren G. Kake3; 1Simon Fraser University, Canada; 2University of Saskatchewan, Canada

Most high-k dielectric materials known are based on inorganic materials, where large polarization is due to the slight separation of positive and negative charges in response to an applied field. Organic materials on the other hand, tend to have very low dielectric constants because of the low atomic number of their constituents. However, organic materials offer many advantages including easy of processing and mechanical flexibility. Zwitterionic molecules have charged groups that can be spatially separated by tens of angstroms. However, they are underexplored as dielectric materials. We report the synthesis of a novel zwitterionic molecule which melts below 100 °C. The compound was blended with poly(methyl methacrylate) and its dielectric properties were studied. The frequency-dependent capacitance depends strongly on the amount of zwitterion in the film and on the temperature of the device. At low concentrations of zwitterion and low temperatures, the film shows small capacitance (~3 nF/cm²). Above a specific concentration and temperature, capacitance is greater than 10⁶ F/cm², consistent with electrostatic double layer formation. In order to achieve this high of a capacitance value, the bulk of the film must be field-free. As such, we suggest that zwitterions exhibit strong electrostatic correlation behaviour. This interpretation is supported by grazing incidence wide angle x-ray experiments which show evidence of zwitterion crystallization only at high concentrations. The demonstrates a non-electrolyte dielectric with a very high capacitance and illustrates the importance of the nanoscale electrostatic environment on the properties of this class of materials.

5:00 PM EL07.10.07
Depolarization Field Driven Photovoltaic Effect in 2D Ferroelectric α-In₂Se₃
Simranjeet Kaur, Saharir Muhammad Nahal1, SungWoo Nam2 and Arend M. van der Zande1; 1University of Illinois Urbana Champaign, United States; 2University of California Irvine, United States

The ultimate limit of bulk photovoltaic energy conversion efficiency in ferroelectrics at the nanoscale depends on the mechanism of electron and hole separation. Understanding the underlying mechanism will enable new design principles for utilizing the bulk photovoltaic effect (BPVE) in next generation optoelectronic devices, such as self-powered photodetectors or solar cells. In contrast to conventional ferroelectrics, 2D ferroelectric α-In₂Se₃ has two advantages for BPVE based solar cells. First, the band gap is 1.3 eV, close to the ideal value for utilizing the solar spectrum, and much smaller than most wide bandgap ferroelectric oxides. Second, they naturally exist at nanoscale dimensions with stable ferroelectricity down to a monolayer. The key goals are to characterize the thickness dependent BPVE in α-In₂Se₃ and understand the dominant mechanism.

Here, we fabricate graphene-α-In₂Se₃-graphene heterostructures, where the thickness of α-In₂Se₃ varies between 18-50 nm, and characterize the transport under illumination. We use scanning photocurrent and photovoltage microscopy to map the short-circuit current density (Jsc) and open-circuit voltage (Voc). We also measure the transport under varying intensities.

The photocurrent and photovoltage maps show that both the Jsc and Voc prevails only in the region overlapped by the top and bottom graphene. The Jsc is antiparallel to polarization. All these observations confirm the BPVE in the heterostructures. The transport measurements under illumination show that the Jsc and Voc suffer from different exponential thickness. The direction of the photocurrent and its exponential decay with thickness confirm the depolarization field as the origin of the photovoltaic effect in α-In₂Se₃. We also find that the depolarization field is inversely proportional to thickness and reaches 158 KV/cm for 18 nm α-In₂Se₃. Moreover, the depolarization field model allows us to predict a nonmonotonic trend of photovoltage with thickness where it is expected to peak for 6 nm thick α-In₂Se₃. The transport measurements depict that Jsc & Voc intensity³ where β varies from 0.6 to 1.2 with increasing thickness. The photosresponsivity reaches 1.8 mA/W under 1 W/cm² intensity for 18 nm α-In₂Se₃. This is comparable to other 2D ferroelectrics and almost 4 to 2200 times higher than conventional bulk ones.

Conductive domain walls (DWs) hold promise for nanoscale, energy-efficient multi-level diodes and neuromorphic circuitry. In CsGeX3, caesium and halogen vacancies are intrinsic point layers. The Bi2O2Se-based top-gated field-effect transistor device shows excellent semiconductor device properties, including high carrier mobility (~28,900 cm^2/Vs at 1.9 K and 450 cm^2/Vs at room temperature) and superior current on/off ratio with the almost ideal subthreshold swing. In addition, the moderate bandgap (~0.8 eV) of Bi2O2Se makes its device suitable for room temperature operation while requiring only a relatively low operation voltage. These fascinating properties, chemical stability in the ambient environment, and easy accessibility make Bi2O2Se a promising semiconductor candidate for future ultra-small, high-performance, and low-power electronic devices. Moreover, as the Bi-O layer in Bi2O2Se is structurally compatible with many perovskite oxides with interesting physical phenomena, it is feasible to fabricate heteroepitaxy/superlattices between Bi2O2Se and perovskite oxides to pursue novel emergent physical phenomena in hybrid heterostructures. The device study combines an epitaxial ferroelectric Pb(Zr0.2Ti0.8)O3 (PZT) layer with the Bi2O2Se layer. The ferroelectric polarization of the PZT layer serves as a control parameter to modulate the semiconducting behaviors of the Bi2O2Se layer. The as-grown polarization leads to charge depletion and, consequently, low conduction. Switching the polarization direction results in charge accumulation and enhances the conduction at the Bi2O2Se layer. The origin of this modulation is attributed to a change in the electronic structure due to the ferroelectric polarization states, evidenced by X-ray photoelectron spectroscopy and cross-sectional scanning tunneling microscopy/spectroscopy. Control of the conduction at this new heterostructure delivers a pathway of non-volatile controlling on layered semiconductors for next-generation transistors.

8:00 AM EL07.11.01

Giampietro Second Harmonic Generation from SnS with Ferroelectric Stacking Redwuan A. Mostafa, Yi-Bing Zhao, Ting-Kai Wang, Michael E. Gnecco, *Liu Jia, Bei-Rui Liu; 1National Taiwan University, Taiwan; 2Academia Sinica, Taiwan; 3Taiwan International Graduate Program, Taiwan; 4The University of Tokyo, Tokyo, Japan; 5Tamkang University, Taiwan

In recent years, substantial attention has been directed towards two-dimensional SnS, a member of the group IV monochalcogenides, owing to its exceptional physical properties. Theoretical predictions have emphasized the potential of SnS monolayer to display significant second harmonic generation (SHG) due to its in-plane ferroelectricity. However, the synthesis of monolayers with considerable lateral dimensions remains challenging due to the formidable inter-layer forces between SnS layers. For a large SnS bulk crystal, the layers are typically stacked with an antiferroelectric order (AB stacked), and the ferroelectric property disappears. In this work, we successfully fabricated a sizable flake (approximately 8x8μm) consisting of a few layers of SnS with ferroelectric stacking (AC stacking), which enables optical measurement feasible. We found giant SHG from AC-SnS, surpassing that of MoS2 monolayers by 50 times. The SHG susceptibility was experimentally estimated as 85 pm/V, which is much stronger than the value (~2 pm/V) of a typical nonlinear crystal such as BBO and KTP crystals. We have also investigated the angle-resolved SHG patterns and found that there is good agreement between experimental and theoretical data. We further developed angle-resolved SHG microscopy as a tool for identifying single or multiple domains in SnS flakes. Orientations of polarization in different domains have been clearly obtained by this technique. From the results of cross-sectional transmission electron microscopy, we found some regions that the stacking order of layers is neither AB nor AC stacking. We have also investigated the effect of stacking disorder to the angle-resolved SHG patterns.

9:15 AM EL07.11.03

Defects and Domain Walls in Soft Ferroelectric CsGeX3 (X = Cl, Br, I) Kristoffer Eggstad, Benjamin A. Williamson, Dennis Meier and Sverre M. Selbach; Norwegian University of Science and Technology, Norway

Conductive domain walls (DWs) hold promise for nanoscale, energy-efficient multi-level diodes and neuromorphic circuitry. In CsGeX3, caesium and halogen vacancies are intrinsic point defects that can induce electrons and holes, respectively. Controlling the formation and position of vacancies can in principle give switchable local n-type or p-type conductivity at DWs and enable new concepts for DW-based circuitry. This requires a material where mobile point defects of both positive and negative charge can accumulate at DWs. CsGeX3 is here chosen as our model system due to the possibility of having mobile caesium and halogen vacancies.

We use density functional theory (DFT) to study intrinsic point defects and DWs in CsGeX3. Using hybrid DFT we investigate electronic structure and defect formation energies in bulk, showing highly mobile holes and free electrons, as well as relatively shallow defect levels. Additionally, a study on point defect mobility in bulk, reveals exceptionally mobile anion vacancies with migration barriers comparable to Li vacancies in the best solid-state electrolytes. Furthermore, we investigate possible DWs and show that parallel and head-to-tail Y-type 71-degree DWs are the most stable DWs. Moreover, the mobility of DWs, with and without point defects in their vicinity, has been studied, showing extremely mobile anion vacancies, with migration barriers comparable to Li vacancies in the best solid-state electrolytes.

9:30 AM EL07.11.04

Two-Dimensional MOF-Based High-Performance Ferroelectric Field-Effect-Transistors with an Ultralow Off-State Current Jinyu Li; Southern University of Science and Technology, China

Two-dimensional (2D) ferroelectric oxides open a new realm of nonvolatile memory and computing devices, while metal-organic framework (MOF) materials offer tremendous possibilities to design and optimize ferroelectric performance. Building a ferroelectric field-effect transistor (FeFET) by integrating a 2D MOF ferroelectric gate with a 2D semiconducting channel provides new strategies towards ultralow power nonvolatile memory devices, yet no 2D MOF was found to be ferroelectric yet. Here we successfully develop 2D ferroelectric MOF nanosheets, \{CuIIL2\}-MOF, and confirm its ferroelectricity down to 7 nm. A large polarization of ~14.2 μC/cm2, a small coercive field of ~33.3 V/μm, and excellent endurance ~10^6 cycles are found in 2D \{CuIIL2\}-MOF nanosheets. This enables us to fabricate FeFETs using 2D \{CuIIL2\}-MOF as the gate and MoS2 as the channel, achieving an on/off ratio of 10^7 with the ultralow off-state current of 100 fA and tunable memory window, making it exceptionally unknown FeFETs and very promising for next-generation ultralow power memories and computing devices.

9:45 AM EL07.11.05

Understanding The Formation of Ferromagnetic CuCr2Se4 Nanocrystals Samantha Harvey, Jonathan DeStefano, Jun-Haw Chu, Daniel R. Gamelin and Brandi M. Cossairt; University of Washington, United States

Spinels (AB2X4) are a unique class of materials that exhibit a range of magnetic, optical, and magneto-optical properties tunable through choice of A and B site cations. While many of the oxides have been synthesized at the nanoscale, research into nanocrystalline chalcogenide spinels is lacking. Amongst these the copper chromium chalcogenides are of particular interest for their high Curie temperatures (>350K) and large magneto-optical Kerr effects. Only a handful of reported syntheses for these materials exist, with conflicting magnetic properties (e.g. superparamagnetic vs. ferromagnetic), minimal mechanistic understanding, and no optical data. In this study, we delve deeper into the synthesis of this material. Binary copper selenium forms as an intermediate followed by Cr diffusion into the lattice. Upon ramping the reaction temperature, magnetism is slow to turn on as evident by magnetic susceptibility measurements. After approximately 40 minutes at 340°C ferromagnetic ordering appears concurrently with a change in lattice parameter, crystallite size, and stoichiometry suggesting annealing and cation diffusion. Magnetic circular dichroism data of nanocrystal films is similar to magneto-optical Kerr rotation spectra of single crystals exhibiting a NIR feature that overlaps with telecommunications wavelengths. Current and future directions involving doping, cation exchange, and spectrally-resolved microscopy are also discussed.
Amplifying Spin-Orbit Torque Efficiency via a Crystallographic Approach

Yulan Chen, A. El-Ghazaly, Chao-Yao Yang and Yen-Lin Huang; National Yang Ming Chiao Tung University, Taiwan

Currently, transition-metal oxide based spintronics have sparked a tremendous research interest thanks to their non-trivial properties in solid-state physics and soon become potential candidates to participate into the spin-orbit torque (SOT) technology in the third generation of magnetoresistive random access memory. Recent studies have highlighted the ability of epitaxially grown SrIrO$_3$ to generate a spin current with remarkable charge-to-spin conversion efficiency. However, a comprehensive study of crystallographic dependence of SOT effect in single crystal SrIrO$_3$ thin films remains lacking. To address this gap, we prepare SrIrO$_3$(001)/La$_2$Sr$_{17}$MnO$_{33}$/SrTiO$_3$(001) epitaxial bilayers on the SrTiO$_3$ single crystal substrates by using pulsed laser deposition technique. The SrIrO$_3$ layer serves as a spin generator with orthorhombic symmetry, facilitating the study of anisotropic SOT effects, while LSMO functions as a ferromagnetic layer with in-plane magnetic anisotropy for spin detection. Employing a loop-shift method on Hall bar devices with different crystallographic orientations, we observed that applying current along the [100] direction of SrIrO$_3$ resulted in nearly five times higher SOT efficiency compared to applying current along the [100] direction, as indicated by the peak shift ($H_{\theta}$) relative to the sensing current amplitude. This outcome reveals a robust correlation between the crystal structure and the SOT effects, offering an ideal platform for manipulating SOT properties in TMO-based spintronic devices.

Understanding Magnetic Nanochain Interactions for Reconfigurable Soft Actuators

Amra El-Ghazaly, Yulan Chen and Ludovico Cestarollo; Cornell University, United States

When scaled down to micrometer dimensions, magnetic actuators along with other micromagnetic devices strongly depend upon their nanoscale behavior. For example, magnetoretoelectromagnets (MREs), which are composites of a polymer matrix and a magnetic filler, will stretch, bend, and generally behave in a manner that is intrinsically linked to the properties of the magnetic filler. However, the extent by which a material can bend and deform is proportional to its elasticity and inversely proportional to the cube of its thickness. Thus, high-resolution actuation and bending of MREs at the microscale requires an MRE of thickness similarly at the microscale and a magnetic filler that is much smaller – on the order of nanometers. In this talk, we will present a direct comparison of actuation by microparticle-filled and nanoparticle-filled elastomer thin films, illustrating that higher actuation response at small applied magnetic fields (<100 mT, typical of integrated devices) can be achieved by the nanoparticle films [1]. Therefore, MRE microactuators using magnetic nanoparticles are desirable. However, magnetic particles are known to lose their anisotropy and ferromagnetic behavior as the dimensions are reduced to the nanoscale. Thus, nanoparticle MRE actuation can be further increased with improved nanostructures having increased remanent magnetic moment.

We will show that synthesis of high saturation magnetization Fe$_{65}$Co$_{35}$ (230 emu/g) magnetic nanoparticles addresses this obstacle head on, bringing both anisotropy and strong ferromagnetism with improved nanostructures having increased remanent magnetic moment.
Furthermore, we successfully fabricated a reconfigurable magnetic composite film by incorporating the optimal concentration of magnetic nanochains into an elastomer matrix. A soft actuator was made with two separate magnetic panels. The panels could be either encoded with the same magnetization orientation or opposite magnetization orientation to achieve various actuation modes. Subsequent reprogramming could be achieved through the application of a magnetic field to one or both panels. This actuator exhibited shape-morphing behaviors in the form of a twisted or bent configuration, respectively, in response to the magnetic field and could be repeatedly reprogrammed. Thus, we demonstrated the construction of reconfigurable magnetic soft actuators capable of large-scale, efficient deformation in small actuation fields (less than 400 Oe). This research emphasizes the potential of magnetic nanochains as effective magnetic fillers and determines the optimal concentration of this magnetic filler for the development of reconfigurable, highly-elastic actuators.

SESSION EL07.13: Bulk Ferroics
Session Chairs: Kevin Crust and Aileen Luo
Friday Afternoon, April 26, 2024
Room 342, Level 3, Summit

1:30 PM EL07.13.01
Energy Storage Properties of Samarium-Doped Bismuth Sodium Titanate-Based Lead-Free Ceramics Xiaoyu Tang1, Ziming Hu1, Vladimir Kovář2, Bin Yang1, Graham Smith1 and Haixue Yan1; 1Queen Mary University of London, United Kingdom; 2Slovak Academy of Sciences, Slovakia; 3University of Chester, United Kingdom

Due to worldwide environmental regulations, lead-free relaxors, namely Bi4_xNa8_xTio3−x−6Bi2O3 (BNT-6BT) are being extensively studied as an alternative candidate for energy storage applications. Here, Sm was introduced at different A sites of the relaxor system; specifically, the Sm-doped BNT-6BT system was designed to replace Bi (BNT-Bi), Na (BNT-Na), and both the Bi and Na ions (BNT-BiNa) by Sm ions. It was found that the BNT-Bi sample possesses high piezoelectricity ($d_{33}=117.3$ pC N$^{-1}$), whereas the BNT-Na and BNT-BiNa ceramics show exceptionally high values of the energy storage density and efficiency. To define the energy storage performance, a new concept based on determining the recoverable energy storage intensity is proposed in the present work. This allows bypassing the high applied electric fields in determining the value of the energy storage density. An ultrahigh recoverable energy storage density (4.41 J cm$^{-3}$), excellent energy storage efficiency (83.96%) and superhigh recoverable energy storage intensity (19.17×10^3 J K$^{-1}$ cm$^{-2}$) were achieved in the BNT-BiNa ceramics simultaneously. Furthermore, the energy storage characteristics exhibit an excellent stability over a wide temperature range from 25°C to 150°C. Thus, the developed Sm-doped BNT-6BT ceramics show great potential for piezoelectric and high-power energy storage applications.

This paper has been published in Chemical Engineering Journal 473 (2023) 145363, https://doi.org/10.1016/j.cej.2023.145363

1:45 PM EL07.13.02
Field Sensitive Ba0.5Sr0.5TiO390%Bi40.0110.5O3 Ceramics with Super High Dielectric Tunability Wanting Hu, Haixue Yan, Xuyao Tang, Samrawit D. Hailu and Isaac Abrahams; Queen Mary University of London, United Kingdom

Barium strontium titanate(Ba0.5Sr0.5TiO3, BST) is a promising candidate for tunable components but the tunability of BST is relatively low and the mechanisms of tunability and the impact of electric fields on the dielectric properties of BST ceramics require more comprehensive research. Here, by introducing Hf and adjusting the content of Sr, the transition in BST ceramics turn to the diffuse phase. There are at least two distinct polar structures, which is suggested by different current peaks in current-electric field loops. The developed ceramics show super high dielectric tunability (up to 68%) which can be attributed the different polar structures having significantly sensitive to applied electric fields. Compared to pure BST ceramics or other doped variants, the designed BST exhibit nearly twice the increase in dielectric tunability and hold great potential for widespread use in tunable devices including phase shifters, resonators, filters, voltage-controlled oscillator.

2:00 PM EL07.13.03
Facile Mechanochemical Synthesis of Lead-Free Piezoelectric Perovskite Potassium Sodium Niobate Incorporated with Tungsten Latha Nataraj, Anthony Roberts, Scott Walck, Tucker Moore, Kenneth Strawhecker and Kristopher Darling; US ARL, United States

A quest for non-toxic alternatives to conventional lead-based ferroelectric and piezoelectric materials has led to avid research in complex perovskite oxides and systems characterized by morphotropic phase boundary due to the abrupt increase in the dielectric and piezoelectric constants occurring in this region. Niobate perovskites like the (K,Na)NbO3 (KNN) family have emerged as some of the most important lead-free ferroelectric and piezoelectric materials. Engineering of facile, economical, and environmentally safe synthesis methods for such materials pose challenges to ensuring chemical homogeneity and achieving desired structures. Further, it has been demonstrated that doping positively influences properties such as morphology, texture, crystalline structure, and polarization of KNN. Here, we report solvent-free mechanochemical synthesis of single-phase lead-free piezoelectric perovskite oxide (W-KNN) of KNN incorporated with Tungsten (W), using a simple high-energy ball-milling process with shorter processing times and lower calcination temperatures than those reported in literature. The characterization of the derived powder confirms the structure, morphology, crystallinity, and chemical composition of the material synthesized. Local piezoelectricity is confirmed on the synthesized material for various application-specific device configurations. The presented method could also pave the way for a rapid, facile, and faster synthesis mechanisms at lower processing temperatures for other promising functional oxides.

2:15 PM EL07.13.05
Novel Photocaloric Effects in Archetypal Ferroelectrics for Solid-State Cooling Applications Claudia Cazorla; Universitat Politècnica de Catalunya, Spain

Solid-state cooling represents an energy efficient and ecologically friendly solution to the environmental problems posed by conventional refrigeration technologies based on compression cycles of greenhouse gases [1-3]. Upon small and moderate magnetic, electric and/or mechanical field shifts, promising caloric materials experience large adiabatic temperature variations ($\Delta T$)$=-10$ K and $\Delta S$)$=10-100$ J K$^{-1}$kg$^{-1}$, as a result of phase transformations entailing large isothermal entropy changes ($\Delta S$). Solid-state cooling relies on such caloric effects to engineer multi-step refrigeration cycles. Nevertheless, conventional magneto-, electro- and mechano-caloric effects present a series of critical drawbacks that keep hindering their practical implementation in commercial refrigeration devices. For example, operation temperature conditions should be close to zero-bias transition points, since otherwise the required driving fields grow unfeasibly too large, but these only serendipitously occur at ambient conditions. Here, we will show, based on advanced first-principles simulation methods, that macroscopic light-driven phase transitions in ferroelectrics have the potential to overcome such a materials selection limitation. In particular, we demonstrate for the archetypal ferroelectric KNNO that the existence of giant photocaloric effects (i.e., $\Delta T$)−10 K and $\Delta S$)−100 J K$^{-1}$kg$^{-1}$, that is, induced by light absorption, over a vast temperature span of several hundreds of Kelvin containing room temperature. Our results can be qualitatively generalized to other ferroelectrics displaying similar types of ferroelectric to paraelectric phase transitions [4].


2:30 PM EL07.13.06
Light-Induced Color Change and Negative Photoconductivity in Bandgap Engineered Lead Titanate Ceramics Yang Bai1, Suhas Yadav1, Ofir Rudich2, Or Shafir2 and Ilya Grinberg2; 1University of Oulu, Finland; 2Bar-Ilan University, Israel

Motivated by the principle of above-bandgap photovoltage and thus the theoretical possibility of breaking the Shockley-Queisser limit, research interest in bandgap engineering of conventional ferroelectric materials is on the rise. Due to the reduced bandgaps and the resultant interaction between the incident photon energy and the unit cells and domains, many fundamentally interesting phenomena have been observed in ferroelectrics under visible light, including photo-excited domain switching and photoferroelectric cumulative effect. These phenomena could result in optical and optoelectrical applications far beyond the bulk photovoltaic effect. This talk will report a newly synthesized PbTiO$_3$-based ceramic that is modified to achieve a narrow band gap, which has been predicted via calculations by the density functional theory (DFT). This new material changes its color from maroon to brown when exposed to visible light, accompanying with negative photoconductivity. A hypothesis to explain this behavior could be that the photo-excited electrons might reduce Ti$^{4+}$ to Ti$^{3+}$, causing the color change.

Large Magnetic Proximity Effect in Manganite Oxide Heterostructures

Suryakanta Mondal, Naveen Negi and Bhagwati Prasad; Indian Institute of Science Bangalore, India

The fabrication of spintronic devices necessitates the use of multi-layer structures made up of diverse magnetic materials. Such magnetic structures lead to a wide range of interface effects, prominent among which is the proximity effect. Manganite oxide thin film heterostructures are potential candidates for a comprehensive exploration of these proximity effects, primarily because manganites showcase emergent phenomena due to the dynamic interplay among charge, spin, orbital, and lattice degrees of freedom [1]. Some of their fascinating properties are colossal magnetoresistance and metal-insulator transitions. These properties arise from the intricate interactions among charge carriers, spin ordering, and lattice distortions, and they can be modulated by external stimuli like magnetic or electric fields. The physical attributes of manganites, such as Sm1-xSr2MnO3 (SSMO), undergo significant changes with alterations in the Sr doping percentage. Depending on the doping ratio, SSMO can exhibit ferromagnetic, antiferromagnetic, or even mixed magnetic phases [2]. The extensive variety of phenomena that can be tuned based on Sr concentration in SSMO highlights its scientific importance and makes it a compelling subject for the study of diverse properties [3, 4]. In this study, we investigated the magnetic proximity effect in SSMO bilayer and tri-layer heterostructures. Initially, we deposited a single layer of ferromagnetic metal (FMM) and an antiferromagnetic insulator (AFI) onto a SrTiO3 (STO) substrate using the pulsed laser deposition (PLD) technique. Their magnetic attributes were assessed with a SQUID magnetometer, and the results were consistent with earlier reports. Subsequently, we laid down a bi-layer stack of FMM/AFI and a tri-layer configuration of AFI/FMM/AFI on the STO substrate. We observed a marked increase in magnetic moment across these structures, indicating that the magnetic proximity effect in the heterostructures was the main contributor. In conclusion, manganite heterostructures present a promising avenue for further exploration of novel electronic and magnetic phenomena at their interfaces. References: 1. Y. Tokura, Reports Prog. Phys. 69, 797 (2006). 2. Kurubakov et al., Journal of Physics: Condensed Matter. 20, 104233 (2008). 3. Bhagwati Prasad, et al.; Advanced Materials 27, 3079 (2015). 4. Bhagwati Prasad and M. G. Blamire, Appl. Phys. Lett. 109, 132407 (2016).
magnitude in magnetization has been observed in the doped compounds because of the development of ferromagnetic properties. All the doped compounds showed an enhancement in MCE performance compared to the pristine compound. The compound La0.8Ca0.2MnO3 exhibited a maximum change in magnetic entropy of 0.07 J kg⁻¹ K⁻¹ when subjected to an applied field of 5 T. The Nd and Co co-doped La0.8Nd0.2Cr0.5Co0.5O3 compound showed the highest magnetic entropy change of 6 J kg⁻¹ K⁻¹, whereas the Gd and Co co-doped La0.8Gd0.2Cr0.5Co0.5O3 compound showed magnetic entropy change of 4 J kg⁻¹ K⁻¹, both under a 5 T applied field. Due to the substantial rise in magnetic entropy change, these materials have potential for use in magnetic refrigeration applications at low temperatures.

5:05 PM *EL07.14.05
Tunneling in Ferroelectric Heterostructures: A Tale of Two Interfaces 
Nagarajan Valanoor; UNSW Sydney, Australia

The various demonstrations of robust ferroelectricity down to a few unit cells at room temperature has triggered the quantum era of ferroelectrics. Nearly two decades ago the concept of a ferroelectric tunnel junction (FTJ) was brought to the fore leading to a flurry of activity in the field of polarization control of tunneling current and related tunneling electro-resistance (TER) effects studies. In this presentation we cover two types of new ferroelectric devices based on the tunneling effect, both founded on the control of electrode/ferroelectric interface in an II oxide heterostructure.

The first part of the talk discusses our recent demonstration of a ferroelectric resonant tunneling diode (RTD), which exploits the switchable electric polarization state of the quantum-well (QW) barrier to tune the device resistance at room temperature. We show robust room-temperature ferroelectric-modulated resonant tunneling and negative differential resistance (NDR) behaviors in all-perovskite-oxide BaTiO3/SrRuO3/BaTiO3 RTDs. The resonant current amplitude and voltage are tunable by the switchable ferroelectric polarization of the ultrathin BaTiO3 layers with the NDR ratio modulated by ~3 orders of magnitude and an OFF/ON resistance ratio exceeding a factor of 20 000. An average tunnel lifetime of 0.47 fs on the resonant states is obtained, which is orders of magnitude smaller than those obtained in semiconductor QWs. This work appears in Ma et al., Adv. Mater. 2022, 34, 2205359.

In the second study we explore how electronic phases at the interfaces can be deterministically harnessed to modulate the TER. We find a large tunneling electroresistance (TER) of 6 orders of magnitude when inserting a 0.5 nm-thick La0.8Ca0.2MnO3 layer between the Pt/BaTiO3 interface in Pt/BaTiO3/Nb:SrTiO3 ferroelectric tunnel junctions (FTJs), benefitting from the double interface effect. That is, both the BaTiO3/Nb:SrTiO3 and La0.8Ca0.2MnO3/BTO interfaces are synchronously metal or insulator phases in response to the ferroelectric polarization switching, thus amplifying the difference in resistance between the high resistance state (OFF state) and low resistance state (ON state). It is found that a thicker La0.8Ca0.2MnO3 layer leads to the decrease of the TER. This is attributed to the decreased barrier height/width at the BaTiO3/Nb:SrTiO3 interface as revealed by analysis of the electron transport mechanism. We show it occurs by Fowler–Nordheim (FN) tunneling. Our reports provide a pathway, namely interface control of the oxide heterostructure, to achieve high-performance ferroelectric tunneling devices for future oxide electronics at the nanoscale.

The speaker would like to acknowledge the support of an Australian Research Council (ARC) Discovery Project and Australian Research Council Centre of Excellence in Future Low-Energy Electronics Technologies (Project No. CE170100039) grant.

SYMPOSIUM EL08

Plasmonics and Metasurfaces—Design, Materials and Applications
April 22 - May 7, 2024

Symposium Organizers
Yao-Wei Huang, National Yang Ming Chiao Tung University
Min Seok Jang, Korea Advanced Institute of Science and Technology
Ho Wai (Howard) Lee, University of California, Irvine
Pin Chieh Wu, National Cheng Kung University

Symposium Support
Bronze
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* Invited Paper
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** Keynote Speaker
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SESSION EL08.01: Photonics Resonance Designs for Biomedical Imaging, Sensing and Spectroscopy Application
Session Chairs: Ho Wai (Howard) Lee and Pin Chieh Wu
Monday Morning, April 22, 2024
Room 340/341, Level 3, Summit

8:45 AM EL08.01.02
Integrating Surface-Enhanced Raman Spectroscopy and Electrokinetics for Bacterial Identification in Wastewater
Yinui A. Zhang, Liam Herndon, Punnag Padhy, Babatunde Ogunlade, Alexandria Boehm and Jennifer A. Dionne; Stanford University, United States

Antibiotic-resistant bacterial infections claim over 1.2M lives annually and are projected to be the main cause of death in 30 years [1]. Elevated pathogen levels in wastewater are one of the first indicators of disease outbreaks, making wastewater a powerful tool for surveilling the infections present in a community [2]. However, bacterial WBE presents outstanding challenges; current culturing or fluorescence-based methods [3] to identify bacteria are slow and costly, and not suitable for high-throughput screening of diverse bacterial species. Further, the complex substances in wastewater can interfere with chemical probes or cause false negative results.

In this study, we develop a generalized enrichment with Raman-machine learning spectroscopy (GERMS), employing surface-enhanced Raman spectroscopy (SERS) [4] and integrating it with electric fields and machine learning models [5], to enable rapid and amplification-free bacteria identification in filtered wastewater, even at low concentrations down to 10⁴ cells/mL. To
achieve this, we first synthesize gold nanorods designed to electrostatically bind with bacteria, enabling SERS measurements from the cell surfaces. We perform SERS measurements on various bacteria, including Staphylococcus aureus, Staphylococcus epidermidis, and Escherichia coli, across a concentration range spanning from $10^9$ down to $10^3$ cells/mL. Spectral clustering analysis reveals that as the concentration decreases, bacterial signals become progressively more challenging to distinguish from the background wastewater. Furthermore, we incorporate electrokinetic effects into SERS by employing gold microelectrodes to apply external electric fields and leveraging dielectrophoresis [6] to rapidly displace and enrich bacteria within minutes. Microscopy directly visualizes the enrichment of bacteria with nanorods, leading to a remarkable increase in Raman signal intensities by up to tenfold under external electric fields for bacterial concentrations from $10^9$ down to $10^3$ cells/mL. This enhancement has the potential to extend the detection sensitivity to environmentally-relevant concentrations. In addition, through data science approaches, we identify biologically significant “fingerprint” Raman peaks that characterize proteins, nucleic acids, and lipids on bacterial surfaces. This study holds promise for the rapid identification of bacterial species for wastewater-based epidemiology.


**EL08.01.03**

**Evaluating The Refractometric Sensing Performance of Plasmonic Titanium/Hafnium Nitride Nanohole Arrays**

Maha Ibrar1, Megan Knobeloch, Zachery Mccurtain, David Crandall and Sara Skrabalak; 1Indiana University Bloomington, United States

Noble metals, such as gold and silver, have conventionally been the preferred materials for plasmonic applications owing to their elevated electrical conductivity, surface plasmon frequencies within the visible spectrum, and chemical stability. However, they are increasingly expensive to utilize, incompatible with conventional CMOS process, difficulties in large-scale manufacturing, and have low melting temperatures at the nanoscale. In this perspective, refractory group IVB metal nitrides present a remarkable ability to modulate their plasmonic behavior within the visible to near-infrared range as alternatives to noble metals. These materials can exhibit exceptional resistance to high temperatures, mechanical robustness, compatibility with CMOS technology, chemical inertness, and outstanding compatibility with prevailing electronic platforms. Thus, these properties render group IVB metal nitrides, especially titanium nitride (TiN) and hafnium nitride (HfN), highly promising candidates for diverse plasmonic applications. In this study, we have investigated the optical properties of TiN and HfN thin films using variable angle spectroscopic ellipsometry, focusing on the Ar/N$_2$ ratio to improve the metallic properties of thin films. X-ray diffraction and Raman spectroscopy have been thoroughly carried out on thin TiN and HfN films to assess the stoichiometry and structure of thin films with different gas flow rates. In addition, periodic nanohole arrays of TiN and HfN (especially HfN is a hard material, called conductive ceramic) were successfully fabricated by electron beam lithography (EBL) and induced coupled plasma reactive ion etching (ICP-RIE) to evaluate the refractometric sensing of plasmonic assays. Finally, to explore the potential of plasmonic nitrides as alternatives to noble metals, the refractive index sensitivities of TiN and HfN nanohole arrays were investigated using a custom micro-spectrometry setup under different mediums. The refractive index sensitivities for TiN and HfN nanohole arrays achieved 180 and 631 nm/RUI, respectively. This study provides unique insights into the behaviors of TiN and HfN nanohole arrays in refractometric sensing applications, and the full potential of refractory metal nitrides in plasmonics is yet to be realized.

**EL08.01.04**

**Temporal Vs Stable Plasmonic Anticounterfeit Tags for Structural Health Monitoring Studies**

Hao Wang, Ashish Pandey, Nanhong Deng and Haogang Cai; New York University, United States

Proliferation of counterfeit goods has resulted in exorbitant economic fallout, device reliability issues, and health and safety concerns. Hence, developing anticounterfeit platforms has become imperative for reliable and cost-effective authentication, tracking of products, and detection of potential tamper activity. Here, we report covert anticounterfeit platforms where plasmonic nanoparticles (NPs) were used to develop tags to authenticate goods. The two platforms developed are Unique images and Physical Unclonable Functions (PUFs). Fabrication of Unique images is imperative for reliable and cost-effective authentication, tracking of products, and detection of potential tamper activity. Here, we report covert anticounterfeit platforms where plasmonic nanoparticles (NPs) were used to develop tags to authenticate goods. The two platforms developed are Unique images and Physical Unclonable Functions (PUFs). Fabrication of Unique images entails assembling plasmonic nanoparticles in arrays with the help of templates, while PUFs result from light scattering from randomly drop casted NPs. These techniques allow critical goods to be facilely tagged, and the resultant pattern from either a nanoparticle assembly or individual NPs is analyzed with darkfield optical microscopy imaging. Au and Ag NPs were prioritized due to their tailorable optical properties in the visible range. The sensitivity of metal nanoparticles (particularly Ag) to the environment was also leveraged as a monitor of structural health and to show evidence of tampering. Functionalized Ag NP inks were used to create tags that serve as temporal sensors where changes in color response were tracked with variable exposure times to ambient environmental conditions. These temporal sensors are authenticated with machine learning protocols that keep track of the optical changes with time.

**EL08.01.05**

**Scalable Manufacturing, Transfer and Integration of Metasurfaces for Biosensing**

Hao Wang, Ashish Pandey, Nanhong Deng and Haogang Cai; New York University, United States

Building upon a long-established history of plasmonic and nanophotonic biosensors, the recent advancements in metasurfaces have brought to light exciting new possibilities, such as tailor-designed high-Q resonances, spectrometer-less and imaging-based sensing. However, there is still a major challenge towards the widespread implementation of metasurface technology, for either sensing or wavefront engineering: optical metasurface manufacturing largely relies on electron beam lithography (EBL), which provide high resolution at a price of low throughput. It is difficult for EBL to offer either high-volume production or large area metasurfaces. Moreover, EBL-compatible substrates are planar and bulky, usually orders of magnitude thicker than the metasurface itself. Conventional substrates not only nullify the reduced footprint advantage of metasurfaces, but also limit their application scenarios. To address these challenges, we demonstrate scalable manufacturing of metasurfaces using the self-assembly approach known as nanosphere lithography, which is versatile in terms of material selection, nanopattern geometry and dimension tunability. Through a process called ‘Marangoni convection’, polystyrene (PS) latex beads float at the air-water interface and eventually self-assemble into hexagonally close-packed pattern upon addition of surfactant. Nanosphere hexagonal arrays can be formed on a wider range of substrates, and then used as masks for metal deposition or etching to create complementary geometries of nanohole and nanodisc arrays, respectively. Oxygen plasma is used to etch the PS beads for fine tuning of the feature size in the nanoscale. After removing and cleaning of the PS beads layer, the metallic nanopatterns can be directly used as plasmonic metasurfaces for biosensing, or used as etching masks for pattern transfer into the underlying dielectric materials. Recently, dielectric metasurfaces are drawing increasing attention for sensing applications due to their advantages of negligible ohmic loss and high-Q resonances, compared to the plasmonic counterparts. Taking gold nanohole arrays as an example, the metasurface geometric parameters are tuned by following the determination of the original PS bead size, the nanohole diameter is determined by the Oxygen plasma etch, while the thickness by electron beam deposition. We started with 600 nm PS beads assembly on glass coverslips, and etched the diameter to 360 nm for gold deposition of $50 \text{ nm}$. For the optofluidic integration, a polydimethylsiloxane (PDMS) chamber was formed in a mold, and then bonded on top of the metasurface after Oxygen plasma treatment. Microfluidic tubes were inserted to the PDMS chamber, forming inlet and outlet channels. In the medium of DI water, a transmission resonance dip was found within the visible to near-infrared range as alternatives to noble metals, the refractive index sensitivities of TiN and HfN nanohole arrays were investigated using a custom micro-spectrometry setup under different mediums. The refractive index sensitivities for TiN and HfN nanohole arrays achieved 180 and 631 nm/RUI, respectively. This study provides unique insights into the behaviors of TiN and HfN nanohole arrays in refractometric sensing applications, and the full potential of refractory metal nitrides in plasmonics is yet to be realized.

**EL08.01.06**

**Terahertz Monitoring of Gas-Matter Interactions: Exploring Interatomic and Interfacial Dynamics through Palladium Nano-Film Hybrid Metasurfaces**

Jinwoo Lee1,2, Jongsu Lee1, Geon Lee1,2, Ryu Yang-Sang2 and Minah Seo1,2; 1Korea Institute of Science and Technology(KIST), Korea (the Republic of); 2Korea University, Korea (the Republic of); 3Seoul National University, Korea (the Republic of)

Terahertz (THz) technology is an attractive optical sensing platform that offers accurate approaches for the real-time investigation of intrinsic materials in non-invasive and non-contact manners. In addition, using metasurfaces that have been extensively researched recently, diffraction-limit and absorption cross-section-limit can be overcome [1]. Here, we monitored molecular dynamics by gas-matter interactions including interatomic and interfacial reactions such as absorption, desorption, adsorption, and catalytic reaction. In-situ THz measurement using nanometer-sized systems introduced to the Palladium (Pd) based interatomic and interfacial gas-matter interactions. Interatomic interaction which is atomic scale changes can be measured using our geometrically optimized nano-slot structure, which consists of a narrow gap of approximately 14 nm between a gold wall and a deposited Pd metal thin film. Furthermore, we manipulated nano-slot structures to maximize the sensitivity of THz signals in terms of water, formed by the Pd catalytic reactions, and their absorption. Our proposed experiment aims to analyze the dynamics of interatomic hydrogenation, interfacial oxygen adsorption, and water-forming reactions in a highly consistent and dependable manner, enabling real-time analysis [2]. The molecular dynamics are interpreted by THz transmission measurement under the various gas concentrations including N$_2$, H$_2$, and O$_2$. The molecular dynamics can be determined by
inspecting resonance frequency shifts and transmittance changes in the transmitted resonance signals that were filtered by our nano-slot structures. The Pd hydrogenation process, the oxygen adsorptions, and the catalytic water formation reactions according to the various concentrations of H₂, O₂, and N₂ were dynamically measured by resonance frequency and transmittance response.

The atomic scale response, such as hydrogen absorption, desorption into the Pd lattice, and catalytic water formation response which is a relatively huge scale can be measured in a reliable manner using such a long wave-length light. In addition, by interpreting inclinations that are plotted on the map composed of the amount of resonance frequency and transmittance response, not only the three different dynamics can be classified, but also a complex hidden process of water-forming reactions can be tracked.

Acknowledgement: NRF (2023R1A2C2003898, CAMM-2019M3A6B303638, 2021R1A2C2009236), KIST (2E32451)

References

Keywords: Metamaterial, Terahertz spectroscopy, Palladium film

10:00 AM EL08.01.07
Passive and Active Metasurfaces for Wireless Telemetry Sensors
Hanwei Wang, Xiaodong Ye, Yulei Shen, Yun-Sheng Chen and Yang Zhang; University of Illinois Urbana-Champaign, United States

In this talk, I will discuss both the theoretical design and experimental realization of metasurfaces aimed at enhancing the efficiency and operational range of wireless charging for surgically implanted biosensors. I will delve into several design concepts of metasurfaces including auto-reconfigurability, magnetic mode forming, and Parity-Time (PT) symmetric metasurfaces, which hold the potential for achieving unity efficiency. My discussion will extend to the inverse design principles and their impact on mode optimization. Further, I will explore the practical applications of these theoretical concepts by introducing the metasurface as a wearable device designed to sustainably power a surgically implanted bio-potential sensor, encompassing electromagnetic compatibility with both in vitro and in vivo demonstrations.

10:00 AM EL08.01.08
Designing Spoof Plasmonic Metasurfaces for Microwave Frequencies and Applications in Biological Processing
Zachary Nichols and Chris D. Geddes; University of Maryland, Baltimore County, United States

Plasmonic metasurfaces are a growing subclass of metamaterials which are materials whose properties are based on their structure rather than their composition and can be tuned and designed for different applications as a result. Metasurfaces are the two-dimensional analogs of three-dimensional metamaterials and plasmonic metasurfaces are those that use electron oscillations in metals, termed plasmons, to achieve their desired properties. Most applications of plasmonic materials have been limited to the visible and UV frequency ranges of light since lower frequency photons have insufficient energy to excite plasmons in metals, however “spoof plasmons” which mimic normal plasmons, have been created in the terahertz and microwave frequency ranges by utilizing subwavelength metal structures in periodic arrays. Spoof plasmonic metasurfaces (SPMs) are metasurfaces that can mimic plasmonic metasurfaces at lower frequencies by utilizing properties of spoof plasmons. In this work, we have designed several SPMs for use in the microwave frequency range using a combination of computational modeling and physical testing. SPMs were designed in-silico using finite-difference time-domain (FDTD) methods and then fabricated for physical testing with microwave irradiation. Once designed, these SPMs were assessed for their utility as a sample processing platform for biological samples such as microbes, nucleic acids, and proteins in a variety of laboratory assays such as genomic sequencing or diagnostic polymerase chain reaction (PCR). While many applications of metasurfaces to biological problems have been focused on sensing biological signals and imaging, this work is focused on using their properties to process biological samples via light-matter interactions and their products. Thus far this work has shown promise in applying SPMs to a new area of biological processing as well as exploring existing metasurface design principles for alternative applications.

10:15 AM EL08.01.10
Fluorophore Induced Plasmonic Current (FIPC) for The Detection of Biological Species for The Purposes of Assay Development and Onsite Detection
Dan Pierce; University of Maryland, United States

The recent COVID-19 pandemic has made it abundantly clear that there is a growing need for the capacity to have analytically precise detection of pathogens be performed as quickly as possible for the best public health outcome. Fluorophore Induced Plasmonic Current (FIPC) is a newly developed testing modality that is based upon the principles of modern fluorescence detection, but differs in its implementation and applicability. Where a traditional fluorescence-based assay would require a laboratory environment and an expensive fluorimeter, an FIPC only requires a current detection device and an excitation source to achieve similar results. Based on the properties of FIPC wherein a fluorophore that is excited close to the surface of a plasmonically active metal nanoparticle film is able to transfer a portion of its excitation energy to the film, these proposed assays revolve around this property for the detection of various fluorescent tags and probes for the analytical detection of DNA and proteins. The goal of this presentation is to demonstrate the advances made in the assay development side of FIPC research, and to highlight its strengths and identify its shortcomings when compared to traditional fluorescence detection.

10:30 AM EL08.01.11
Low-Loss Plasmonics with Nanostructured Potassium and Sodium-Potassium Liquid Alloys
Ankun Yang; Oakland University, United States

Alkali metals have low optical losses in the visible to near-infrared (NIR) compared to noble metals. However, their high reactivity prohibits the exploration of their optical properties. Recently sodium (Na) has been experimentally demonstrated as a low-loss plasmonic material. Here we report on a thermo-assisted nanoscale embossing (TANE) technique for fabricating plasmonic nanostructures from pure potassium (K) and Na-K liquid alloys. We show high-quality-factor resonances from K as narrow as 15 nm in the NIR, which we attribute to the high material quality and low optical loss. We further demonstrate liquid Na-K plasmonics by exploiting the Na-K eutectic phase diagram. Our study expands the material library for alkali metal plasmonics and liquid plasmonics, potentially enabling a range of new material platforms for active metamaterials and photonic devices.

SESSION EL08.02: Metasurfaces, Plasmonics and Breaking News Presentations
Session Chairs: Yao-Wei Huang and Min Seok Jung
Monday Afternoon, April 22, 2024
Room 340/341, Level 3, Summit

1:45 PM EL08.02.01
Meta-Optics for Image and Spectral Classification
Jason G. Valentine; Vanderbilt University, United States

Here, we demonstrate how meta-optics can be designed, and realized, to work in concert with a digital back-end for a range of tasks including image and spectral classification. In the case of image classification, the meta-optic serves to off-load computationally expensive tasks into an optical front-end, speeding computational speed while lowering energy consumption. For spectral classification, meta-optics serve as complex filters which are used in conjunction with a digital neural network to achieve a compact flow cytometer capable of classifying up to four unique fluorophores, and their combinations.

2:15 PM EL08.02.02
Printable, Emissivity-Adaptive and Albedo-Optimized Radiative Covering for Dynamic Radiative Thermal Management
Jiachen Li1,2,1; Kaichen Dong1,3; Ruizhan Guo1; Tiancheng Zhang1 and Junqiao Wu1,2,1; University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States; 3Tsinghua University, China

Radiative cooling technology utilizes thermal emission to cool buildings and uses outer space as a natural heat sink. Traditional radiative cooling materials focus on static, cooling-optimized material properties to maximize the cooling power, but the constant strong cooling causes overheating in cold climates, which increases energy budget in the HVAC system. Recently, advances in temperature-adaptive structures have been made to solve the overheating issue. However, great challenges remain in their fabrication feasibility, and their unoptimized solar heating that may override the radiative cooling benefit.
In this work, we develop a printable, emissivity-adaptive and albedo-optimized covering (PEAC) based on recyclable materials with roll-to-roll fabrication. With a metasurface embedded with the phase change material vanadium dioxide, PEAC automatically switches its sky-window emissivity from 0.25 to 0.85 when the surface temperature exceeds a preset transition temperature, whereas delivering an albedo that is optimized for maximal year-round energy saving or thermal comfort in a given climate. Numerical simulations and outdoor experiments show that PEAC outperforms radiative cool roofs in terms of annual energy saving in most climates, especially those with substantial seasonal variations. PEAC can also be applied to objects in addition to building roofs and walls, such as space objects, tents, and vehicles.

2:30 PM BREAK

3:00 PM EL08.02.04
Low-Dimensional Phonon-Polariton Materials for Higher-Order Hyperbolic Dispersion and Efficient Thermal Transport Guanyu Lu1, Zhihao Pan1, Christopher R. Gubbins2, Ryan A. Kowalski1, Xiun Li1, James R. McBride1, Rinkle Juneja2, Mackey Long1, Lucas Lindsay3, Simone De Liberato2, Deyu Li1 and Joshua D. Caldwell1; 1Vanderbilt University, United States; 2University of Southampton, United Kingdom; 3Oak Ridge National Laboratory, United States

Phonon polaritons are stimulated by coupling infrared photons with the polar lattice vibrations. Such quasi-particles offer low-loss, highly confined electromagnetic energy propagation at subwavelength scales. Here, we discuss the launching and manipulation of higher-order hyperbolic phonon polaritons (HPhPs) in low-dimensional materials.1 Additionally, we discuss how non-equilibrium phonon polaritons in these materials can further enhance thermal transport as additional energy carriers.2 HPhPs in low-symmetry polar crystals offer ray-like light propagation with out-of-plane or in-plane hyperbolic wavefronts at deep-subwavelength scales. While hyperbolic dispersion in HPhPs implies multiple propagating modes at a given frequency, experimentally launching and probing the higher-order modes, especially for in-plane HPhPs, remains challenging. We report the experimental observation of higher-order in-plane HPhP modes, stimulated on the 3C-SiC nanowire (NW) α-MoO3 heterostructures. This demonstrates the advantage of leveraging both the low-dimensionality and low-loss nature of polar NWs to launch higher-order HPhP modes within two-dimensional α-MoO3 crystals.

One-dimensional polar NWs not only bridge the wavevector mismatch between free-space light and the higher-order, high-momenta HPhPs but could also significantly impact thermal transport. While optic phonons typically contribute minimally to thermal conductivity, their hybridization with photons as phonon polaritons could facilitate conductive heat transfer in nanostructures. Although some signs of progress in phonon-polariton-mediated heat conduction have been made, experimental efforts so far suggest only very limited contribution from such modes. Here, by combining nanoscale real-space mapping of phonon polaritons within 3C-SiC NWs with direct thermal transport measurements of these NWs (coated with gold as an efficient polariton launcher), we unambiguously demonstrate phonon-polariton-mediated heat conduction, resulting in orders of magnitude enhancement compared to equilibrium predictions.


3:15 PM EL08.02.05
An Abnormal Single Molecule Detection by Plasmonic InGaN Quantum Dots Thi Anh Nguyen Nguyen and Kun-Yu Lai; National Central University, Taiwan

Detecting single molecules is a formidable challenge. Surface-enhanced Raman spectroscopy (SERS) is one of the few techniques that can achieve the goal. To verify the presence of single molecules with SERS, the biaxial etalon is the most adopted approach since it is a statistical result from thousands of spectra, rather than the conclusion based on the blinking signals at a few selected spots. However, the biaxial method relies on an undesirable nature of SERS, i.e., the hot spot (SERS-active regions) is too small (< 10 nm) to cover two or more molecules. Since it is extremely difficult to control the size of a hot spot in a scalable manner, only a very limited portion (~1%) of the diluted molecules can yield detectable Raman signals.

In this work, we demonstrate an abnormal single-molecule signal by SERS, covering 89.6% of the scanned spots. The result was achieved by making the hot spot big enough to simultaneously boost the signals from two or more single molecules. The hot-spot expansion was accomplished by coupling the localized surface plasmons at every Au nanoparticle with electrons confined by the subsurface InGaN quantum dots (QDs). This SERS configuration allows all of the dense Au nanoparticles to become the intensity-enhancing boosters. Thus, any single molecule adsorbed on the SERS substrate can be easily captured by the Au-QD complexes, making single-molecule detection a prevailing event, instead of a rare instance.

With the greatly expanded SERS-active region, the single molecules can deliver stable signals by staying within the “hot surface” before and after the thermal diffusion upon laser excitation. This is not achievable with the conventional hot spots, where blinking signals are often observed by the SERS detection of diluted analytes. Our approach not only changes the biaxial principle, but also allows researchers to analyze the molecular dynamics with reliable data.

SESSON EL08.03: Thermal Emission with Nanostructure and Nonreciprocal System
Session Chairs: Ho Wai (Howard) Lee and Pin Chieh Wu
Monday Afternoon, April 22, 2024
Room 340/341; Level 3, Summit

3:30 PM EL08.03.01
Harnessing The Infrared: Materials and Structures for Breaking Reciprocity and Control of Thermal Radiation Harry A. Atwater; California Institute of Technology, United States

In this talk I will discuss materials and photonic design concepts that allow us to experimentally observe breaking of optical reciprocity for thermal radiation, as well as metastructures that allow for considerable control of the thermal emission angular distribution. Thermal radiation—the process through which all objects with a finite temperature radiate electromagnetic energy—has generally been thought to obey reciprocity, where the absorbed and emitted radiation from a body are equal for a given wavelength and angular channel. This equality, formalized by Gustav Kirchhoff in 1860, is known as Kirchhoff’s law of thermal radiation and has long guided designs to control the emitted radiation. There is considerable interest and numerous theoretical proposals for design of nonreciprocal absorbers that violate the Kirchhoff thermal radiation law. Until recently however, there were no experiments demonstrating this concept. I will discuss direct observation of the inequality between the spectral directional emissivity and absorptivity for an InAs photonic metamaterial arising from the non-diagonal permittivity tensor of InAs at the epsilon-near-zero condition under an externally applied magnetic field. The magneto-optic response of magnetic Weyl semimetals is characterized by non-diagonal permittivity governed by the nontrivial Berry curvature that exists between recombinant Weyl nodes. I will also discuss reciprocity breaking in the magnetic Weyl semimetal Co3Sn2S2, confirmed via observation of a net reflectance modulation that is nearly an order of magnitude higher than that of the typical inverse magneto-optical Kerr effect in ferromagnets, without the concurrent application of any external magnetic field, and discuss implications of these findings.

4:00 PM EL08.03.02
Thermal Imaging through Hot Emissive Windows Civil Samuel Prasad1, Henry O. Everitt2 and Guru V. Naik1; 1 Rice University, United States; 2 DEVCOM Army Research Laboratory - South, United States

The challenging problem of enhancing thermal emission in some directions while suppressing it in others is exacerbated for hot windows because they must remain transparent in the same spectral window. This complex problem has prevented applications such as infrared imaging through hot windows, whose own thermal emission is strong enough to blind the camera [1]. Here, we demonstrate a solution to this long-standing challenge by replacing the hot emissive window with one coated with an asymmetrically emitting thermal metasurface. By engineering the imaginary index of refraction to produce an asymmetric spatial distribution of absorption losses in its constituent nanoscale resonators, the metasurface suppresses thermal emission towards the camera while being sufficiently transparent for thermal imaging. We create the constituent resonators of the asymmetric loss metasurface by coupling nanoscale Si discs with distinct losses [2, 3, 4]. These silicon nano-discs separated by SiO2 spacer support a quasi-bound state in the continuum (q-BIC) mode. These photonic modes couple to each other under normally incident input excitation with coupling strength that can be tuned by varying the spacer thickness. We identify that, when the resonators are weakly coupled, the eigenmodes of the system are distributed asymmetrically across the resonators with a large fraction of photon energy confined in the lossless resonator and hence causes strong asymmetry in the far-field thermal radiation from the metasurface [4].
The asymmetry in energy confinement also causes the resonance dip in the transmission spectra to be narrow and as a result, enhances the overall transmission in the spectral bandwidth of the thermal camera. Thus our metasurface design, inspired by non-Hermitian optics, balances the need for good transmittance and emissivity asymmetry required to achieve thermal imaging through an emissive hot window. Our metasurface window, operating at 873 K, enhanced the thermal imaging contrast by nearly 2 times when compared to a conventional window at the same temperature. This demonstration illustrates the power of using the imaginary index as a design parameter for nanophotonic thermal devices, thereby enabling novel functionalities for energy, imaging, and sensing applications.

Reference


Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]

11:15 AM EL08.04.03
Zero Diffraction: A Novel Approach for High-Contrast Switching of Light
Patrick Goerm, Andreas Henkel, Sven O. Schumacher, Christopher Knoth and Maximilian Buchmüller
University of Wuppertal, Germany

The ultrafast electro-optic Pockels effect is widely used for modulating light in terms of intensity, phase, and polarization, because controlling these parameters is the basis of modern information and communication technology. However, other applications, including displays, scanners, or solar concentrators, also require the control of geometric parameters of light, such as its pathway in space. Until today, the efficient spatial control of light remains challenging.

The common approach for achieving spatial control involves modifying optical components. These modifications often rely on the mechanical movement of lenses, mirrors or gratings, which is much slower compared to modulations based on the Pockels effect. Recent reports propose novel approaches based on interference. [1] In these cases, the optical components remain mostly unchanged, but their interaction with light strongly depends on the light’s properties like phase or momentum leading to a limited set of operation parameters.

Here, we propose a novel approach for controlling the diffraction of light at a leaky waveguide grating using the ultra-fast Pockels effect. The leaky waveguide grating is illuminated by two symmetrical incident plane waves. By tuning the relative phase between the two waves, the diffraction can be entirely suppressed, termed zero diffraction. [2] Therefore, this phenomenon enables to control the diffraction of light with infinite contrast. Remarkably, it not only occurs at singular spectral positions but on continuous curves in the energy–momentum space.

In analogy to our recent report, we first investigate a standalone grating and a symmetric waveguide grating under symmetric dual-plane wave incidence. Simulations using rigorous coupled wave analysis (RCWA) show that the diffraction efficiency can be controlled with an average contrast below 100. Zero diffraction cannot be found in either of these cases.

In the next step, we introduce leakiness and find zero diffraction for plane waves. We demonstrate the experimental feasibility of these theoretical findings using real laser beams instead of plane waves. For that purpose, a symmetric waveguide grating is placed between two lithium tantalate (LiTaO$_3$) wafers of opposite crystal direction. The high refractive index of the LiTaO$_3$ introduces leakiness, while the opposite crystal direction maximizes the relative phase shift when applying an electric field across the entire waveguide stack. After creating symmetrically propagating beams, we measure the optical power diffracted at the waveguide grating as a function the applied field strength and find a maximum contrast of 1236.

This way, we also show how zero diffraction can be applied in a nonlinear waveguide in order to control trapping and detrapping of light. The position where a directed laser beam is detrapped from the surface can be selected with an electric field without any mechanics. Laser displays based on zero diffraction would be more efficient than liquid crystal displays as are not based on absorption. Instead, they extract the light only where it is needed. At the same time, such laser displays could be completely transparent and promise immense possibilities in terms of color rendering due to the narrow spectrum of the laser.

[1] M. Meudt, A. Henkel, M. Buchmüller, and P. Görrn, 

11:30 AM EL08.04.04
Metamaterial-Controlled Parity-Time Symmetry in Non-Hermitian Wireless Power Transfer Systems
Hanwei Wang, Xiaodong Ye and Yang Zhao; University of Illinois at Urbana-Champaign, United States

Wireless power transfer (WPT) technologies contain two main categories, radiative and non-radiative. Non-radiative WPT utilizes the magnetic near-field to carry energy and is more commonly used due to its advantages of high-power volume and safety. The receiving (Rx) resonator couples with the transmitting (Tx) resonator through magnetic mutual induction. Inductive WPT systems can be described as non-Hermitian systems through coupled-mode theory. Power transfer in such systems is efficient when forming PT-symmetric states, which could be guaranteed by the physical symmetry in a strong coupling regime. However, spontaneous symmetry breaking happens in the weak coupling regime as the increasing of the Tx-Rx separation, where the resonant states become anti-PT-symmetric.

Relay resonators can be used to increase the overall coupling and, therefore, increase the maximum Tx-Rx separation for the PT-symmetric state. The PT-symmetric states in such systems are also known as the topological edge state for magneto-inductive waves, which have been used for mid-range WPT and frequency-robust WPT. However, one drawback of the relay resonators is the potential involvement of higher order resonant states of the system; many of the states are anti-PT symmetric. To avoid these states, spatial arrangement of the relay resonators needs to be symmetric and the geometry of the Tx and Rx resonators need to be identical. Such requirements are impractical in many applications, such as free-positioning WPT.

Metamaterials, demonstrating excellent ability in manipulating electromagnetic and acoustic fields and waves, show great potential in solving this challenge. Researchers have developed metamaterials to control the PT-symmetry for above-unity transmission and reflection, nanoscale sensing, and coherent perfect absorption. However, such an approach remains challenging for WPT systems due to the lack of accurate control in the metamaterial’s resonance mode. In our previous works, we have demonstrated a quasi-Hermitian metamaterial that can achieve on-demand field-shaping for magnetic resonance imaging and WPT. In this conference presentation, we will extend the theory by showing metamaterial-controlled PT-symmetry in a non-Hermitian WPT system.

We derive the states of the system and show that a PT-symmetric state can be achieved with certain metamaterial’s configuration. The sizes of the Tx and Rx do not need to be identical, and their physical positions are not limited as long as operating in the strong coupling regime. We prove that the state is stable when the system operates in a strong coupling regime. We theoretically and experimentally demonstrate the transition between anti-PT-symmetric and PT-symmetric states controlled by the metamaterial’s configuration. We further show that the PT-symmetric state can be achieved with different spatial arrangements of the Rx resonator. This technique largely increases physical freedom of Tx and Rx and provides a paradigm for designing many-body WPT systems.

11:45 AM EL08.04.05
Ultrafast Collapse of Molecular Polaritons to Pure Molecular Transition in Plasmonic Photoswitch-Nanoantennas
Joel Kuttruff1, Marco Romanelli2, Esteban Pedroza-Villalmanzo3, Jonas Allerbeck4, Jacopo Fregoni5, Valeria Saavedra-Becerril2, Ioakim Andréasson6, Daniele Brida7, Alexandre Dmitriev3, Stefano Corni2 and Nicolò Maccaferri6
University of Wuppertal, Germany

Zero diffraction, a phenomenon that can suppress diffraction at a leaky waveguide grating, is achieved by illuminating the grating with two plane waves. This approach was applied experimentally in a symmetric waveguide grating placed between two lithium tantalate (LiTaO$_3$) wafers of opposite crystal direction. The high refractive index of LiTaO$_3$ introduces leakiness, while the opposite crystal direction maximizes the relative phase shift when applying an electric field across the entire waveguide stack. After creating symmetrically propagating beams, the diffraction is completely suppressed as the applied field strength increases.

This method can be used to control the spatial distribution of light, which is beneficial for applications in wireless power transfer (WPT) and other optical technologies. The technique can be extended to create optical elements with complex functionalities, such as beam shaping and spatial filtering, using metamaterials to control the PT-symmetry for above-unity transmission and reflection, nanoscale sensing, and coherent perfect absorption. However, implementing this approach remains challenging due to the requirement of accurate control in the metamaterial's resonance mode.

In our previous work, we demonstrated a quasi-Hermitian metamaterial that can achieve on-demand field-shaping for magnetic resonance imaging and WPT. In this conference presentation, we will present our recent advancements in extending the theory to show metamaterial-controlled PT-symmetry in a non-Hermitian WPT system. We will derive the states of the system and show how to achieve a PT-symmetric state with certain metamaterial's configuration. The sizes of the Tx and Rx do not need to be identical, and their physical positions are not limited as long as operating in the strong coupling regime. We prove that the state is stable when the system operates in a strong coupling regime.

We theoretically and experimentally demonstrate the transition between anti-PT-symmetric and PT-symmetric states controlled by the metamaterial’s configuration. We further show that the PT-symmetric state can be achieved with different spatial arrangements of the Rx resonator. This technique can significantly increase the physical freedom of Tx and Rx and provides a paradigm for designing many-body WPT systems.

SESSION EL08.05: Low Dimensional Metasurfaces and Metamaterials
Session Chairs: Ho Wai (Howard) Lee and Jason Valentine
Active Exciton Metasurfaces Using Exciton Polaritons in Monolayer TMDs

Thomas Bauer and Jorik Van de Groep; University of Amsterdam, Netherlands

Monolayer transition metal dichalcogenides (TMDs) like WS2 exhibit strong exciton resonances in the visible spectral range that govern their optical response. The excitonic light-matter interaction in these 2D quantum materials is inherently strong and highly tunable, which can be leveraged to realize mutable flat optical elements as well as novel spin-valley coupled information carriers. To unleash the full potential of exciton-enhanced wavefront shaping and active optical switching in atomically thin metasurfaces, it is essential to gain a detailed understanding of the exciton’s quantum mechanical properties and its coupling to hybrid light-matter quasiparticles known as exciton polaritons.

Recently, it was shown theoretically that excitonic polaritons can exist as excitations from the continuum of three-dimensional electromagnetic modes even for atomically thin layers of materials. Coupling to such 2D exciton polaritons (2DEPs) was subsequently demonstrated experimentally in a free-standing monolayer membrane via photoluminescence excitation and outcoupling through a photonic crystal. Realizing such a strongly coupled light-matter state in on-chip photonic environments promises new opportunities for tunable wavefront shaping, photonic sensing, as well as probing of fundamental quantum-mechanical properties of light scattering by excitons.

However, direct integration of coherently coupled 2DEP functionality into nanopatterned monolayers on substrates has so far remained elusive due to the stringent requirements on the dielectric environment as well as monolayer quality to support 2DEPs.

Here, we experimentally demonstrate active control of coherent coupling to 2DEPs in a monolayer of WS2 on a quartz substrate, allowing for enhanced photonic functionality given directly by the geometry of the monolayer itself. We accomplish guiding along the monolayer by managing the refractive index contrast between the top and bottom side via a 230nm thick capping layer of PMMA. Using guided mode resonances in sub-wavelength gratings structured in nm-sized continuous WS2 monolayers, we realize polarization-selective dynamic phase control of light scattered coherently off the hybrid light-matter state. The sub-wavelength nature of the grating together with the high quality and homogeneity of the initial monolayer leads to an electrically and/or thermally tunable phase modulation of the reflected light at an excitation close to the 2DEP guided mode resonance.

Further utilization of photonic metasurface concepts allows for active amplitude switching of higher diffraction orders via binary blazed gratings, leading to expected modulation depths exceeding 80% stemming from an atomically thin optical element. This opens a path to full active control over the complex optical response in tailored atomically thin metasurfaces via exciton resonance tuning.

Asymmetric Propagation of Hyperbolic Polaritons in MoO3 and β-Ga2O3 Heterostructures

Saurabh Dixit1, Maximilian Obst2, José Á. Cuervo3, Giulia Carini4, Ryan Kowalski1, Aitana T. Martin-Luengo1, Gonzalo Alvarez Perez3, Katja Diaz-Granados Santos1, Aditha Senarath1, Niclas Müller4, J. Michael Klop6, Lukas Eng5, Susanne Kehr1, Thomas G. Folland6, Pablo Alonso Gonzalez2, Alex Paarmann4 and Joshua D. Caldwell1; 1Vanderbilt University, United States; 2The Pennsylvania State University, United States; 3Technische Universität Dresden, Germany; 4University of Oviedo, Spain; 5Max Planck Society, Germany; 6Helmholtz-Zentrum Dresden-Rossendorf, Germany; 7The University of Iowa, United States

Opposite signs of the dielectric permittivity along different principal directions of optical materials (hyperbolic anisotropy) allow for exotic quasiparticles to be formed due to the hybridization of photons and phonons (phonon polariton) in the mid-infrared spectral region. Phonon-polaritons in such hyperbolic materials enable the confinement of electromagnetic waves at the nanoscale, which offers mechanisms to induce large enhancements of the optical response and reduce the footprint of photonic devices such as molecular sensors, polarizers, waveplates, optical modulators, IR sources and detectors, and many others. To design nanophotonic devices, it is necessary to engineer the characteristic features of phonon polaritons, like propagation direction and distances. It has been demonstrated that characteristic features of hyperbolic phonon polaritons can be engineered via the choice of crystal symmetry. Hyperbolic polaritons in crystals with varying symmetries from hexagonal, such as boron nitride (h-BN), exhibit isotropic propagation in plane, whereas reducing to orthorhombic structures like MoO3 and V2O5, results in directional propagation. Monoclinic systems, such as β-Ga2O3 or CdWO4, with further reduced symmetry exhibit exotic phenomena in the form of shear, whereby the polaron wavelength and direction of propagation change with changing frequency. This provides an additional degree of freedom to manipulate propagation polarization. By employing twisted low symmetry structures, such as twisted slabs of MoO3, highly directional propagation with minimal divergence can be observed (canalization) at specific ‘magic’ angles. Yet, it remains unclear if such canalization can be observed in twisted structures of different Bravais lattices. Here, we investigate heterostructures of MoO3 (orthorhombic) and Ga2O3 (monoclinic) to determine the role of twisting with non-degenerate polaron resonances, as well as the potential influence of shear. By investigating a series of MoO3 slabs twisted with respect to the a-axis of β-Ga2O3 we observed the change in the direction of propagation along with asymmetric dispersion via a scattering-type SNOM coupled to a free-electron laser. It is determined that the high anisotropy in the propagation in the twisted structure is driven principally by the twist angle, rather than the inherent shear in the underlying β-Ga2O3, indicating that the propagation direction can be dictated via twist angle, making such heterostructure platforms designable for future nanophotonic devices such as sensors, chiral sources, IR imaging components, and many others.
We achieve a dynamically tunable optical response by integrating an electro-optically tunable lithium niobate layer (LNO) into the resonant metasurface structure and introducing indium tin oxide (ITO) interconnects. By applying electrical bias, we achieve a dynamically tunable phase shift of 236° when the refractive index of the LNO layer varies between 2.212 and 2.208. The optical efficiency of the designed metasurface is >80% for all the considered values of the applied bias, and the Q-factor of the considered resonance is 40,000. In alternative implementations, we use ITO or tungsten disulfide (WS₂) as dynamically tunable materials and present realistic active metasurface designs adapted to the choice of the active material. Finally, we analyze the beam steering performance of the designed metasurfaces considering the cases of both two-dimensional and one-dimensional beam steering.

The designed high-efficiency metasurfaces could be useful for a number of applications such as free-space optical communications, light detection and ranging (LiDAR), and laser additive manufacturing.


2:45 PM EL08.05.05
Weak Coupling of WS₂ to Plasmonic Surface Lattice Resonance

Stanislav Tsioi, Marc Christophersen, Joseph A. Christodoulides, Hsun Jen J. Chuang, Paul D. Cunningham, Adam D. Dunkelberger, Kathleen M. McCready, Nicholas Prosia and Igor Vurgaftman; U.S. Naval Research Laboratory, United States

Weak coupling of light emitters to optical cavities facilitates efficient photon extraction by directing their emission into cavity modes instead of random directions in free space. Monolayer transition metal dichalcogenides (TMDs) are 2D semiconductors with the band direct gap attractive for future nanoscale optoelectronics. The present experimental work investigates weak coupling of monolayer WS₂ to a metasurface cavity, consisting of a lattice of plasmonic nanodisks and supporting surface lattice resonances (SLRs) propagating in its plane. The nanodisks were fabricated from aluminum and WS₂, mechanically transferred on top of the cavity. Angle-resolved photoluminescence (PL) measurements show efficient light emission by WS₂ into the SLRs. The most efficient emission appears to take place into spectrally narrow modes resulting from interference of two counter-propagating SLRs, a previously unreported behavior in metasurface cavities. The obtained results suggest the opportunity to control the interference modes via geometrical factors of the lattice and thus tune the strength of its coupling to emitters, including the possibility of strong coupling.

3:00 PM BREAK

SESSION EL08.06: Nanophotonics and Plasmonics
Session Chairs: Yao-Wei Huang and Arka Majumdar
Tuesday Afternoon, April 23, 2024
Room 340/341, Level 3, Summit

3:30 PM EL08.06.01
Plasmon Enhanced Light Emission in Metal Halide Perovskite Nanowires

Tintu Kurikko1, Qingyu Wang1, Hao Sha2, Shengfu Yang2 and Robert A Taylor1; 1University of Oxford, United Kingdom; 2University of Leicester, United Kingdom

Photonic nanowires based on semiconductor materials have potential applications in light generation, propagation, detection, and amplification at the nanoscale and play a key role in the development of integrated photonic/electronic devices. To achieve the best optical performance for these applications it is crucial to enhance the photon conversion efficiency of the nanowires. A promising way to enhance light emission from nanowires is to combine semiconductors with noble metals. The strong confinement of electromagnetic field resulting from plasmonic structures can effectively transfer surface plasmon resonance energy to semiconductors via excited electrons and thus effectively enhance the photoluminescence (PL) yield. However, the synthesis of hybrid metal-semiconductor nanowires having desirable optical properties has proven challenging due to the non-wetting between the two types of materials.

Here we report plasmon light emission from a hybrid nanowire consisting of noble metal nanowire and semiconductor nanowire materials. The demonstration is performed in a cesium lead halide perovskite-based four-layer structure (CsPbBr3/PMMA/Ag/Si) designed to limit plasmonic losses in the metal while exhibiting efficient surface plasmon–photon coupling at moderate power. We used solution processing to make the nanowires, which were then spin-coated onto a Si substrate coated with Ag nanoparticles. These were produced by using quantized vortices in superfluid helium, which circumvents the non-wetting between the two types of materials. We employ temperature-dependent micro-photoluminescence spectroscopy (from 4 K to 300 K), to study the optical properties of the nanowires. We excite the individual nanowires by considering several configurations with Ag nanoparticle diameters ranging from 7 to 10 nm and PMMA layer thicknesses ranging from 5 to 25 nm to better understand the optical performance. The study, conducted with 100 fs laser pulses at a repetition rate of 76 MHz and at an excitation wavelength of 400 nm reveals that a 5 nm thick PMMA layer and 7.5 nm sized Ag nanoparticles enhanced the PL intensity by approx. 40% compared to pure semiconductor structures at 4 K. In addition, we investigate the emission dynamics of carriers and excitons in the nanowires using time-resolved photoluminescence spectroscopy techniques. Observation shows enhanced carrier recombination dynamics due to plasmonic interactions with the perovskite. These results show a potential way to excite hybrid nanowires at sufficiently low photon density so that single photon excitation/emission could be possible from these structures. Moreover, this fundamental demonstration confirms a proof-of-concept for further work involving plasmon-enhanced light emission from core-shell metal-semiconductor nanowires and opens the door for realizing lead halide perovskite-based micro and nanolasers in the visible range and more broadly for developing on-chip nanophotonic devices.

3:45 PM EL08.05.04
Functional Materials for Next Generation Photonic Chips

Volker J. Sorger, Nicola Peserico, Russell Schwartz, Hao Wang, Chandraman Patil and Hamed Dahir; University of Florida, United States

Emerging and functional materials are critical for next-generation optoelectronic device performance, energy efficiency, and application capabilities. In this presentation we share recent developments on efficient, fast, and compact electro-optic modulators, as well as sensitive photodetectors with high gain bandwidth products, as part of advanced integrated photonic circuits. The second part of the presentation then shows how these emerging device-level technologies enable performance gains for photonic-electronic heterogeneous integrated AI chips to accelerate machine learning applications such as matrix-matrix multiplications and convolution operations.

4:15 PM EL08.06.03
Disordered Meta-Doublets for Unidirectional and Synergetic Imaging in The Mid–Infrared

Roni Audhakas, Maksym Zhelyeznyakov, Anna Wirth-Singh and Arka Majumdar; University of Washington, United States

Recent advances in metamaterials have enabled the realization of complex optical functionalities within a compact form factor. The vast number of design degrees of freedom in such systems provides the ability to manipulate optical waves in the spatial and spectral domain, thereby enabling the development of photonic devices for a broad range of applications. Here, we propose an all-silicon metamaterial platform for advanced imaging applications of the mid-infrared wavelength range. Specifically, we design large aperture, all-silicon meta-optic doublets for use in the mid-infrared wavelength range. We employ temperature-dependent micro-photoluminescence and use a CsPbBr₃/PMMA/Ag/Si four-layer structure designed to limit plasmonic losses in the metal while exhibiting efficient surface plasmon–photon coupling at moderate power. The phase profiles of our optimized unidirectional and synergistic imaging at a wavelength of 4 µm reveals that a 5 nm thick PMMA layer and 7.5 nm sized Ag nanoparticles enhanced the PL intensity by approx. 40% compared to pure semiconductor structures at 4 K. In addition, we investigate the emission dynamics of carriers and excitons in the nanowires using time-resolved photoluminescence spectroscopy techniques. Observation shows enhanced carrier recombination dynamics due to plasmonic interactions with the perovskite. These results show a potential way to excite hybrid nanowires at sufficiently low photon density so that single photon excitation/emission could be possible from these structures. Moreover, this fundamental demonstration confirms a proof-of-concept for further work involving plasmon-enhanced light emission from core-shell metal-semiconductor nanowires and opens the door for realizing lead halide perovskite-based micro and nanolasers in the visible range and more broadly for developing on-chip nanophotonic devices.

4:30 PM EL08.06.04
Electrolyte-Gating for Metasurfaces and Large-Area Fabrication

Vivian Ferry; University of Minnesota, United States

Alternative materials for metasurfaces enable new properties and lay the foundation for advantage applications. This talk will discuss two strategies for new, tunable metasurfaces. The first part of the talk will discuss the use of electrolyte gating to control the optical properties of materials, focusing on La₁₋ₓSrₓCoO₃₋₄ (LSCO) as an exemplary case. We fabricate electric double layer transistors using LSCO and an ion gel, and under application of positive gate voltage gating facilitates the formation and migration of oxygen vacancies, and a transition from a perovskite phase to an oxygen-vacancy-ordered brownmillerite phase. This is accompanied by substantial change in optical properties, as measured with spectroscopic ellipsometry. The talk will discuss how
In this study, free standing gold (Au) membranes with embedded arrays of split-ring resonator (SRR) were fabricated using modified nanospherical-lens lithography. The diameter of the polystyrene nanosphere used is 2 mm. The SRR-shaped photoresist (PR) patterns were achieved by exposing ultraviolet light at a tilt angle while rotating the sample and subsequent PR development. A thin Au layer was evaporated onto the rotating sample at an oblique angle and the evaporated Au only covered the surface area, resulting the Au membranes with embedded SRR arrays. The Au membrane was released from the substrate by dipping it into the solvent and was recovered onto a stainless-steel plate with micron-sized holes. The Au membrane suspended within the micron-sized hole is the free-standing gold Au membrane with embedded SRR arrays. Surface plasmon resonance (SPR) of the fabricated SRR is in the mid-infrared, which was confirmed by the theoretical simulation. The structural parameters of the SRR were tuned so the SPR is within the molecular infrared signature region between 400 to 4000 cm⁻¹. An aminothiophenol (4-ATP) molecules were applied to the Au membrane and their absorption signal around 1400 and 1600 cm⁻¹, which are correspondent to the vibrational modes of C=O band and N-H scissoring, are greatly enhanced. Therefore, the proposed gold membrane with embedded SRR array can be ideal platform for surface enhanced infrared absorption spectroscopy.

**5:00 PM EL08.07.03**

**Arrays of Split-Ring Resonator Embedded in a Free-Standing Gold Membrane for Surface-Enhanced Infrared Absorption Biosensing Platform**

Chieh-Chun Chang¹,² and Yun-Cheng Chang¹,²
¹Academia Sinica, Taiwan; ²National Taiwan University, Taiwan

In our fabrication process, nanocomposite films consist of vertically aligned gold (Au) nanoparticles within ferromagnetic (La,Sr)MnO₃ (LSMO) oxide matrices, achieved through pulsed laser deposition. X-ray diffraction confirms the highly epitaxial nature of the (001)-oriented ferromagnetic LSMO film along, while X-ray reflectivity attests to the uniformity of electron density and high-quality surfaces and interfaces with a film thickness of approximately 30 nm. Detailed analysis through atomic force microscopy and scanning electron microscopy reveals the formation of Au nanoparticles with diameter of around 45 nm within the LSMO matrix. X-ray photoelectron spectroscopy of the Au 4f and Mn 2p core levels highlights that the electronic structure of the nanocomposite displays a correlation between Fermi energy and electrical conductivity.

Notably, Fourier transform infrared (FTIR) microscopy uncovers a highly reflective band observed between approximately 12.2 µm and 8 µm optical phonon wavelengths. Ellipsometry microscopy further demonstrates the presence of double negative materials in our engineered nanocomposite. Further, we employed scanning near-field optical microscopy nano-FTIR, providing high-resolution insights with 10 nm spatial resolution. This technique not only enables chemical analysis but also characterizes local electromagnetic fields, offering a comprehensive understanding of the intricacies within our magneto-plasmonic nanocomposite.

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**5:00 PM EL08.07.05**

**Laser-Based Facile Fabrication of Plasmonic Gold Nanostuctures and Their Sensory Applications**

Do-Hyun Kang, Nguyen H. Minh, Ga-Eun Han, Jae Sung Yoon, Kwanoh Kim and Yeong-Eun Yoo; Korea Institute of Machinery and Materials, Korea (the Republic of)

Plasmonic nanostuctures presenting localized surface plasmon response (LSPR) have attracted great attention in diverse sensory applications. Susceptible change of LSPR peak wavelength to the environmental stimulus, such as molecular bonding, has been exploited to detect rare biomolecules at extremely low concentrations. In addition to such biomolecule sensing, the LSPR peak change to the distance variation between individual plasmonic nanostructures has been used to equipoment-free colorimetric sensing of mechanical strain. Various nanolithography techniques have been employed to craft plasmonic metal nanostructures to realize the above-mentioned sensor applications; however, there is still a need for a low-cost, simple, fast, and scalable fabrication method to achieve reliable and reproducible LSPR sensors. Herein, we introduce a laser scribing-based technique for rapid formation and patterning of plasmonic gold nanostructures. In our process, a high-power laser beam melts a thin gold film on glass or quartz substrates, and subsequent dewetting of the melted gold results in nano-island structures consisting of surface-bound gold nanoparticles with an average diameter of 42 nm. We have successfully applied the plasmonic structures to the highly-sensitive and selective immunosensor of the SARS-CoV-2 nucleocapsid protein, enabling the diagnosis of recently prevalent infectious disease, COVID-19. On the other hand, we have also developed a technique to transfer the gold nanostructures from the hard quartz substrate to the soft and flexible elastomer tape, aiming to create convenient colorimetric strain sensors capable of detecting mechanical motions of human bodies or mechanical behaviors of building structures.

**5:00 PM EL08.07.07**

**Molecular Reporter-Immobilized Ag-Au Shell-Satellite Nanoassemblies for a SERS-Based Galactose Sensor**

Eun Hae Heo and Hyejin Chang; Kangwon National University, Korea (the Republic of)

Galactosemia is a genetic metabolic disorder caused by a deficiency of galactose-degrading enzymes, leading to the accumulation of galactose and its metabolites in the body. The early
excitation of in-plane HPhPs but also offers the ability to fine-tune the far-field response by introducing controlled twists in the hypercrystal lattice relative to the lattice of the new HPhPs. This strategy for galactose SERS detection is based on a capillary tube-based SERS biosensor that demonstrates its potential as an early galactosemia diagnosis platform.

5:00 PM EL08.07.09 Nano-Material Design and Fabrication, Hybridized with Various Nanostructures for Gigantic THz Electromagnetic Wave Modulation and Their Biochemical Applications
Minah Seo1,2, Geon Lee3 and Jinswo Lee1,2, 3Korea Institute of Science and Technology, Korea (the Republic of); 2Korea University, Korea (the Republic of)

Large-scaled metamaterial design and fabrication, hybridized with various nanostructures for gigantic terahertz (THz) electromagnetic wave modulation and their applications. Their potential applications as highly sensitive target molecule-specific sensors, amplifying interactions between light and materials, are particularly noteworthy [1-2]. On the one hand, the terahertz (THz) waves offer non-destructive interactions with molecular modes for the sensing purpose, and reasonable process capabilities in terms of fabrication size. Metamaterials operating at this range, with similar-sized structures (micrometer scale), can be manufactured using photolithography methods on a wafer-to-chip basis. Notably, a large-area nanoscale process was successfully developed by selectively combining different techniques based on their intended purpose. This structure takes the form of a slot-shaped antenna, with a width of hundreds of nanometers and a high aspect ratio, extending tens of micrometers in the transverse direction. To enhance sensitivity and minimize noise levels, over 1,000 antennas per sensor chip were designed and arranged in an array configuration. The design of the metamaterial was thoughtfully engineered to enable the tuning of its resonant frequency by adjusting the antenna's length. Furthermore, the additional nanostructures including nanowires, self-assembled nanoparticles, 2D materials such as MXene, graphene, and catalytic materials as well were integrated to get further functionality. This innovative feature allows excellent detection of trace amounts of biomaterials, leading to several groundbreaking research outcomes at the forefront of the field.

In conclusion, we successfully produced nanoscale THz metamaterials using various process equipment, enabling high field enhancement, thus improving sensing and imaging ability. These THz metamaterial sensing chips demonstrated the ability to detect even DNA nucleotides, COVID viruses, micro-plastics, and trace biochemical substances with greatly improved sensitivity compared to existing light sources [3-4]. Its unique and powerful capabilities offer significant advancements in sensing and control applications, promising to revolutionize electro-optics and open up new possibilities across various industries.

References

Acknowledgment: The National Research Foundation of Korea (NRF) (2023R1A2C2003898), and KIST Institutional Program (No. 2E32451)

Keywords: Metamaterial, Terahertz spectroscopy, nanostructures

In summary, the presence of TiN nanoparticles significantly influences the structural, morphological, electrical, and optical properties of CsFAMA perovskite. The incorporation of TiN nanoparticles leads to improved absorptance, enhanced crystallinity, larger grain sizes, and increased efficiency of perovskite solar cells. These findings contribute to the ongoing efforts to advance the development of high-performance perovskite-based photovoltaic devices.
The study systematically explores biaxial van der Waals (vdW) crystals, focusing on α-MoO₃, wherein HPhPs exhibit pronounced sensitivity to the crystal's basal plane direction. The isofrequency contours in these cases take on a hyperbolic geometry, a stark departure from the circular contours observed in uniaxial vdW materials like h-BN. This biaxial hyperbolicity in vdW crystals opens up unprecedented opportunities for manipulating and tailoring infrared light waves and energy flow at the nanoscale, offering intriguing optical phenomena such as negative refraction, topological transitions, light canalization, and twist photonics.

The research confronts the longstanding challenge of momentum mismatch for far-field excitation of phonon polaritons. Previous studies have proposed patterning the vdW crystal with various materials to surmount this limitation. This work, however, introduces the concept of a photonic hypercrystal, involving periodic structural modulations in a hyperbolic material. By employing α-MoO₃ as a model system, we demonstrate the feasibility of far-field excitation of in-plane HPhPs, showcasing a new dimension of control over light-matter interactions.

In essence, this study represents a transformative advancement in the understanding and utilization of in-plane hyperbolic vdW crystals. The results not only deepen our comprehension of the intricate interplay between light and these hypercrystals but also lay the foundation for the practical realization of phonon-polariton-based devices. These findings hold broad implications, extending from the realm of nanophotonics to the burgeoning field of twist photonics, opening up a new chapter in the exploration of advanced photonic technologies.

References:

Nonlinear Optical Colloidal Three-Dimensional Metacrystals Ye Zhang and Chad A. Mirkin; Northwestern University, United States
Atomic and molecular structure inversion symmetry breaking in naturally occurring crystals dictate their physical properties including nonlinear optical effects, piezo-/ferroelectricity, and nonreciprocal charge transport behavior. With metamaterials composed of nanoscale building blocks (i.e., meta-atoms), the spatial inversion symmetry violation on planar surfaces leads to spin-controlled photonics as well as nonlinear optical metasurfaces. While low-symmetry three dimensional (3D) metacryals can be synthesized, limitations in long-range order and control over resulting symmetries inhibits the investigation of the symmetry-property relationships in these systems. Here we present a DNA-mediated gold nanoparticle assembly approach to create 3D colloidal crystals which can be designed to deliberately access high- or low-symmetry phases. By manipulating particle shape, size, and DNA design, we effectively tune the crystal symmetries of the superlattices in a controllable manner. Access to these different symmetries and facile transitions among them enable us to explore the symmetry-directed functionalities of these colloidal crystals. Further, we investigate how the resulting crystal symmetry relates to their nonlinear optical interactions and identify that the non-centrosymmetric crystal functions as an effective nonlinear optical metacytal, where second harmonic generation (SHG) arises from the asymmetrical distribution of the local electric field around the close-packed plasmonic nanoparticles. Moreover, this non-centrosymmetric colloidal metacytrel represents the first 3D nonlinear optical metamaterial developed through a bottom-up approach and exhibits a high maximum SHG conversion efficiency, notably surpassing the efficiencies observed in the majority of plasmonic 2D metasurfaces by two orders of magnitude.

9:15 AM | E108.08.05 Modeling The Nonlinear Optical Response of ENZ Films Adam Ball1, Ray Secondo2, Yaqub Mukhtar3, Samprity Saha1, Jingwei Wu1, Dhruv Fomra1,2, Jacob Khurgin1 and Nathaniel Kinsey1,2, Virginia Commonwealth University, United States; 2Azhimut Corporation, United States; 3Air Force Research Laboratory, United States; 4NIST, United States; 5Johns Hopkins University, United States

The epsilon-near-zero (ENZ) regime of optical materials represents the transition point between metallic (negative permittivity) and dielectric (positive permittivity) response, similarly characterized by strong alterations in reflection, transmission, and absorption. This intriguing region of optical response has given rise to range of unique effects in both the linear and nonlinear optics fields, including wavelength expansion, slow, and fast field confinement. In particular, the ability of the ENZ regime to enhance various nonlinear optical effects has garnered significant attention in recent years. Among them, a key is the ability to modulate the refractive index of the ENZ film on the order of unity on a picosecond timescale via nonlinear optical excitation. This has given rise to a significant interest in utilizing ENZ films for a number of optical devices including saturable absorbers, nonlinear activation functions, optical switches, and more. However, key to designing these devices is understanding the nonlinearity and modeling the change in complex index (permittivity) that will be experienced for a given excitation. In this talk we will highlight our recent efforts to model the intensity dependent index of Drude-based ENZ thin films, highlighting the Nonlinear Epsilon Near Zero (NLENZ) Calculator application available online via nanohub.org. We will introduce the basic theory of the non-parabolic conduction band and how it gives rise to nonlinear response of ENZ materials. We will then provide a high level outline of the models for interband and intraband nonlinearities, culminating in the use of the NLENZ app to predict the nonlinear properties of the material, using only experimental parameters and the material band structure, which can then be extracted and used in combination with other FEM or FDTD solvers for complex device design. We expect this tutorial style talk to be of interest to researchers and materials scientists who are interested in working with ENZ materials in new devices or developing new materials with an ENZ response, and hope to support the further development and study of these unique effects by furthering the ability of the community to simulate material and device responses incorporating ENZ.

9:45 AM BREAK

10:15 AM | E108.08.06 Analysis of Near-Field Patterns generated by Propagating Polaritons Minsoo Jang, Sergey Menabde, Jacob Heiden and Min Seok Jang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Polaritons are quasi-particles that are excited by the coupling of light and charges within a material. They are closely related to the motion of charges in matter, which gives them a deep connection to material properties. Additionally, in specific low-dimensional materials, they exhibit a high level of light-matter interaction and confinement. Polaritons hold significant value in the field of nanophotonics, and current research is underway in areas such as light absorption, thermal emission, biosensing, and beam deflection. However, directly measuring the complex propagation of polaritons remains a challenging aspect of research due to the difficulty of near-field measurements. Scattering type scanning near-field optical microscopy (s-SNOM) enables the simultaneous measurement of the amplitude and phase of the near field by utilizing a metallic atomic force microscopy (AFM) tip as a near-field detector and the interferometric coupling of this signal with the base signal. Typically, s-SNOM excites complex propagating polaritons through the tip and material edges and images them. In the past, Fourier transform (FT) was used on the image profile to extract real momentum, but the damping term was determined through direct fitting or by directly fitting the momentum from the beginning. This method poses challenges in mixed signal analysis and background removal. Additionally, for edge-launched polaritons, the polariton momentum can shift depending on the edge angle, but this shift has not been considered in recent high-effective-index materials like hBN or MoO3.

In this study, we first present a standardized method for analyzing the complex momentum of propagating polaritons. To analyze polariton momentum, we fit the FT signal of propagating polaritons with a function obtained by FT of the analysis model. We confirmed a perfect fit and also revealed the relationship between the full-width half-maximum (FWHM) of the FT signal and the damping of propagating polaritons, confirming a specific ratio of q. This method of FT makes it easier to analyze comprehensive signals compared to the traditional direct fitting method and offers an advancement in analyzing the loss of polaritons based on the existing Fourier transform approach. Secondly, we established an analytical model for tip and edge polaritons and experimentally demonstrated edge-oriented momentum shifts that occur during measuring process in edge mode. We measured polaritons on hBN transferred onto crystalline gold. Polaritons launched from the clear atomic gold edge generate modes known as hyperbolic phonon-polaritons (HPP) and hyperbolic image polaritons (HIP) that propagate on both the glass substrate and crystalline gold. We measured the polarization by rotating gold edge at 45-degree angles and confirmed that the degree of shift matched the theoretical model. Furthermore, for HIP, it was observed that HIP exhibited a maximum momentum shift of approximately 8% even at a high effective index of 12.54.

10:30 AM | E108.08.07 Plasmonics Platforms for Strong Coupling Matthew T. Sheldon; University of California, Irvine, United States

Nanophotonic and plasmonic architectures present a compelling platform for investigating strong coupling phenomena. These nanofabricated optical structures enable precise tailoring of electromagnetic modes on sub-wavelength scales, leading to significant coupling interactions within near-field "hot spots". Recent advancements from our laboratory have showcased ultrastrong coupling to vibrational modes using innovative plasmonic cavity designs. The sub-wavelength localization of these platforms facilitates strong coupling to fewer molecules compared to traditional Fabry–Perot (FP) cavities, potentially limiting contributions from "dark states" in plasmon chemistry. A notable feature of plasmonic-based cavities is their compatibility with established surface science techniques, such as confocal molecular Raman spectroscopy. With these tools, our recent studies have uncovered unique temperature-dependent dehydrogenation behavior of transition metal salt films on plasmonic substrates, suggesting resonant thermal energy transfer when vibrational strong coupling is present. This discovery hints at the potential of pronounced thermal gradients within the near-field of plasmonic substrates.

Furthermore, our research delves into the design of cavities that support radiaot modes with higher q-factors that lead to stronger coupling interactions with molecular samples. Preliminary results indicate that these sub-radiant cavity modes with quadrupolar field symmetry achieve very strong coupling with molecular samples, while offering a modification of the usual optical selection rules for bright and dark (N-1) polariton states.

11:00 AM | E108.08.08 Visualizing Chiral Plexcitons at Room Temperature Using Tip-Enhanced Photoluminescence Thomas P. Darlington1, Kevin W. Kwock1, Matthew Strasbourg2, William Hayes1, Nicholas Boris3 and P. James Schuck1; 1Columbia University, United States; 2Montana State University, United States

Chirality is a fundamental property of nature, arising naturally in many systems, ranging from the structure of molecules to the spiral arms of galaxies. Structural chirality leads to circular dichroism, where photons of right or left handedness experience contrasting refractive indices for a particular molecular enantiomer. This phenomenon plays a crucial role in the chemical identification of molecules in the food and drug sciences. In the field of quantum optics, chiral single photon sources have gained increased interest due to their inherent non-ripropionicity, allowing for realization of novel optical devices such as single photon isolators and circulators. A requirement in many quantum optical applications is the realization of polarization states through strong coupling of a cavity optical field with a material dipole excitation. In this regime, substantial recent work has focused on plexcitons, strongly coupled excitons with nanocavity plasmon-polaritons, due their ultra-confined cavity volumes (<10 nm³). These small volumes allow for strong coupling to be readily achieved at elevated temperatures, with Rabi splittings of 50 – 400 meV in a wide array of excitonic systems ranging from quantum dots to monolayer transition metal dichalcogenides, to molecular J-aggregates. However, despite the explosion of the scientific efforts on the topic, chirality in plexcitonic systems has yet to receive significant experimental attention.

In this presentation I will show our recent experimental efforts on imaging chiral plexcitonic states formed with commercial CdSe/ZnS quantum dots with a gap-mode plasmonic cavity. Using tip-enhanced photoluminescence (TEPL), we are able to map out the nanocavity quantum dot response, revealing a naturally asymmetric spatial profile for nanocavities formed with commercially available silver nano-optical probes and gold substrates, a common cavity geometry. Our nano-optical measurements further show positional control of the quantum dot emission
energy, with an upper and lower polarization branches forming in the TEPL spectrum depending on the probe-dot separation and orientation, demonstrating the plexciton nature of the emission. Using a novel nano-optical imaging method that integrates TEPL with single photon avalanche photodiodes (SPADs) and time correlated single photon counting hardware, we map out the degree of circular polarization as a function of probe-dot position, showing polarization ratios as large as 80%, that is controllable by varying the x,y,z position of the nano-optical probe. Our results demonstrate the ability to imprint chiral behavior on quantum-emitter-based polarizations using plasmonic nanocavities, and provide important insight into development of chiral quantum optical devices.


11:15 AM *EL08.08.10* Perspectives of Design, Materials, Manufacturing and Applications for Optical Metasurfaces Junsuk Rho; Pohang University of Science and Technology, Korea (the Republic of)

In this talk, I will represent Al-designed metasurfaces, new materials and three low-cost manufacturing: 1) nanoimprinting with high-refractive-index dielectric particle embedding resin (PER), 2) bandgap engineering of hydrogenated amorphous silicon (a-Si:H), and 3) atomic-layer coating on imprinted resin. a-Si, TiO2, and ZrO2 PERs are used for metasurfaces at infrared (940 nm), visible (532 nm), and ultraviolet (325 and 248 nm), respectively; measured efficiencies reach 47% (940 nm), 91% (532 nm), 72% (325 nm), and 49% (248 nm). PER metasurfaces with an inverse design provide 3D, full-color holography at visible. The bandgap of a-S:H is engineered to suppress optical losses, realizing metasurface efficiencies of 42% (450 nm), 65% (532 nm), and 75% (635 nm). We deposit an atomic layer on resin for 12-inch metasurfaces, achieving measured efficiencies of 61% (450 nm), 78% (532 nm), and 65% (635 nm). Finally, the recent development of mass production and manufacturing of metasurfaces and nanophotonic structures, and future direction with a bigger vision will be discussed.

**SESSION EL08.09: Photonics Metastructure Designs for Imaging and Display Technologies**

**Session Chairs: Min Seok Jang and Ho Wai (Howard) Lee**

**Wednesday Afternoon, April 24, 2024**

**Room 340/341, Level 3, Summit**

**1:30 PM *EL08.09.01* Metasurfaces for Future Sensing, Imaging and Display Technologies**

Mark L. Brongersma; Stanford University, United States

Metamaterials are a new, emerging class of high-performance materials that derive their unique, physical properties from the way they are structured. In this presentation, I will focus on the creation of 2-dimensional metamaterials (i.e. metasurfaces) by nanopatterning glass, semiconductor and metal films. I will argue that these metasurfaces are ideal building blocks for the next generation of optical elements and optoelectronic devices.

I will highlight how metasurface functionalities can start to impact a variety of optical sensing, imaging and display technologies. For example, I will show how one can create transparent optical sensors on glass substrates that can extract valuable information from an optical scene. I will also discuss the use of integrated metasurfaces for new imaging modalities. The proposed optical elements can be fabricated by scalable fabrication technologies, opening the door to many commercial applications.

**2:00 PM *EL08.09.02* Highly Collimated and Polarized Light Emitting Metasurface for AR displays**

JP Berenguer1, Fenghao Xu2, Qitong Li1, Jung-Hwan Song1, Mark L. Brongersma1 and Siddharth Doshi1; 1Stanford University, United States; 2Stanford University, United States

Major technical challenges must be overcome in order for augmented reality (AR) technologies to fulfill its revolutionizing promises. Current solutions for AR displays suffer from very low efficiencies and large form factors, mostly due to the use of grating-based waveguides and polarizing optical elements. Therefore, there is a growing need for nanophotonics designs that can focus light emission at desirable in-coupling locations for maximum throughput and with a high degree of polarization to avoid the use of bulk polarizers.

Here, we present and characterize a directional and polarized light-emitting metasurface based on a generic GaN LED. We engineered arrays of Mie nanoresonators that combine an actuator and a micro-scanner, and flash LiDAR, based on diffractive elements, were adopted to address those issues. However, they still suffered from low durability and significant power consumption. Metasurface-based beam steering device offers several breakthroughs, including miniaturization, reduced power consumption, reduced heat generation and higher frame rates.

**2:15 PM *EL08.09.03* Photonics Metastructure Designs for Imaging and Display Technologies**

Sangjun Han; Pohang University of Science and Technology, Korea (the Republic of)

We demonstrate a novel depth sensing system that utilizes metasurfaces and photonic crystal surface-emitting lasers (PCSELs), realizing structured light generation and facial recognition in monocular depth sensing. Our single-shot system projects approximately 45,700 infrared spots from an about 300^2 m^2 metasurface area, which is 233 times smaller than the commercial LiDAR, based on vertical-cavity surface-emitting laser (VCSEL) array. Our proposed system addresses the limitations of traditional structured light depth sensing technology, offering significant advantages in terms of size, power consumption, and potential for integration into wearable devices.

**2:30 PM BREAK**

**SESSION EL08.10: Wave Front Control Metasurfaces—Design and Fabrication**

**Session Chairs: Yao-Wei Huang and Min Seok Jang**

**Wednesday Afternoon, April 24, 2024**

**Room 340/341, Level 3, Summit**

**3:30 PM *EL08.10.01* Single-Gate Active Beam Steering Graphene Metasurface**

Sanjion Han; Jinsook Kong and Min Seok Jang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Optical beam steering is a next-generation technology with applications in optical communications, laser patterning, three-dimensional laser point clouds and LiDAR systems. Conventional beam steering devices based on mirrors rotated by motors have a 360° field-of-view, but suffered from its bulky size and high heat generation. MEMS-based LiDAR, which combines an actuator and a micro-scanner, and flash LiDAR, based on diffractive elements, were adopted to address those issues. However, they still suffered from low durability and significant power consumption. Metasurface-based beam steering device offers several breakthroughs, including miniaturization, reduced power consumption, reduced heat generation and higher frame rates.

Active metasurface beam steering device can be implemented utilizing liquid crystals, phase change materials, or carrier injection into Transition metal dichalcogenide monolayers or conductive oxides. However, previous studies have faced challenges such as a small field-of-view within a few degrees, poor diffraction efficiency or directivity. In conventional electrically tunable beam steering devices, they generally require a complex circuit driver inside to individually control each metatom. Those system may also involve dielectric breakdown problems between adjacent metatom. To scale up to practical beam steering technologies in the future, it is necessary to simplify the driving mechanism and improve performance.
Leveraging Correlations between The Statistics and Spectral Properties of Random Metasurfaces for Multi-Wavelength Cryptography

Steven Brunton and Arka Majumdar; University of Washington, United States

Randomness and disorder are abundant in nature and help in sustaining the environment around us. In particular, random optical media encountered in various varieties of insects, birds and...
marine organisms are naturally optimized to offer survival advantage in their respective habitats. Historically, photonics researchers have focused their attention on periodic and ordered systems, and randomness has often been viewed as undesirable. In recent years, the broad range of functionalities exhibited by random optical media have prompted researchers to explore materials with tailored disorder for various applications. As opposed to their periodic counterparts, the vast design space afforded by disordered photonic devices provides greater flexibility in achieving tailored optical responses. However, the expanded design space makes it challenging to map the structural degrees of freedom of random photonic devices to their optical properties. This necessitates the identification of a tractable set of parameters that can be used to characterize random optical media. Here, we investigate correlations between the configuration statistics of random metasurfaces and their spectral response. Our metasurfaces consist of a two-dimensional array of silicon nanoparticles with random widths on a silica substrate. We explore the effect of tuning the probability distribution characterizing the nanoparticle widths on the wavelength-dependent transmissivity of the random metasurface in the 400 – 800 nm wavelength range. Furthermore, we exploit the correlations between the configuration statistics of the random metasurfaces and their spectral properties to design a photonic device encoding spectrally encrypted image data in the visible wavelength range. Our findings open up new insights into the optical properties of random media and provide avenues for developing such systems for a broad range of applications.

5:00 PM EL08.11.03
Engineering The Properties of Metal Nanoparticle Arrays for Optoelectronic Applications
Gavin Farmer, Chris Litter, Athanasios Sylianos and Usha Philopito; The Pennsylvania State University, United States

This work focuses on the fabrication of ordered metal nanoparticle arrays with tunable particle diameter and inter-particle distance. The nanoparticle arrays were formed by a sequential solid state de-wetting process, using evaporated gold to fill the dimples of an anodized alumina membrane. The results show a direct correlation between the particle size and inter-particle distance, factors that are determined by both the geometry of the dimples in the membrane as well as the volume of the evaporated gold. An experimental threshold for the evaporated gold film was determined, such that beyond a certain limit the existing nanoparticles were unable to preserve their ordering and spacing. This technique allows for fabricating ordered nanoparticle arrays with diameters ranging from 55 nm to about 85 nm, with inter-particle spacing ranging from 10 nm to about 40 nm. This work is significant because ordered arrays of metal nanoparticles exhibit localized surface plasmon resonance, a phenomenon that can be taken advantage of in sensing applications.

5:00 PM EL08.11.04
Aqueous Synthesis of Silver Nanocubes and Their Sensing Capabilities
Annabella Talbott1, Anika Guo2,2, Nigel Nig1 and Ying Bao1; 1Western Washington University, United States; 2University of Oregon, United States

Nanocubes are of great interest because they have shown promise in many fields like biomedicine, imaging, and sensing because of their chemical and physical properties. A focus has been put on controlling the morphology of metallic nanoparticles since specific characteristics (size, shape, composition, and structure) can impact the nanoparticles’ properties and applications. Among these structures, sharp tips are of interest for enhancing related applications, as they allow for “hot spots” on the nanoparticles. Specifically, silver nanocubes (AgNCs) are desirable for sensing due to the “hot spots” located at their sharp corners, as well as the heightened plasmonic properties of silver. Typically, AgNCs are synthesized through a polyol process, but other methods are being explored due to the polyol process having been found to be toxic to the environment. In this work, an aqueous method of synthesizing the AgNCs was employed, and the effects of specific components of the synthesis and their resulting impact on the AgNCs were studied. This was done using UV-Vis spectroscopy and scanning transmission electron microscopy (STEM) to characterize the size and morphology of synthesized AgNCs. The refractive index sensitivity of varied sized AgNCs has been evaluated which shows a larger cube size has higher refractive index sensitivity. Furthermore, the synthesized AgNCs also were used for sensing iodide with the assistance of copper. In the future, the sensitivity of detecting iodide using various-sized AgNCs will be studied. The sensing of iodide using coated AgNCs will also be studied.

5:00 PM EL08.11.06
Effect of pH on The Self Assembly of Janus Particles
Maria Ifreum1, Mohan K. Dey1, Alisha Prasad2, Jin G. Lee2, Shirin Parvin3, Meng Lu4, Ram Devireddy4, Bluvnesh Bhatti1 and Manas R. Garita1; 1Louisiana State University, United States; 2Catalent Pharma, United States; 3University of Colorado, Boulder, United States; 4Iowa State University of Science and Technology, United States

The use of pH-adjusted self-assembly in Janus particles is a promising approach for controlling Raman scattering. These Janus particles, known for their asymmetry in composition and properties, provide distinct benefits for crafting precise nanostructures in surface-enhanced Raman scattering (SERS) applications. The study investigates using pH-controlled self-assembly of Janus particles to observe the changes in their Surface-Enhanced Raman Scattering (SERS) and Raman signals. Characterization methods such as scanning electron microscopy (SEM) and focused ion beam (FIB) technology were implemented for detailed information regarding the shape, size variation, and inter-assembly structure of Janus particles. Various analytical techniques, including TEM, EDAX, and elemental mapping, were employed to assess the assembled Janus particles by examining their elemental composition and how it is distributed. By adjusting the pH of the solution, electrostatic interactions between the Janus particles were manipulated, leading to controlled aggregation and spatial arrangement. As the pH value rises, the gap between the particles widens. At specific pH levels, the self-assembly of Janus particles occurs, forming ordered nanostructures that concentrate analyte molecules. This spatial confinement caused significant changes in electromagnetic field intensity and Raman signals. Optimal pH selection enables control over interparticle spacing, plasmonic coupling, and electromagnetic field distribution, leading to remarkable modulation of Raman signals. This research also focuses on analyzing electromagnetic fields, uncovering how electric and magnetic fields are distributed between Janus particles when exposed to excitation light. A decrease in Raman Intensity with the increasing number of Janus particles were observed at the Raman wavenumber. Using Finite-Domain-Time-Difference (FDTD) simulations, a decrease in electromagnetic field intensity with the number of particles were also observed, which validates our experimental finding. Analyzing the structure and optical and electromagnetic properties of Janus particles will further help us understand their behavior and potential applications. pH-tuned Janus particle self-assembly shows promise in creating sensitive and selective Raman sensing platforms. This research advances our understanding of Janus particle assembly for SERS-based sensing, with broad applications in areas like chemical analysis, bioassays, and environmental monitoring.

5:00 PM EL08.11.07
Visible Light Mediated Deposition of Pt Nanocatalyst on Refractory Plasmonic Titanium Nitride Nanoparticles
Hiritha Sharad Jeyashangarraj1, Sanchari Chowdhury and Naomi Helsel; New Mexico Institute of Mining and Technology, United States

Plasmonic photocatalyst can efficiently absorb light to generate photocreated electrons to drive energy intensive catalytic reactions including CO2 reduction, water splitting and solar energy conversion. We have successfully synthesized composite plasmonic catalysts by visible-light-induced deposition of transition metal nanocatalysts such as Pt on refractory plasmonic titanium nitride (TiN) nanoparticles. Titanium nitride nanoparticles can absorb broad spectrum solar light to generate photocreated electrons which reduce transition metal precursor salts to deposit the metal atoms on the surface. We could deposit different size of Pt nanocatalysts on titanium nitride by varying the photodeposition process conditions such as light intensities and duration of light illumination. We are studying the effect of light intensity, irradiation time and wavelength dependence of Pt precursor reduction rate to understand the reaction mechanism of Pt nanocatalysts deposition. The hypothesis of this study can be used to develop a visible light mediated synthesis of single atom plasmonic catalysts under mild conditions, which has been a bottleneck for their widespread applications.

5:00 PM EL08.11.08
Large-Grain Thin Films of Biaxial Hyperbolic α-MoO3 Using Alkali Metal Compound-Assisted Vapor Transport Deposition
Ryan Spangler1, Joshua D. Caldwell2, Patrick E. Hopkins1 and Jon-Paul Maria1; 1The Pennsylvania State University, United States; 2Vanderbilt University, United States; 3University of Virginia, United States

As the application space of mid-IR technologies continues to expand, materials with new and advanced properties become of interest. α-MoO3 is a transparent, layered semiconductor that can exhibit biaxial hyperbolicity of the dielectric function, where the optical properties can be switched from out-of-plane hyperbolic to in-plane hyperbolic by varying the mid-IR wavelength. This opens up opportunities for planar emitters, non-reciprocal plasmon waveguides, and directional collimation of energy within nanomaterials via long-lifetime hyperbolic phonon polaritons. However, research on these properties has been predominantly performed on samples of exfoliated flakes of α-MoO3, with thin film fabrication techniques being relatively undeveloped. This is in part due to the difficulty of producing the large grains necessary for many polaritonic experiments of in-plane anisotropic crystals. Furthermore, the experimental flexibility of α-MoO3 studies has been historically limited and it is of great interest to repeatedly produce large single crystals in thin film form. In this work, a physical vapor transport technique is developed which uses alkali metal compounds to promote grains possessing lateral dimensions of hundreds of µm to few mm. We observed that this technique overcomes the poor film texturing and morphology that is observed in α-MoO3 grown on most substrates. Data will be presented on the film morphology and crystalinity as functions of different growth parameters including substrate composition and preparation, growth temperature, and presence of alkali metal compounds. Additionally, the applicability of this synthesis technique to the nanophotonics community will be demonstrated by characterizing the optical and hyperbolic phonon polariton properties of the synthesized films. This synthesis technique opens up new capabilities for controllable fabrication of large-area α-MoO3 crystals for nanophotonics and polaritonics research.
Conventional camera systems can only detect light intensity while losing important information about the target scene, including depth, polarization, and spectrum. In order to further obtain the multi-dimensional light-field information of the target object, it is often required to use bulky and expensive instruments. Metasurface is composed of an array of optical antennas that can manipulate the amplitude, phase, polarization, and spectrum of light at the subwavelength scale. By replacing conventional diffraction-defractive of refractive elements with metasurfaces in imaging systems, one may be able to build optical sensors for high-performance multidimensional light sensing with low size, weight, power, and cost. Here, we will present our group’s recent effort to replace conventional camera lenses with metaelements. By leveraging the unique capability of metasurface to tailor the vectorial field of light, in combination with an advanced image retrieval algorithm, we aim to build compact camera systems that can capture multi-dimensional light field information of a target scene in a single shot under ambient illumination conditions.

9:15 AM EL08.12.03
Direct Measurement of Radiation Pressure Forces on Membrane Lightsails Lior Michaeli, Ramon Gao, Michael Kelzenberg, Claudia Hail, John Sader and Harry A. Atwater; California Institute of Technology, United States

We report direct measurement of radiation pressure forces exerted on a 100-nm-thick silicon nitride lightsail membrane. Our sensitive measurements rely on three key components: a noise-robust common-path interferometer with picometer resolution, rational design of the tethered lightsail for enhanced mechanical susceptibility, and an off-resonant driving scheme for quasi-static, linear dynamics. Ultrathin lightsails, propelled to relativistic speeds by laser radiation pressure, are being actively explored as a new generation of interstellar spacecraft probes, spearheaded by the Breakthrough Starshot Initiative [1,2]. Realizing laser-driven lightsails necessitates precise characterization of the optical forces on a material platform capable of exhibiting mechanical, beam-ringing, and thermal stability. For a laser power density of 200 W/cm² at 514 nm, we measure displacements of ~10 pm, resulting from optical forces of ~30 N. Contrary to optical trapping of microscopic objects, motion is induced by a collimated laser beam filling substantial part of the lightsail, mimicking the initial acceleration stage of interstellar lightsails. Furthermore, to predict the tilt-dependent dynamics of subwavelength thick lightsails, we characterize the non-intuitive trend of the optical force versus incidence angle in the range of ±20° for TE and TM polarization. Our study represents a critical milestone in realizing an experimental testbed for lightsail characterization, thus advancing the development of laser-driven spacecraft, and opening the door for manipulation of macroscopic objects through optical forces.

9:30 AM *EL08.12.04
Let’s Twist Again: High-Quality-Factor Metasurfaces to Enhance Spin In Molecules and Monolayer Materials Jennifer A. Dionne; Stanford University, United States

Many inversion-asymmetric materials, including chiral molecules and certain van der Waals materials, exhibit a differential absorption of left and right circularly polarized light that is nearly five orders of magnitude less than their absorption of unpolarized light. Such weak differential absorption challenges applications such as single molecule circular dichroism spectroscopy, all-optical enantio-specific synthesis, and efficient valleytronic data encoding for quantum information. Here, I describe approaches to enhance helicity-dependent optical absorption, emission, and carrier relaxation in molecules and monolayered materials. We rely on high-quality-factor (high-Q) metasurfaces, which, when placed in the near-field of a molecular or monolayer sample, precisely control the amplitude, phase, and polarization of light. Each metasurface enables substantial and uniform-sign enhancements of both the electric and magnetic fields of light, with local photon spin fields that can be enhanced by several orders of magnitude.

First, we show how high-Q metasurfaces enable circular dichroism from a molecular monolayer. We fabricate silicon metasurfaces and functionalize them with short, ~10-mer DNA oligonucleotides. We measure their circular dichroism in a home-built table-top polarization sensitive spectrometer, and also show how this technique is sensitive to changes in the CD

10:00 AM BREAK

10:30 AM *EL08.13.01
Novel Dielectric Metasurfaces for DUV Photonics Bo Ray Lee, Ting An Shu, Pei Ying Ho, Mao Feng Jiang, Yu Chieh Peng, Kuan-Heng Chen, Jia Hua Lee, Yu Chia Chung, Yu Jie Wang, Der-Hsien Lien, Tzu-En Lin, Chao-Hsin Chien, Ray Hua Horng and Ming Lun Tseng; National Yang Ming Chiao Tung University, Taiwan

Deep ultraviolet (DUV) light covers wavelengths from 200 nm to 300 nm and has diverse applications including imaging, sensing, and medical treatments. Developing efficient and robust metasurfaces is crucial for improving the relevant DUV technologies. Here, we present innovative DUV dielectric metasurfaces providing field enhancement and several unique properties. By employing the photon doping effect and including a quasi-bound state in the continuum in the design, we realize a Si metasurface capable of showing a DUV plasmonic resonance. The field enhancement and durability of biochemistry-related solvents of the sample enable its applications for DUV sensing applications. In addition, to generate strong field enhancement, we use low-loss HfO2 to create a dielectric metasurface. Combining HfO2's optical properties with novel designs results in multiple high-quality factor resonances and significant field enhancement. These results will advance the development of ultrasmall biosensing devices within this crucial wavelength range.

11:00 AM EL08.13.02
Extremely Confined THz Phonon Polaritons in HS2 and HS62 Ryan Kowalski1, Gonzalo Alvarez Perez2, Maximilian Obst3, Katja Diaz-Granados Santos2, Giulia Carini4, Aditha Senarath1, Saurabh Dixit1, Niclas Müller4, J. Michael Klopf5, Thomas G. Folland6, Lukas Eng3, Susanne Kehr3, Pablo Alonso Gonzalez2, Alex Paarmann4, Richard Haglund1 and Joshua D. Caldwell1; 1Vanderbilt University, United States; 2University of Oviedo, Spain; 3Technische Universität Dresden, Germany; 4Fritz-Haber Institute, Germany; 5Helmholtz-Zentrum Dresden-Rossendorf, Germany; 6The University of Iowa, United States

Plasmonics and polaritronics have enabled the field of nanophotonics to reduce the wavelength of light to length scales far below the diffraction limit, leading to optoelectronic devices miniaturization and enhanced light-matter interactions. Traditionally, complex heterostructures were necessary to achieve the desired confinement capabilities. Coherently coupled vibrations in polar dielectrics, or phonon polaritons, are an attractive alternative to realize these goals as they use a different mechanism intrinsic to the material, to compress light. Quality phonon polariton materials possess a large splitting between the transverse optic (TO) and longitudinal optic (LO) phonons, which results from a strong internal electric dipole. Within the TO-LO splitting, or Reststrahlen band, the dielectric permittivity becomes negative, opening the door for phonon polaritons. Traditionally, the dominant spectral range for phonon polaritons is
the mid-infrared (mid-IR), despite a rich potential for nanophotonic materials at far-infrared (far-IR) and terahertz (THz) frequencies where molecular vibrations and rotations are observed. The transition of plasmonics and polaritronics into the far-IR and THz has been stunted due to a lack of materials that can host phonon polaritons.

Transition metal dichalcogenides (TMDs) are commonly studied in the near-infrared (near-IR) and visible wavelengths, specifically for the excitonic properties in MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$. However, the phonon resonances of these TMDs are not strong and do not possess large TO-LO splitting, making them a poor candidate for infrared nanophotonics. Conversely, Group-IVB TMDs such as HfS$_2$ and HfSe$_2$ have exceptionally large Reststrahlen bands ($>100$ cm$^{-1}$), a priority for phonon polaritonics. They are also two-dimensional (2D) van der Waals crystals, making them even more attractive for nanoscale optics. Furthermore, due to the crystals’ anisotropy, the dielectric permittivity between the in-plane ($\varepsilon_{xx}$) and out-of-plane ($\varepsilon_{xy}$) directions differs with respect to the incident wavelength, which separates the Reststrahlen band into two dispersion bands, elliptic ($\varepsilon_{xx}^* > 0$) and hyperbolic ($\varepsilon_{xx}^* < 0$). In the hyperbolic regions, the isofrequency contour becomes an open hyperbola with extraordinary waves that do not have a momentum ($k$) limit, facilitating extreme compression of the free-space wavelength ($k = 2\pi/\lambda$).

In this study, we use polarized Fourier transform infrared (FTIR) spectroscopy to extract the anisotropic IR permittivity of HfS$_2$ and reveal the exceptional TO-LO splitting in the mid- to far-IR. Within these broad bands, we image the near-field optical signal of phonon polaritons and measure confinement of the free-space wavelength by a factor of more than 100. Finally, by varying the substrate permittivity, we demonstrate tunable control of the coupling strengths between the hyperbolic phonon polaritons and epsilon-near-zero polaritons in HfSe$_2$. By examining an underexplored class of materials, this work directs the search for quality nanophotonic materials, in particular those that facilitate access to far-IR/THz wavelengths, a spectral range that suffers from limited optical materials.

11:15 AM  *EL08.13.03*
Metasurfaces for Light Detection and Ranging  Patrick Genevet; Colorado School of Mines, United States

Metasurfaces are versatile optical components that can distribute optical power in desired regions of space, thus holding great potential for on-chip integration of miniaturized optoelectronic and imaging systems[1]. Using metasurfaces, we reported advanced LiDAR technology that leverages from ultrafast low FoV deflectors cascaded with large area metasurfaces to achieve large FoV (150°) and high framerate (kHz)[2]. Additionally, achieving wide-angle 3D imaging is becoming essential nowadays for autonomous robotic systems, yet most of the available solutions fail to simultaneously measure backscattered from multiple directions. Inspired by arthropods eyes, we conceive a metasurface can overcome the limitation of curved optics, achieving panoramic vision. On-chip vertical integration of directional metalessesthe on top of a planar array of detectors enables a powerful insect-inspired LiDAR vision that is capable of 3D imaging over a wide field of view[3]. The use of our disruptive LiDAR technology with advanced learning algorithms offers perspectives to improve perception and decision-making process of ADAS and robotic systems.


11:45 AM  *EL08.13.04*
Silicon Nanophotonics for Multi-Omic Marine Detection  Halleh Balch1, Sahil Dagli2, Varun Dolia1, Kai Chang1, Greg Doucette2, William Usi1, Chris Scholin3 and Jennifer A. Dionne1;
1Stanford University, United States; 2NOAA/National Center for Coastal Ocean Science, United States; 3Monterey Bay Aquarium Research Institute, United States

The oceans are host to diverse marine microorganisms that are capable of cycling nearly all chemical elements and are responsible for over half of the oxygen on earth, forming a key part of our carbon cycle. Yet, studying the marine microbiome remains an outstanding challenge. Very few marine microbes have been successfully cultured under laboratory conditions and culture-independent methods like metagenomics and mass spectroscopy are incompatible with the real-time and in situ measurements necessary to study how physico-chemical drivers impact microbial nutrient cycling.

Here, we present our approach based on high quality factor silicon nanophotonics to simultaneously and rapidly measure multiple ‘omic’ signatures from marine ecosystems. Our metasurfaces are composed of sub-wavelength silicon nanobars on sapphire substrates. First, by introducing small biperiodic perturbations to the lateral block dimension, free space radiation can be coupled into guided mode resonances to produce high-Q resonances with Q factors exceeding 10$^3$ in aquatic environments. We demonstrate in simulation and experiment that by varying the biperiodic perturbation from 10 nm to 50 nm, the quality factor can be modulated from 10$^2$-10$^4$ and that the local electric field can be driven to the silicon surface, increasing the overlap between the field and the bonding surface by nearly four-fold. We experimentally demonstrate that by introducing tapered photonic mirrors, the resonator cavity length can be reduced by 10X while retaining Q-factors exceeding 3000, and that the long resonance lifetimes together with the increased field penetration at the binding surface results in strong spectral shifts of the resonance mode due to small perturbations to the local dielectric environment. We fabricate our metasurfaces by e-beam lithography and demonstrate that the optical responses of individual resonators can be spatially resolved as individually addressable finite ‘pixels’ and simultaneously read out on a 2D InGaAs CCD array in a cross-polarized reflection configuration.

Using this platform, we demonstrate quantitative and amplification-free detection of DNA and the harmful algae bloom toxin, microcystin, which poses a threat to drinking and agricultural water supplies. We selectively target nucleotides and the toxin microcystin on the same multiplexed platform using tailored surface functionalization of self-assembled monolayers (SAM) and a competitive antibody binding assay. We observe in both calculations and experiments that consecutive molecular layers generate 0.5 nm - 4 nm shifts to the resonant wavelengths as sequential water supplies. We selectively target nucleotides and the toxin microcystin on the same multiplexed platform using tailored surface functionalization of self-assembled monolayers (SAM) and a competitive antibody binding assay. We observe in both calculations and experiments that consecutive molecular layers generate 0.5 nm - 4 nm shifts to the resonant wavelengths as sequential water supplies. We selectively target nucleotides and the toxin microcystin on the same multiplexed platform using tailored surface functionalization of self-assembled monolayers (SAM) and a competitive antibody binding assay. We observe in both calculations and experiments that consecutive molecular layers generate 0.5 nm - 4 nm shifts to the resonant wavelengths as sequential water supplies. We selectively target nucleotides and the toxin microcystin on the same multiplexed platform using tailored surface functionalization of self-assembled monolayers (SAM) and a competitive antibody binding assay. We observe in both calculations and experiments that consecutive molecular layers generate 0.5 nm - 4 nm shifts to the resonant wavelengths as sequential water supplies.
Elastic Electrochemical Active Metasurfaces

Yu-Jun Lo \(^{1,2}\); 1Academia Sinica, Taiwan; 2National Taiwan University, Taiwan

Tunable Metal-CP-Metal Metasurface with Intrinsically Reflective IR-Electrochromic Conducting Polymer (CP)

Ting-Hsuan Chen \(^{1,2}\) and Po-Chun Hsu; 1Duke University, United States; 2The University of Chicago, United States

Electrochemical conducting polymers (CPs) have made significant contributions on actively tunable applications from visible light to infrared (IR), including metasurfaces, plasmonics, and personal thermoregulation. By varying their charge concentration and localization, the interaction between CPs and electromagnetic waves is therefore modulated. Until recently, most CP-based IR-electrochromic studies focused on thin-films toggling between transmissive and absorptive state, due to the trade-off between electrical conductivity and ionic diffusion kinetics. Compared with the transmission modulation strategies, electrochromism based on intrinsic reflectance opens the opportunities to create substrate-agnostic devices.

In this presentation, we propose a tunable metal-Cp-metal tunable metasurface by incorporating lossy metals with CP to achieve large tunability of absorption and emission in mid-to-long IR spectrum. The device utilizes the CP as the active material to modulate between reflective and absorptive states. Our study shows the active material, chemically synthesized camphor sulfonic acid doped polyaniline (PANI-CSA), can simultaneously achieve intrinsic reflectance and large mid-IR electrochromic contrast. The IR-spectroscopic ellipsometry and electrochemical characterization explains the correlation between the electrochemical kinetics and the charge localization during the modulation processes. Finally, we will discuss and compare the several materials and design properties that affect the overall performance and efficiency in IR electrochromic metasurfaces.

2:30 PM ^EL08.14.04
Gap-Plasmon-Enhanced NbN Superconducting Photon Detectors at Single-Photon Level Yu-Jun Lo \(^{1,2}\); 1Academia Sinica, Taiwan; 2National Taiwan University, Taiwan

Single-photon detectors have been widely studied for decades because of their unique capability to resolve photon numbers, enabling many applications in quantum information technologies. Compared to other types of single-photon detectors, niobium nitride (NbN) superconducting nanowire single-photon detectors are promising candidates and are commercially available today. However, the absorption coefficient of superconducting NbN in the visible range is typically low, resulting in low quantum efficiency and low signal-to-noise ratios. In the present work, we use a novel approach to enhance the visible-light photoresponse in NbN superconducting microwave photon detectors (SMPDs) by integrating them with gap plasmon resonators (GPRs). This talk describes how we observe the plasmonic NbN SMPDs can achieve a 233-fold enhancement in the phonon-electron interaction factor (\(\gamma\)) compared to pristine NbN SMPDs under resonant conditions with illumination at 532 nm. The nonlinear photoresponse in the visible region is attributed to the gap-plasmon-induced heating that breaks the superconducting state to normal. In addition, an impressive detection efficiency of 98\% was achieved using these plasmonic SMPDs. Our results open new opportunities for designing sensitive quantum detectors for quantum information processing, quantum optics, imaging, and sensing at visible wavelengths. The detailed mechanisms and possible applications will be discussed.

3:00 PM BREAK

3:30 PM ^EL08.06.02
Strong Field Enhancement Based on Manipulation of Anapole State in Dielectric Metasurface Wen-Hui (Sophia) Cheng and Meng-Hsueh Tsai; National Cheng Kung University, Taiwan

Resonant metamaterials and metasurfaces cause by light-matter interaction in sub wavelength structures have been a hot research topic recently due to its potential in progressing the conventional devices. Anapole, a new hybrid mode is formed by overlapping toroidal dipole (TD) and electric dipole (ED) mode. Since the far field radiations of TD and ED are antiphasic, destructive interference between them will turn this hybrid mode into a dark mode with strong near field. In addition, the electric field can be further enhanced by incorporating the slot effect, which happens to fulfill the continuity of electric displacement field at interfaces of low-refractive-index and high-refractive-index material. In this work, we propose a dielectric metasurface which can support anapole mode and introduce slot effect to manipulate field enhancement. The structure is composed of a concentric circle and ring, with a middle bar connecting them. We find the middle bar and gap are critical and give rise to the tunability. From the multipole decomposition, a combination of TD and ED with same amplitude can be corresponded to the anapole mode. It shows that the middle bar creates a path for displacement current passing through it, supporting the nonradiative mode with high quality factor. The strong near field enhancement and high Q demonstrated is believed to be useful for many applications including PL control and nonlinear effect.

Keywords: Anapole, Slot effect, Metasurface, Dielectric, Field enhancement

4:00 PM ^EL08.14.06
Electrochemically Active Metasurfaces Po-Chun Hsu; The University of Chicago, United States

Electrochemistry is a powerful tuning knob for inducing drastic material property change. By applying an electrical bias while using counterions to maintain charge neutrality, electrochemistry can vary the carrier density or even trigger a phase transformation in an electrically addressable manner. Electrochemistry is an ideal tool in many applications where tunable range, scalability, or non-volatility is crucial. However, electrochemically active metasurfaces are still largely underexplored, probably due to the lack of a property database to perform metasurface design and optimization. More co-development is needed among fundamental materials science, metasurface design, and electrochemical device engineering. In this talk, I will present two examples of electrochemically active metasurfaces. (i) Conducting polymer near-perfect dynamic thermal emitter. We conducted infrared ellipsometry to measure the potential-dependent optical property and designed a tunable MIM near-perfect absorber for wearable variable emittance (WearVE) devices for personal thermoregulation. (ii) Reversible metal electrodeposition for active beam steering metasurface. Because reversible electrodeposition can create and dissolve metals on demand, active metasurface can be achieved by creating and dissolving the meta-atoms affecting the periodicity. As a proof of concept, we will demonstrate a reflection-type beam steering metasurface based on this principle and discuss the outlook and future challenges and opportunities.

4:30 PM EL08.14.07
Stop Coloring Inside The Lines- Meniscus-Guided Printing of Nanoparticle Films John R. Crockett. Kyung Sun Park, Yen-Chi Chen, Ying Diao and Qian Chen; University of Illinois at Urbana-Champaign, United States

Meniscus-guided printing has become a well-known technique for the application of polymer films. The ability to control orientation and thickness along with the ease of scaling have made it a low cost and effective process that is even used in manufacturing OLED displays. This research investigates the use of meniscus-guided printing for the simultaneous self-assembly and deposition of anisotropic gold nanorods. Through varying the speed, concentration of nanorods, energy of surface interactions, and size of substrate we have achieved deposition of several patterns with features from the millimeter to the nanoscale. This method can alleviate the necessity of costly and time-consuming templating or lithography steps, instead by controlling the confinement of the solution, and its interaction with the substrate, nanoparticle films can be templated and printed simultaneously.

SESSION EL08.15: Poster Session III
Session Chairs: Ho Wai (Howard) Lee and Pin Chieh Wu
Thursday Afternoon, April 25, 2024
Flex Hall C, Level 2, Summit

5:00 PM EL08.15.01
Realizing Full-Spectral Image Encryption In The Infrared Using An Electrically Tunable Metasurface and a Matched Detector Romul Audikhan\(^1\) and Michelle Povinelli\(^2\); 1University of Washington, United States; 2University of Southern California, United States

The ability of metasurfaces to manipulate optical waves in the spatial and spectral domain has provided new avenues for the development of compact and secure data storage platforms. Here we present an encryption system consisting of an electrically tunable metasurface and a matched detector for secure encryption of grayscale images in the 8 – 12 \(\mu\)m wavelength range. In the proposed scheme, the encrypted image corresponds to the spatially varying thermal intensity of the metasurface as captured by its matched detector. In contrast to previous metasurface-based encryption schemes, the current approach leverages the full spectral response of the associated photonic devices to achieve secure encryption while circumventing the need for an increased device size. Using examples of single and multi-image encryption, we show that the optical properties of either the metasurface or matched detector alone do not reveal any meaningful information about the encrypted image, thereby validating the security of the proposed scheme. The electrical tunability of the metasurface provides additional security as the image can only be retrieved by operating it at a predefined voltage level. We believe that our results provide intriguing possibilities for the development of compact and secure object tagging and anti-counterfeiting applications in the infrared.

5:00 PM EL08.15.02
Manipulating Confined Infrared Light via Polaritonic Design of Sub-Diffractional \(\alpha\)-MoO\(_3\) Wedges Ethan Ray\(^{1,2}\), Mingze He\(^2\), John Buchner\(^2\), Saurabh Dixit\(^2\) and Joshua D. Caldwell\(^2\); Duke University, United States

Stop Coloring Inside The Lines- Meniscus-Guided Printing of Nanoparticle Films

John R. Crockett. Kyung Sun Park, Yen-Chi Chen, Ying Diao and Qian Chen; University of Illinois at Urbana-Champaign, United States

Meniscus-guided printing has become a well-known technique for the application of polymer films. The ability to control orientation and thickness along with the ease of scaling have made it a low cost and effective process that is even used in manufacturing OLED displays. This research investigates the use of meniscus-guided printing for the simultaneous self-assembly and deposition of anisotropic gold nanorods. Through varying the speed, concentration of nanorods, energy of surface interactions, and size of substrate we have achieved deposition of several patterns with features from the millimeter to the nanoscale. This method can alleviate the necessity of costly and time-consuming templating or lithography steps, instead by controlling the confinement of the solution, and its interaction with the substrate, nanoparticle films can be templated and printed simultaneously.

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Thursday Afternoon, April 25, 2024
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5:00 PM EL08.15.01
Realizing Full-Spectral Image Encryption In The Infrared Using An Electrically Tunable Metasurface and a Matched Detector Romul Audikhan\(^1\) and Michelle Povinelli\(^2\); 1University of Washington, United States; 2University of Southern California, United States

The ability of metasurfaces to manipulate optical waves in the spatial and spectral domain has provided new avenues for the development of compact and secure data storage platforms. Here we present an encryption system consisting of an electrically tunable metasurface and a matched detector for secure encryption of grayscale images in the 8 – 12 \(\mu\)m wavelength range. In the proposed scheme, the encrypted image corresponds to the spatially varying thermal intensity of the metasurface as captured by its matched detector. In contrast to previous metasurface-based encryption schemes, the current approach leverages the full spectral response of the associated photonic devices to achieve secure encryption while circumventing the need for an increased device size. Using examples of single and multi-image encryption, we show that the optical properties of either the metasurface or matched detector alone do not reveal any meaningful information about the encrypted image, thereby validating the security of the proposed scheme. The electrical tunability of the metasurface provides additional security as the image can only be retrieved by operating it at a predefined voltage level. We believe that our results provide intriguing possibilities for the development of compact and secure object tagging and anti-counterfeiting applications in the infrared.

5:00 PM EL08.15.02
Manipulating Confined Infrared Light via Polaritonic Design of Sub-Diffractional \(\alpha\)-MoO\(_3\) Wedges Ethan Ray\(^{1,2}\), Mingze He\(^2\), John Buchner\(^2\), Saurabh Dixit\(^2\) and Joshua D. Caldwell\(^2\); Duke University, United States
The mid-infrared (mid-IR) spectrum of light is crucial for various applications, including thermal imaging, molecular sensing, and free-space communication. However, the application of long free-space wavelengths of mid-IR light is limited in chip-scale devices due to the diffraction limit. This problem can be circumvented by using hyperbolic materials where the dielectric permittivities along the principal crystal directions exhibit opposite signs in the mid-IR spectral region. It has been well-demonstrated that hyperbolic materials (e.g., h-BN, α-MoO3, α-V2O5) can confine high-momentum (short wavelength) electromagnetic waves in the form of hyperbolic phonon polaritons (HPPs) - quasi-particles made from the hybridization of charged dipole phonons and photons (an external light source). The propagation behavior of these HPPs can be tuned and confined in deep sub-diffraction volumes using sub-wavelength structures, which offer distinct opportunities in the form of chip-scale nano-phononics devices for integrated optics and photonics applications.

In this work, we investigate sub-wavelength wedges of a hyperbolic material (α-MoO3) to demonstrate in-plane focusing of electromagnetic waves beyond the diffraction limit and a transition of polaritonic propagation in the forbidden direction of the α-MoO3 crystal. We design our wedges by optimizing lateral dimensions and wedge thickness using 3D numerical simulations via COMSOL Multiphysics. Numerically, we observed transitions from adiabatic compression to standing wave in polaritonic modes through changing wedge vertex angles ($\theta$). For 10°< $\theta$<30°, we observe a compression factor (i.e. ratio of wavelength in the waveguide to the adiabatically compressed region in the wedge) of 2.89 (at 700 cm-1) and 1.42 (at 900 cm-1) that converge to 1 upon increasing vertex angle. Further, we investigate the effect of geometrical confinement at vertex angles 120°< $\theta$<150° on propagation direction and found that a high vertex angle of wedge enables the propagation of HPPs in the forbidden direction. After establishing these theoretical foundations, we fabricated such wedges and characterized them with scattering-type Near-field Optical Microscopy (s-NSOM). Through s-NSOM, we found the presence of adiabatically compressed waves confined at the tip of the wedge at lower vertex angles and node formation along the forbidden propagation direction at high vertex angles. This work offers a novel tunable parameter for manipulating mid-IR light propagation in α-MoO3 sub-wavelength structures. Further, these findings open avenues for chip-scale mid-IR nanophotonics devices and optical components with the ease of van der Waals integration for integrated optics and photonics applications.

5:00 PM EL08.15.03

New Design Principle of Chemically Tunable Bulk Hyperbolic Metamaterials

Hyunsung Lee1, Jong-Young Kim2 and In Chung1; 1Seoul National University, Korea (the Republic of); 2Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of)

Conventional hyperbolic metamaterials are fabricated to form artificial nanoscale structures that are designed to interact with light uniquely. In addition to removing the difficulty in theoretical prediction of the structures to induce desired properties, their structures had to be realized by technically challenging nanofabrication techniques. Herein, we present a new facile design principle to realize hyperbolic metamaterials with a hyperbolic dispersion tunability. Using two exfoliated inherent hyperbolic materials as a building block, hexagonal boron nitride (h-BN) and graphite/graphene, we developed the facile synthesis method to obtain their heterostructured nanohybird powders via self-assembly between two functionalized building blocks. Afterwards, the resulting powders were consolidated into dense bulk pellet using spark plasma sintering. The final bulk products comprise the alternating nanoscale layers of h-BN and graphite/graphene. Depending on the mixing ratio and thickness of the constituent building blocks their microstructures were delicately altered, consequently serving as a fine tool to control the hyperbolic responses. Remarkably, embedding a trace of rhombohedral boron nitride (r-BN) also anisotropically changes both type-I and type-II hyperbolic resonance modes and negative permittivities, thus indicating that r-BN acts as a `dopant' in h-BN/graphite metamaterial system. For the first time, our work demonstrates the real bulk metamaterials with finely tunable hyperbolic dispersions by modulating chemical compositions. Negative permittivities are observed for the incident infrared light along both the in-plane and out-of-plane directions. Our achievement can serve a potential platform to rationally design and conveniently realize scalable bulk metamaterials without need of complicated fabrications.

5:00 PM EL08.15.05

Terahertz Time Domain Transmission Spectroscopy of Magnetic Nanoparticles for Frequency Selective Surface Application

Kousik Pradhan1, Sumit Saxena1, Shobha Shukla1, Siddhartha Duttagupta1 and Sriganesh Prabhu1; 1Indian Institute of Technology Bombay, India; 2Iowa Institute of Fundamental Research, India

Terahertz time-domain spectroscopy (THz-TDS), is an effective method for characterizing materials and monitoring processes. Metals, electronics, 2D materials, and even superconductors have all been tested with this technique, which does not require physical touch to extract accurate results. Terahertz (THz) spectroscopy has developed as a method for investigating dielectric and transient photoductive characteristics of materials over the past few decades. Since it can measure electrical resistance without touching the sample and has a temporal precision of a few picoseconds. Due to the low energy of THz radiation and the narrow pulse width, THz-TDS technology is non-destructive when used for extracting visual data from materials (picosecond range). This paper reveals optical parameters extraction methods using by THz transmission spectroscopy technology. In summation, materials with a low absorption of terahertz radiation can benefit from the adaptability of transmission methods, while materials with a high absorption capacity can take advantage of the advantages of reflection methods. To measure the magnetic material's optical properties like refractive index and absorption coefficient, we employ a transmission-type terahertz time domain spectroscopic instrument. The observations and analysis are performed in both the time domain and frequency domain, and we examine the transmission of terahertz radiation through a polymer based magnetic nanoparticle substance at frequencies from 0.1 to 3 terahertz (THz). In the past few years, magnetic materials based on frequency selective surfaces (FSS) have become indispensable in the design of gigahertz (GHz) and terahertz (THz) millimeter-wave filters, polarizers, absorbers, EMI shielding, antenna reflectors, and radar applications. In this research, ferrite was used to produce a microstructured FSS on a quartz substrate. Frequency Domain (FD) solvers included in the CST MWS commercial software package, which is based on the Finite Integration Technique (FIT), are used to evaluate the FSS's efficiency. Here, we demonstrate a terahertz filter made from arrays of circular holes in a quartz substrate, which acts as a frequency selective surface (FSS). We shall show the properties of FSS terahertz-wave transmission using a finite difference time-domain approach. Researchers looked examined the suggested design over a range of frequencies from 0.2 THz to 3 THz. The proposed structure's complementary behaviour is also statistically analysed. We evaluate the proposed layouts by investigating their most elemental characteristics, such as their transmittance and polarisation. The response of the proposed structure to a broad variety of incidence angles is also investigated. Additionally, at the frequency selective surface of the magnetic material, polarisation insensitivity is achieved for the TE and TM stimulated mode. This research presents the detailed layout and analyses of the evaluated parameters for the proposed terahertz wave filter. The suggested terahertz wave filter's parameters are then fine-tuned. The filter we describe has the potential to be widely used in future terahertz wave systems due to its low manufacturing costs and simple design.

5:00 PM EL08.15.06

Dynamic Tuning between a Reflecting Mirror and a Transmitting Window by Nano Sphere Lithography and Electrochemistry

TsongYu Huang and Cheng-Yuan Xiao; Ming Chi University of Technology, Taiwan

In the ever-evolving landscape of technology, electronic devices such as displays, solar panels, and touchscreens have become indispensable to our daily lives. These devices rely on a critical component known as transparent conductive electrodes. In the past, indium tin oxide (ITO) was the common material for these electrodes. However, ITO has certain drawbacks. Its inherent oxide nature makes it brittle and susceptible to damage, and indium is a precious metal, with high cost. To overcome these challenges, researchers have explored novel nanostructures that serve as alternatives to traditional ITO electrodes. Yet, most of these nanostructures come with a drawback, i.e., they tend to possess fixed conductivity and transmittance values after production, lacking the ability for dynamic modulation.

To address this limitation, in this work we combine nanosphere lithography, indium tin oxide deposition, and the electrodeposition of silver to design and fabricate a dynamic tuning between a reflecting mirror and a transmitting window. To fabricate such a device, first of all, we spin-coated polyethylenepolyoxynolene for a uniform mask. The corresponding spacing among nanospheres was further modified by reactive ion etching. Next, ITO was deposited to form a countinous hollow hole array. The next, the electroplating of silver was carried out. By controlling parameters of electrochemical reaction, we could fine tune the corresponding thickness of silver and the open of hole array for actively manipulating transmittance of the proposed devices. The electroplating behavior of the device and the transmittance for different thickness and morphology of the device were further predicted by two simulations. The first simulation focused on the transmittance of the proposed device by tuning the periodicity and the opening of the devices and the thicknesses of both ITO and silver. The second simulation involves the electrochemistry reaction. The potential variables included material parameters of electrodes and electrolytes, applied current, electrodeposition area, and thickness to anticipate the experimental outcomes.

5:00 PM EL08.15.07

Configurationally Tunable Mie, Plasmonic and Diffractive Structural Colors in a Single Design

Youngei Kim1,2; Joshua D. Caldwell1 and Jerome Hyun2; 1Vanderbilt University, United States; 2Ewha Womans University, Korea (the Republic of)

We have developed a structural color design capable of displaying Mie resonant, plasmonic, and diffractive colors within a single design, depending on the configuration of imaging setup. Previous research achieved two distinct colors arising from the same resonance mechanism by introducing anisotropy into the structural parameters of a 2D array and selectively displaying each color based on the polarization. In this study, however, we store and display multiple colors within a single design by employing a 1D metaldielectric grating composed of TiO2 nanowires sandwiched between two Ag layers. Choice of polarization allows for either an electric dipole Mie resonance or a localized surface plasmon resonance to occur independently.

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Metasurfaces have become one of the cornerstones of modern nanotechnology. In planar optics, they enable the precise control of phase, amplitude, and polarization of light at the nanoscale.

A Battery-Free Stretchable Strain Sensor Using Plasmon-Based Structural Color

10:45 AM


Here, we introduce a battery-free, soft, and stretchable strain sensor using structural color that combines plasmon resonance and interference effects. The device structure comprises 4 stacked layers: a high-refractive-index (n=1.55) polymer, a low-refractive-index (n=1.33) polymer, gold nanoparticles, and a black silicone substrate. Structural coloration emerges from the interference of reflected light from gold nanoparticles, where plasmon resonance takes place, with the reflected light at the interface of the top high and low-refractive-index layers. Applied strain changes the thickness of a low-refractive-index polymer layer to induce different structural colors. This color can be adjusted by modifying the thickness of the low-refractive-index polymer layer and the gold nanoparticle size. Given our structural color layer is ultra-thin, under 1 μm, its flexibility is easily adjustable with additional PDMS layers. A particular device displayed a reflection peak of 730 nm (red) at 0% strain and 665 nm (green) at 60% strain. Moreover, our sensor adapted to finger joints and exhibited a distinct color shift during finger bending.

The scaling of lasers and in-particular of surface emitting lasers is a multi-decade long question that has been investigated since the invention of lasers in 1958. It is an important question with numerous applications. In this talk, I will propose and discuss an intriguing solution to this question that we named the Berkeley Surface Emitting Laser (BerkSEL) and it is the world’s first scale-invariant laser. In the second part of the talk, I will discuss our demonstration of the first deterministic quantum light source in silicon that emits single photons in the telecom band. The NA. We also demonstrate the color modes from the 1st order diffraction. All resonance mechanisms and imaging configurations depend solely on the two spatial parameters and their combination: the period and the width of the nanowire. Finally, we demonstrate four levels of encoded images produced from a single set of the gratings under different imaging setups. These findings open up new possibilities for applications, such as image encryption and data storage, and so on.

SESSION EL08.16: Metastucture Designs and Fabrication for Light Manipulation and Sensing
Session Chairs: Ho Wai (Howard) Lee and Ruzan Sokhoyan
Friday Morning, April 26, 2024
Room 340/341, Level 3, Summit

10:30 AM EL08.16.01
Probing The Impact of Interfaces on Thin-Film Lithium Niobate Electro-Optic Device Performance
Matthew Yeh1, David R. Barton1,2, Gavin Smith1, Evelyn L. Hu1 and Marko Loncar2; 1Harvard University, United States; 2Northwestern University, United States

Thin-film lithium niobate on insulator (TFLN) has emerged as a strong candidate platform for integrated classical and quantum photonics due to its large linear electro-optic (EO) effect and wafer-scale availability. Driven by breakthroughs in nanofabrication, the EO interaction strength has greatly improved over the bulk, unlocking a new class of devices such as high-bandwidth and energy-efficient modulators, ultrafast pulse generators, and microwave-to-optical transducers. Despite rapid advances in device functionality, however, material understanding has fallen behind. In particular, it is generally recognized that the reliability of TFLN modulators is subject to unstable EO response at dc and low frequencies. This instability is especially disruptive to the advancement of large-scale photonic circuits and cryogenic applications such as quantum photonics, which require precise index reconfigurability and low-power operation. Post-processing techniques such as thermal annealing have been developed to reduce these deleterious effects, but the microscopic origins of instability remain unclear.

Here, we combine measurements of the material structure, electronic properties, and EO device performance to identify a mechanistic insight for low-frequency instability in TFLN. All devices are fabricated on 600 nm thick x-cut lithium niobate on insulator wafers, and we explore modifications to the fabrication process that affect both bulk and interface properties. First, we correlate electronic transport measurements with improvements in the EO response magnitude to show that annealing reduces charge leakage pathways in TFLN. However, SIMS measurements of the elemental composition show that simultaneously additional dielectric relaxation pathways are introduced; annealing in the presence of a cladding oxide creates an interface by which lithium can diffuse out of the TFLN.

Next, we show through XPS that the etch chemistry and acid cleans used in our thin-film processing dramatically affect the surface chemistry of TFLN. Dry etching with a Ar plasma reduces Nb and creates a damaged amorphous surface layer, whereas employing a C2F6-based chemistry creates a prominent F peak stemming from the formation of LiF, salts or fluoropolymers. The surface Li:Nb ratio can be restored both by specific chemical cleans that remove the damaged layer or thermal annealing. Surprisingly, forming metal contacts to LN surfaces that have been cleaned or annealed actually reduces the EO response magnitude and degrades the stability. Together, these measurements indicate that the metal-TFLN interface also plays a key role in determining EO device performance.

11:00 AM EL08.16.03
Investigation of The Nanoparticle – Support Interaction Effects of Plasmonic Gold Nanoparticles Deposited on Steel and Aluminum
Rosemary L. Calabro1,2, John Burpo1, Stephen F. Bartolucci2 and Joshua A. Maurer2; 1United States Military Academy, United States; 2U.S. Army DEVCOM Armaments Center, United States

Plasmonic nanoparticle (NP) based sensors have been developed to detect a wide range of analytes based on the principles of localized surface plasmon resonance (LSPR). With LSPR, the peak wavelength of absorption and scattering can shift, broaden, narrow, or be amplified or suppressed based on an interaction with the analyte of interest, allowing an optical readout. However, factors such as a near-field coupling, size effects, and surface environment of the NPs can also influence the LSPR properties. Practical implementation of LSPR based sensors requires deposition of the NPs on a substrate, however most studies thus far have focused on very crystalline or pristine materials. We investigated the NP-substrate interaction effects of gold nanoparticles (AuNPs) on two industrially relevant substrates: steel and aluminum. AuNPs were drop cast on the substrates and the change in reflectivity was measured. The spectral properties were also compared to AuNPs in solution. Near field-coupling of the AuNPs was observed when the samples were transferred from water to isopropyl alcohol due to partial nanoparticle agglomeration, however this coupling effect was not observed when the particles were deposited from the isopropyl alcohol to the substrates, despite being aggregated together on the substrate. This suggests that the AuNP coupling effect to the substrate is much stronger than any NP interactions with each other. Shifts in the peak wavelengths were observed when depositing the AuNPs on the substrates, with AuNPs deposited on steel typically exhibiting a redder shift compared to AuNPs on aluminum. Variable angle measurements showed that the AuNPs absorbed strongly at low angles of incidence, with decreasing absorption as the angle increased. Other factors such as the separation of specular and diffuse reflectance, AuNP shape and size, different capping agents, and the surface roughness of the substrates were also considered. The results from this study provide valuable insight into NP – substrate interactions and will help better design LSPR based sensors for a wide range of industrial applications.

11:15 AM EL08.16.04
Scalable Classical and Quantum Light Sources
Boubacar Kante; University of California, United States

The scaling of lasers and in-particular of surface emitting lasers is a multi-decade long question that has been investigated since the invention of lasers in 1958. It is an important question with numerous applications. In this talk, I will propose and discuss an intriguing solution to this question that we named the Berkeley Surface Emitting Laser (BerkSEL) and it is the world’s first scale-invariant laser. In the second part of the talk, I will discuss our demonstration of the first deterministic quantum light source in silicon that emits single photons in the telecom band. The work opens unique perspectives for scalable quantum networks.

11:45 AM EL08.16.05
Light-Controlled Disorder-Engineering of Optical Metasurfaces: Aspects of Design and Applications
Maximilian Buchmueller, Sven O. Schumacher and Patrick Goerrn; University of Wuppertal, Germany

Metasurfaces have become one of the cornerstones of modern nanotechnology. In planar optics, they enable the precise control of phase, amplitude, and polarization of light at the nanoscale, which has led to advances in numerous application fields, including sensing, nonlinear optics, and optical modulators. However, their implementation often requires surface nanostructuring, based on complex design and fabrication methods such as electron-beam lithography of focused ion-beam milling. In addition, exploiting narrow spectral features, e.g., for sensing, is
In conclusion, we hope that this work will lead to the further development of metadevice technologies based on organic semiconductors, with the future aim of improving the effectiveness of methods for both the metamaterial matrix and the organic semiconductor, on either rigid or flexible plastic substrates, without losing modulation efficiency.

Also, another key aspect of our work is to show that it is then possible to shift towards mass-scalable and cost-effective manufacturing techniques exploiting high-throughput deposition based on conjugated polymers with glycolated sidechains, such as the emerging p(g2T-TT) semiconductor.

In our work, we explore for the first time the functioning and the effectiveness of an organic semiconductor-driven metadevice based on a matrix of metal Split-Ring Resonators, which can modulate the amplitude, phase, and frequency of THz pulses, to achieve the highest modulation depth and switch speed possible [3]. Among the plethora of proposed modulating techniques based on organic, electro-mechanical, or thermal stimuli, electrically-tuned THz metadevices represent a flourishing approach that directly benefits from the development of novel and unconventional transistor configurations.

This modulating technique in the THz spectral region, especially in terms of modulating speed. Moreover, this device development comes together with an ongoing study on the THz properties of novel and unconventional transistor configurations.

In support of our approach, we also show that it is possible to modulate surface plasma polarizations (SR-SPPs) to smooth ultra-thin silver films using a Kretschmann-Raether geometry. [3] Typically, it is challenging to utilize SR-SPPs in planar stack geometries, because of their high effective mode index. Nanostructuring ultra-thin metal films (around 20nm thickness), or placing metallic nanostructures in close proximity to the planar film for coupling is technologically challenging and can strongly influence the SR-SPP properties. The new possibilities given by our method promise great potential for sensing single surface binding events and high resolution imaging applications due to their strong field enhancement and localization. First promising results also suggest the possible use of other noble metals instead of silver, such as gold, for biomedical and medical applications.

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**SESSION EL08.17: Nanostructure Design, Fabrication and Characterization**

**Session Chairs:** Boubicar Kante and Ho Wai (Howard) Lee
Friday Afternoon, April 26, 2024
Room 340/341, Level 3, Summit

1:30 PM EL08.17.02

**Electrically Gated Organic-Based Metadevice for THz Amplitude Modulation**

Federico Grandi1,2, Cristiano Bortolotti1,3, Francesco Modena1, Lorenzo Gatto2, Matteo Butti3, Iain McCulloch4, Caterina Vozzi2, Mario Caironi1, Giorgio Ernesto Bonacchini1 and Eugenio Cinquanta2, 1Politecnico di Milano, Italy; 2CNR-IFN, Italy; 3Istituto Italiano di Tecnologia, Italy; 4University of Oxford, United Kingdom

In the last years, the interest in THz technologies has increased rapidly due to their applicability across several application scenarios like telecommunication and sensing, with recent developments overarching the fields of optics and electronics [1]. Despite their scientific and technological appeal, THz waves have a major drawback coming from the absence of optoelectronic techniques and devices that can manipulate such light waves. To solve this issue, one of the most promising approaches relies on the use of metasurfaces [2], engineered composites whose optical properties can be specifically tailored to interact with THz waves. Therefore, research is now focused on trying to design reconfigurable metamaterials, also known as metadevices, able to modulate the amplitude, phase, and frequency of THz pulses, to achieve the highest modulation depth and switch speed possible [3]. Among the plethora of proposed modulating techniques based on optical, electro-mechanical, or thermal stimuli, electrically-tuned THz metadevices represent a flourishing approach that directly benefits from the development of novel and unconventional transistor configurations.

In our work, we explore for the first time the functioning and the effectiveness of an organic semiconductor-driven metadevice based on a matrix of metal Split-Ring Resonators, which can modulate the amplitude of a THz pulse passing through them [4]. This approach has already been shown to work nicely in the microwave spectral region [5] but has not yet been applied in the THz range. The modulability capabilities come from the time it takes for the charge carriers to rearrange in the organic semiconductor, which enables the metadevice to act as an optical transistor, varying THz transmission around a specific frequency (~0.7 THz) with modulation depths of approximately 65%. These performances, which are comparable with current state-of-the-art technologies but with a lower driving voltage (~1 V) result from the unique 3-dimensional charge modulation properties of a new class of organic mixed ion-electron conductors based on conjugated polymers with glycolated sidechains, such as the emerging p(g2T-TT) semiconductor.

Also, another key aspect of our work is to show that it is then possible to shift towards mass-scalable and cost-effective manufacturing techniques exploiting high-throughput deposition methods for both the metamaterial matrix and the organic semiconductor, on either rigid or flexible plastic substrates, without losing modulation efficiency.

In conclusion, we hope that this work will lead to the further development of metadevice technologies based on organic semiconductors, with the future aim of improving the effectiveness of this modulating technique in the THz spectral region, especially in terms of modulating speed. Moreover, this device development comes together with an ongoing study on the THz properties of this emerging class of organic semiconductors, leading to fundamental scientific insights that could also find application in other areas, such as electronics and bioelectronics.


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**Emergent Opportunities with Magnetism for Green Photonics**

Peifen Lyu, Tao Gong and Marina S. Leite; University of California, Davis, United States

Structural color generation exploiting nanophotonics or plasmonic behaviors has burgeoning applications in displays, lasers, sensors and other optical sources due to promising advantages such as durability, environmental friendliness, and compatible integration with monolithic fabrication compared to traditional pigments and dyes. While conventional metals (e.g., Au, Ag and Cu) and their alloys are the focus of current optical research, magnesium (Mg) as an earth-abundant material, with biodegradability and CMOS compatibility, has not been fully explored in photonic applications. In our present works [1, 2], we have already established a novel platform for transient color filters/superabsorbers based on Mg and other dielectric thin films with angle-insensitive responses and capabilities for fast switching of single vivid hues when exposed to water. These results motivate us to now pursue the realization of sophisticated 3D nanostructures that will form the building blocks of degradable/biocompatible devices. Based on our preliminary optical simulations using Finite-Difference Time-Domain (FDTD) for selected nanostructure configurations [3], all of the structures exhibit pronounced blue-shifting of their scattering peak frequency with decreased sizes (i.e. due to the etching process of Mg in water). These resonance shifts beget a plethora of applications in photonic devices. For example, it can produce a smooth transition of hues in color display devices for dynamic color tuning. Besides, we perform near-field scattering measurements with Mg nanostructures in situ to experimentally demonstrate the transient behavior as the Mg dissolves in a controlled manner. This helps us to achieve our long-term goal of realizing Mg-based dyes for next-generation CMOS-compatible and green photonic devices.


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**2:00 PM BREAK**

2:30 PM EL08.17.06

**Synthesis and Photocatalytic Activity of Porous Bimetallic Plasmonic Nanoparticles Formed on Solid Substrates**

Harshitha Rajashekar, Navneet Kumar, John Garcia, Damini Vishubhandarkar and Karthik Shankar; Univ of Alberta, Canada

Plasmonic catalysis aims to extract useful work from the surface plasmon resonance phenomenon to assist in order to drive a chemical reaction. Nanoparticles (NPs) composed of plasmonic metals such as Au, Ag, Cu and Al resonantly interact with light through the excitation of localized surface plasmon resonance (LSPR) modes which subsequently decay to produce highly
energetic “hot carriers”. There are two major technical obstacles that prevent the efficient utilization of hot carriers to drive chemical reactions. The first limitation is that plasmonic NPs are frequently synthesized as colloidal suspensions while a number of heterogeneous catalytic reactions require the catalyst to be anchored to a solid-state support. The second limitation arises due to the relative chemical inertness of noble metals, particularly gold, which prevents the adsorption of most types of reactant molecules on the surface of the plasmonic NP catalyst. As a consequence of the second limitation, plasmonic metal NPs often demonstrate low catalytic activity for many chemical reactions. In recent years, there has been growing interest in bimetallic nanostructures that combine the optical characteristics of plasmonic metals with the catalytic properties of metals such as Pt and Pd. In this work, we attempted the precise fabrication of diverse bimetallic plasmonic photocatalysts with a porous structure to overcome both the aforementioned technical problems. Porous bimetallic plasmonic nanoparticles with large surface areas possess an enhanced capacity to adsorb reactant molecules (compared to their monometallic counterparts) increasing their overall catalytic efficiency. In this work, we present a degrading technique to fabricate porous bimetallic nanostructures on solid substrates and investigate their activity for the vapor phase transformation of CO₂ and H₂O into hydrocarbons at close to room temperature.

We also analyze the photocatalytic ability of the as-fabricated porous bimetallic nanostructures in the decolorization of methylene blue (MB) dye. Scavenger studies indicate photogenerated electrons to be the active species responsible for photocatalytic activity. In both CO₂ photoreduction and dye photodegradation, bimetallic porous Au/Pt NPs outperform monometallic porous Au NPs by nearly 3.3x. These results have important implications for more energy efficient, sustainable heterogeneous catalysis under milder conditions of temperature and pressure. This work also presents the application potential for the use of porous bimetallic photocatalytic catalysts in water remediation and the generation of solar fuels.

Focusing on the application of plasmonic materials, we showed that plasmonic substrates are based on Ag@ZnO nanocomposites deposited on cellulose acetate fibers. Magnetron sputtering combined with 3D nanoprinting can be used to fabricate chiral Au/PbO₂ heterostructures or as an additional ingredient in chiral molecule-directed synthesis to enhance the optical dissymmetry of the nanocrystals further. However, the mechanism by which these chiral structures develop with CPL has remained largely unexplored. Our latest study has revealed that the wavelength of CPL is a critical factor in determining the shape of chiral Au/PbO₂ heterostructures and their resulting chiroptical properties. Here, we further demonstrate that the asymmetry of the initial plasmonic nanocrystals plays a crucial role in generating more chiral nanostructures. Specifically, we utilized silver nanorods with varying aspect ratios as the starting materials. Ag was oxidized at selective sites upon circularly polarized excitation to create chiral structures. Our results indicate that the optical activity of resulting chiral nanostructures increases with the aspect ratio of the starting nanocrystals. Besides, tuning the excitation wavelength with Ag nanorods of a larger aspect ratio can yield higher contrast of chiral morphologies due to the larger number of higher-order modes accessible in these nanocrystals. Our study underscores the importance of carefully selecting the starting material and excitation wavelength to maximize chiral plasmonic nanocrystals’ shape and optical dissymmetry when using CPL as the chirality source. Besides, the non-toxic chiral Ag nanocrystals are more suitable for bio-compatible systems than chiral Au/PbO₂ nanostructures.

We also analyze the photocatalytic ability of the as-fabricated porous bimetallic nanostructures in the decolorization of methylene blue (MB) dye. Scavenger studies indicate photogenerated electrons to be the active species responsible for photocatalytic activity. In both CO₂ photoreduction and dye photodegradation, bimetallic porous Au/Pt NPs outperform monometallic porous Au NPs by nearly 3.3x. These results have important implications for more energy efficient, sustainable heterogeneous catalysis under milder conditions of temperature and pressure. This work also presents the application potential for the use of porous bimetallic photocatalytic catalysts in water remediation and the generation of solar fuels.

In summary, we demonstrated that plasmonic substrates, based on Ag@ZnO nanocomposites deposited on cellulose acetate fibers, can be used for high-performance chiral plasmonic nanostructures. The Ag@ZnO substrates can be fabricated using magnetron sputtering combined with 3D nanoprinting to achieve high-efficiency chiral plasmonic nanostructures.

In this work, we attempted the precise fabrication of diverse bimetallic plasmonic photocatalysts with a porous structure to overcome both the aforementioned technical problems. Porous bimetallic plasmonic nanoparticles with large surface areas possess an enhanced capacity to adsorb reactant molecules (compared to their monometallic counterparts) increasing their overall catalytic efficiency. In this work, we present a degrading technique to fabricate porous bimetallic nanostructures on solid substrates and investigate their activity for the vapor phase transformation of CO₂ and H₂O into hydrocarbons at close to room temperature.

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In conclusion, the development of novel strategies for fabricating chiral plasmonic nanostructures opens up new possibilities for applications in biophotonics, quantum technologies, and optical sensing. Conventional top-down fabrication methods usually fail as the fiber geometry is complementary to that of planar substrates (e.g., wafers). In this presentation, we show on several examples that 3D nanoprinting using direct laser writing circumvents this bottleneck, allowing to implement intricate nanostructures on the end face of optical fibers. This breakthrough allowed us to optically trap microspheres and bacteria with individual single-mode fibers, overcoming a significant limitation of fiber optics.
Plasmonic and Plasmon-Free Nanostructured SERS Sensors

10:30 AM

The practicality of the developed SERS assay was elucidated in various matrices (e.g., maize, rice, and wheat), with recovery values of 95–103%. The successful validation of actual samples' analysis emphasizes the platform's reliability, robustness, and suitability for practical use of multi-target analytes detection, including on-site operation.

Regardless of decades of extensive research, mycotoxins continue to penetrate the food chain through food and feed crops and pose health risks to humans and livestock. Herein, we present a newly developed nanostructured microarray (5 by 5 sensing spots) based on silver-coated porous silicon used as a surface-enhanced Raman scattering (SERS) transducer. The unique microarray was facilitated without the need for any micro/nano-fabrication (clean-room) facilities. The inherent surface void and pore morphology (82±2% and ca. < 9 nm, respectively) were physically optimized to augment the SERS effect while achieving an enhancement factor of > 10^6. Under optimized conditions, three common mycotoxins (aflatoxin B1, fumonisin B1, and ochratoxin A) in feed ingredients and agricultural products were simultaneously assessed using a portable Raman device (1.5 µL sample analyzed in 30 min). The optical response was inversely proportional to the metabolite concentration upon selective interaction with anti-target mycotoxin aptamers modified sensing spots. The calculated limits of detection were 0.01, 0.6 and 0.9 ng/mL (part per billion, ppb) for aflatoxin B1, fumonisin B1, and ochratoxin A, respectively, within the dynamic range of 0.1-1000 ppb. Furthermore, the selectivity, regeneration, and overall shelf-life were thoroughly evaluated while depicting satisfactory performances (no interferences with interfering mycotoxins, four regeneration cycles, and five weeks of stability, respectively). Finally, the practicality of the developed SERS assay was elucidated in various matrices (e.g., maize, rice, and wheat), with recovery values of 95–103%. The successful validation of actual samples' analysis emphasizes the platform's reliability, robustness, and suitability for practical use of multi-target analytes detection, including on-site operation.

**Keynote Speaker**

**JMR Distinguished Invited Speaker**

**Invited Paper**

**Session EN01.01: Organic Photovoltaics**

Application Targets for Next Generation Photovoltaics

April 23 - April 26, 2024

Symposium Organizers

Ardalan Armin, Swansea University
Christopher Brabec, FAU Erlangen-Nuremberg
Nicola Gasparini, Imperial College London
Ellen Moons, Karlstad University

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* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter
Metal halide perovskite solar cells have advanced into a viable option for future renewable energy. Record single and tandem junction all-perovskite solar cells already provide power efficiencies of over ~26% and ~29%, respectively. A next target in photovoltaic energy conversion can possibly be met by developing perovskite triple or even quadruple junction solar cells. While these hold a promise to afford higher efficiencies, they require developing stable perovskite sub cells with bandgaps in the range of 1.8 to 2.3 eV, i.e., a range that has not received much attention so far. These wide-bandgap perovskites often suffer from more pronounced voltage losses due to non-radiative bulk and interfacial charge recombination. In developing new perovskite sub cells, photocurrent spectroscopy and absolute photoluminescence spectroscopy are used in combination with bulk and interface passivation strategies to eliminate these losses. This has enabled to reduce the voltage deficit over a wide range of bandgap. Guided by optical modelling, monolithic multi-junction solar cells have been fabricated by stacking two and three different bandgap perovskite sub cells in series using recombination junctions designed to provide near-zero electrical and optical losses. Collectively, these strategies enable monolithic tandem and triple junction solar cells with a power-conversion efficiency of over 26%.

Moreover, there is still a large performance gap between spin-coated, hero cells and large-scale modules. This is due, among other factors, to the difficulties in maintaining an optimal active layer morphology when switching to industrial fabrication techniques. To bridge this gap, it is paramount to study the photophysics of devices made with scalable techniques, such as blade coating and slot-die coating.

In this work, we demonstrate highly efficient organic solar cells fabricated with spin-coating, blade coating, and slot-die coating techniques, using PM6 and Y12 in o-xylene as electron donor and electron acceptor materials, respectively. We then investigate the differences and similarities between these techniques with a variety of optoelectronic techniques, including transient photocurrent, charge extraction, and GIWAXS, to determine charge carrier dynamics, morphology, photovoltaic performance, and stability.

Finally, this work demonstrates the application of gradient-solvent processed OSCs as semi-transparent devices with over 40% visible transmittance and a fully solution-processed stack.

**Towards Highly Efficient Upscaled Organic Solar Cells: Solvents, Fabrication and The Role of Charge Carrier Dynamics**

Eva Mazzeolini1,2, Richard A. Pacalaj1, Bhushan Patil1, Yuan-Fu4, Rahul Patidar3, Xinhui Lu4, Trystan Watson3, Zhe Li2, James Durrant1 and Nicola Gasparini1, 1Imperial College London, United Kingdom; 2Queen Mary, University of London, United Kingdom; 3Swansea University, United Kingdom; 4The Chinese University of Hong Kong, Hong Kong

Organic solar cells (OSC) using non-fullerene acceptors in the Y6 family have now surpassed 19% efficiency. However, these lab-scale, state-of-the-art devices are usually processed using halogenated solvents, which are not suitable for up-scale. As the solvent used during deposition of the OSC’s active layer has a significant impact on its microstructure, and therefore the device performance, one of the first steps towards industrialization is to start with materials that are already soluble in greener alternatives.

Printed Solar – Green Energy for Industrial, Warehouse and Commercial (IWC) Buildings

Paul Dastoor, Daniel Elkington, Warwick Belcher and Nathan Cooling; University of Newcastle, Australia

Printed solar modules based on organic photovoltaic materials offer significant promise as a next-generation solar energy technology manufactured using roll-to-roll printing. A relatively mature technology, printed solar panels less than 300 g per square metre, is less than 0.3 mm thick and can be adhered to roofing and other structures using adhesives. Moreover, detailed economic modelling has demonstrated that by focusing on low-cost materials and manufacturing techniques, printed solar is commercially compelling even at relatively low device efficiencies and lifetimes [1].

A key application target for printed solar is the Industrial, Warehouse and Commercial (IWC) building sector. The size of the sector is significant with the area of IWC building conservatively estimated to be more than 100 million square metres in Australia [2] and over 4 billion square metres worldwide [3]. Over 70% of IWC roofs are manufactured to the minimum specification and these “slender” roofs are low weight bearing and incapable of supporting the weight of conventional silicon solar panels which typically weigh around 20 kg per square metre.

In this paper we outline our work in developing large area printed solar for IWC applications in Australia, encompassing material synthesis, device development, demonstration installation, economic modelling and recycling. With modelled payback times of less than 2 years for a typical IWC roof, printed solar offers significant potential for sustainable energy generation in the sector.
While the power conversion efficiency (PCE) of single-junction perovskite solar cells (PSCs) has increased to over 26%, there are some challenges to achieving flexible large-area PSCs with good long-term stability for practical applications. In this work, we demonstrate a self-assembled gradient TiO₂ MXene incorporated PEDOT:PSS HTL for promoting flexible large-area PSCs by establishing half-caramelization-based glucose-induced MXene redistribution. Through this process, the TiO₂ MXene nanosheets are spontaneously dispersed and redistributed at the top region of HTL to form the unique gradient distribution structure composed of MXene-Glucose:PEDOT:PSS (MG-PEDOT). Our results show that the MG-PEDOT HTL not only offers favorable energy level alignment and efficient charge extraction, but also improves the film quality of the perovskite layer featuring enlarged grain size, lower trap density, and longer carrier lifetime. Consequently, the power conversion efficiency (PCE) of the flexible device based on MG-PEDOT HTL is increased by 36% compared to that of pristine PEDOT:PSS HTL. Meanwhile, the flexible perovskite solar minimodule (15 cm² area) using MG-PEDOT HTL achieves a PCE of 17.06%. The encapsulated modules show remarkable long-term storage stability at 85°deg C in ambient air (~90% efficiency retention after 1200 hours) and enhanced operational lifetime (~90% efficiency retention after 200 hours) [1]. With the adoption of the flexible transparent electrodes [2] and the introduction of a new modification on the perovskite active layer, the power-per-weight of our flexible PSCs reaches about 8 W/g while the power-per-weight of PEN/ITO-based control about 1-1.5 W/g. The work contributes to the development of flexible PSCs for practical applications.


2:15 PM *EN01.02.03
Natural Sunlight for Stability Testing of Perovskite Solar Cells
Iris Visoly-Fisher; Ben-Gurion University of the Negev, Israel
A major challenge facing the development of perovskite-based solar cells is combining high efficiency with long-term stability. Outdoor stability testing under natural sunlight provides the most relevant test of performance dynamics under operational conditions. Understanding these cells' recovery properties under natural diurnal light-dark cycling can point to methods to extend its lifetime. Sunlight intensity/concentration-dependent studies of perovskite-based devices elucidated the effect of bias applied to the solar cells on its lifetime and degradation mechanisms. Accelerated stability studies under different sunlight concentrations were examined to determine their relevance to degradation at operational conditions.

2:45 PM EN01.02.04
Fabrication of PEDOT Thin Films using Oxidative Chemical Vapor Deposition to Enhance The Stability of Perovskite Solar Cells
Meesam Heydari Gharahcheshmeh; San Diego State University, United States
The practical applications of perovskite solar cells (PSCs) have been hindered by stability issues. One key factor contributing to this limitation is the inherent acidity of the commonly used hole transport layer, poly(3,4-ethylene dioxythiophene):polystyrene sulfonate (PEDOT:PSS), which can compromise the stability of PSC devices. To address this challenge, this study explores an innovative approach that leverages oxidative chemical vapor deposition (oCVD) with antimony pentachloride (SbCl₅) as a liquid oxidant. This method is employed to fabricate stable and ultrathin, highly conformal PEDOT films, offering a promising alternative as a hole transport layer in PSCs. The oCVD-grown PEDOT-C1 thin films, produced using liquid SbCl₅ oxidant, exhibit outstanding optoelectronic properties, precise control over nanostructure, stability, and integration capabilities. These qualities make them a robust and efficient choice for use as a hole transport layer in PSCs. Incorporating oCVD PEDOT-C1 thin films as the hole transport layer in PSCs results in a remarkable PCE of 20.74%. This surpasses the PCE of 16.53% achieved by spin-coated PEDOT:PSS thin films treated with the dimethyl sulfoxide (DMSO) polar solvent. Moreover, PSCs incorporating oCVD PEDOT-C1 thin films demonstrate a notable 2.5x enhancement in stability compared to their PEDOT:PSS-DMSO counterparts. This technological advancement paves the way for the development of PSCs with not only high performance but also enhanced stability.

Keywords: Oxidative Chemical Vapor Deposition, PEDOT, SbCl₅, Oxidant, Perovskite Solar Cells

3:00 PM DISCUSSION TIME

3:15 PM BREAK

SESSION EN01.03: Perovskite Applications
Session Chair: Paul Dastoor
Tuesday Afternoon, April 23, 2024
Room 331, Level 3, Summit

3:45 PM EN01.03.01
Perovskites in Space: Promising Results Aboard Two ISS Missions
Samuel Erickson¹, William Delmas²,³, Calista Lum³, Jorge Arteaga³, Kaitlyn VanSant³, Joseph Luther³, Timothy J. Peshek³, Lyndsey McMillon-Brown² and Sayantani Ghosh³; ¹University of California, Merced, United States; ²Sandia National Laboratories, United States; ³University of California, Irvine, United States; ⁴National Renewable Energy Laboratory, United States; ⁵NASA Glenn Research Center, United States
The rapid commercialization of low Earth orbit (LEO) and NASA’s return to the moon will require next-generation photovoltaic materials with high specific power and defect tolerance. Perovskite solar cells (PSCs) are an excellent candidate for such missions, having demonstrated their resilience against the unique stressors of space. These include rapid temperature cycling with each orbit, high-energy particle radiation, increased ultraviolet light in the AM0 spectrum, and exposure to atomic oxygen. This work discusses the effects of LEO on metal halide perovskite (MHP) samples from two recent Materials International Space Station Experiment (MISSE) missions. MISSE-15, launched in 2021, included eight PSCs of varying architecture and absorber composition to test several prototype devices. The cells were placed in open circuit at zenith orientation (facing normal away from the Earth) outside the ISS for 6 months before returning to Earth for characterization. MISSE-16 included five encapsulated methylammonium lead iodide (MAPI) thin films with different cover glass layers to test the effects of UV radiation. Upon return, all samples were investigated with high-resolution spectroscopy and microscopy. Photoluminescence (PL) emission and recombination lifetime data from the MISSE samples were compared with control devices to quantify how the former changed under LEO conditions.

Ultimately, all MHP samples showed strong PL emission intensity and little sign of chemical degradation. MISSE-16 films were encapsulated with long pass and band pass UV filters instead of standard top glass to expose each sample to specific UV wavelengths. This test was designed to study if and how MHPs would be affected by various UV bands in combination with the space stressors previously described. All five samples exceeded expectations, returning uniform, emissive, and energetically stable. Of the eight PSCs aboard MISSE-15, only the two CsPbBr₂Br cells experienced absorber failure. These cells returned nearly transparent due to CsPbBr₂Br photobleaching. The remaining six PSCs, including two each of MAPI, triple cation, and formamidinium-rich triple cation cells, returned with their absorber layers intact. Unfortunately, all cells experienced degradation to their top electrodes (Al or Ag depending on PSC), resulting in no electrical response in post-flight tests. This appears to be caused by ion migration, likely iodide, between the MHP and the metal. However, all MHP films were stable and emissive in regions without contacts and only slightly altered in areas behind the damaged contacts, further confirming the resilience of MHPs. Future MISSE missions will soon launch containing PSCs with indium tin oxide and Au contacts which are known to prevent ion transfer. Overall, the high stability and PL response of MHP films and cells demonstrates their ability to withstand the harsh environment conditions encountered in space.
Absorption Enhancement in Perovskite based Thin Film Solar Cells using Whispering Gallery Modes of Dielectric Spheres

Tsvetelina Merdzhanova

The aim of the work is to demonstrate a successful and highly efficient energy harvesting and storage under a wide range of light emitting diode (LED) illumination intensities by applying lead halide perovskite cells and modules. The lead halide perovskite cells and modules have demonstrated efficiencies under artificial lighting of more than 30% [1] with a record of 40.1% achieved with an extra thick absorber layer [2]. The main reason is the very close overlap of the external quantum efficiency in lead halide perovskite solar cells with the emission spectrum of an LED lamp. However, there are not many publications showing a combination of perovskite-battery devices working efficiently under low light LED illumination intensities.

Integrating storage technologies in renewable energy systems of the future is one of the most important problems of the moment. Recent development trends in small scale consumer electronics towards implementing “Internet of Things” and smart house/smart cities concepts make it imperative to have cheap, wireless power solutions for electronics that operate all day. The throughput screening, taking into account critical factors such as band gaps, optical absorbance, effective masses, synthesizability, and defect tolerance. As a result, we propose several new candidate materials for fully inorganic photovoltaic absorbers. Additionally, we analyze the overall trends in photovoltaic properties across the various structural types within our classification. We anticipate that this talk will offer valuable insights for discovering and designing new inorganic solar-cell absorbers from an expanded material pool.

References

A fabrication of perovskite solar cells (PSCs) by scalable processes in large-area is prerequisite for the PSCs to fully utilize the inherent advantages of perovskite such as superior charge transport properties, high absorption coefficient, flexible and lightweight form factors. Large-area perovskite solar modules (PSMs) can be utilized in self-powered personal mobility and electronics, smart textiles, custom-shaped building-integrated photovoltaics, and so on.

Although several demonstrations of scalable production of PSCs have been reported, successful demonstration of fully scalable production of large-area PSMs is still lacking. The major obstacles are uniform wet-film formation via scalable process in large-area, and complete phase conversion of perovskite precursor to photoactive phase. Therefore, reliable scalable production methods should be established including wet-film formation and phase conversion steps.

In addition, the direct integration of energy generation and storage devices have attracted a lot of interest recently in order to correspond to the fluctuation of power input from the Sun and increasing demand for self-powered electronics. However, inherent mismatch of voltage and current range for charging and discharge from PSCs to Li-based batteries is a major obstacle to realize the direct integration between them. Additionally, power output from PSCs under continuous light illumination, and storage capacity from charging-discharging cycles from Li-ion batteries should be retained.

In this work, we successfully demonstrate high-performance PSMs and photo-rechargeable batteries by directly integrating PSMs and Li-ion batteries in a single substrate. All the layers constituting PSMs can be fabricated via solution coating, with optimized rheological and interfacial properties, at a low temperature (~160 °C). An electron transporting layer (ETL) is designed to be uniform and compact in large-area, by systematically investigating the effect of leaving group in sol-gel precursor and applying an optimal tin precursor with organic crosslinkers. As a result, high-efficiency over 24% can be achieved, retaining over 90% relative efficiency compared to initial one after over 2000 h. Complete conversion of perovskite precursor to photoactive phase in a large area can be achieved via careful selection of proper antisolvent and bathing in it.

PSMs are carefully designed to have a proper area and structure to exactly match the charging voltage-current range of high-capacity Li-ion batteries. Consequently, over 20% efficiency of PSMs and over 14% of overall charging to storage efficiency can be achieved. The photo-charging can be repeatedly conducted over 50 cycles because of stable power output and storage of integrated PSMs and Li-ion batteries.

**ABSTRACT BODY:**

Perovskite optoelectronic devices have garnered immense attention in recent years due to their exceptional efficiency, low-cost fabrication, and potential to revolutionize the field of photovoltaics. However, enhancing their stability and performance remains a critical challenge [1,2]. This study delves into the systematic investigation of perovskite optoelectronics, focusing on the pivotal role played by the active layer and electron transport layer (ETL) in determining device efficiency and stability [3]. We investigate the role of the electron transport layer (ETL) in enhancing the charge carrier transport and extraction processes. PDI-derivatives, such as PDIN, PDINO, and PDINN which are well-known and used material in organic optoelectronic devices’ electron transport layer, has high electron affinity, charge transport properties, and good chemical and thermal stability etc [4]. However, it was difficult to apply it on the perovskite layer because the alcohol-based solvent was used, so we solved this and applied it to the PSC device of the NIP structure. It was confirmed that by applying PDINN on the PCBM layer, the defects of the PCBM layer were effectively passivated to reduce shunt leakage and at the same time suppress dark current. This process consequently suppresses the thermal degradation of the device and improves the stability of the device. Furthermore, we present a meticulous exploration of various active layer chemical physical process and their impact on the perovskite optoelectronic devices. Until now, it has been known that the grain size in the perovskite active layer is largely influenced by the time and temperature of the annealing process [5]. We note the relationship between the force and buoyancy acting on the active layer by the density of the washing solvent during the washing process, confirming that the lower density washing solvent receives lower buoyancy and consequently induces the formation of a larger grain size. It can be explained by the LaMer model, which represents the speed and time relationship between reaching the supersaturated state from the saturated state, confirming that the dark current is suppressed by reducing grain boundary concentration and passivate the leakage current through it [6]. This, in turn, leads to improved detection performance of the perovskite photodetector. Moreover, we have also conducted research to overcome the shortcomings of perovskite materials that are vulnerable to moisture [7]. A moisture trap capable of trapping water molecules is put into a perovskite solution to remove an infinitesimal amount of moisture remaining over-night stirring, forming a well-oriented perovskite crystal, and preventing oxidation generated by internal moisture meeting the upper electrode when the device is driven, thereby improving device durability. In summary, our research offers valuable insights into the intricate interplay between the active layer composition, ETL properties, and the overall performance and stability of perovskite optoelectronic devices.

**REFERENCES:**

Organic Photovoltaic Sails for Maritime Decarbonation and BIPV Applications

*EN01.08.01

**SESSION EN01.08: Prototypes and PV in the Real World**

**Session Chairs:** Myles Araujo and Nicola Gasparini

**Thursday Morning, April 25, 2024**

**Room 331, Level 3, Summit**
Organic solar cells (OSC)s offer a distinct set of advantages among next-generation photovoltaics, i.e. their flexibility, lightweight design, low-cost manufacturing, and semi-transparency. Substantial efforts have been invested in boosting device efficiency, and this potential is now underpinned by impressive laboratory-scale efficiencies approaching 20%. As efficiency gradually approaches commercialization requirements, the stability of OSCs becomes increasingly paramount in academic research. Numerous factors can influence device stability, including delamination of the photo-active layer or interface triggered by oxygen and water, light-induced chemical alterations in materials, and thermally induced morphological changes. Therefore, it is imperative to comprehend the stability bottlenecks of high-efficiency systems at this stage towards real-world applications.

In this talk, I will elaborate on the stability of various non-fullerene acceptors (NFAs) and different polymer donors for OSC. We established a connection between the molecular structure of Y-series NFAs, specifically the endgroup and side-chain, and their photostability, ultimately affecting the device's lifetime. We also explored the significance of various polymer donors in determining device longevity and highlighted the side-chain-induced degradation pathway in polymer donors. We further provided theoretical tools for understanding the photostability of polymer donors.

Three emerging applications of solar modules are power supply to electrochemical reactors for CO₂ conversion to useful organic substances. Direct connection of these two devices is exactly what we need, because of slight changes in the relative solar spectrum in the relevant near-infrared range. Thus, Triple-SPVM is the best suited for practical use.

Voltage-Matched Configurations for Monolithically Series-Connected All-Perovskite Double- and Triple-Tandem Solar Modules

We designed all-perovskite (PVK) double- and triple-tandem solar modules. Monolithically series-interconnected structures were adopted, because these offer high scalability by exploiting the advantages of thin-film modules over wafer-based crystalline-silicon modules. We revealed the voltage-matched configurations and their variants improve the annually averaged conversion efficiencies outdoor with potentially higher durability and lower costs compared with those of the conventional current-matched configurations.

Although the combination of PVK top cells and crystalline-silicon bottom cells has been realized higher conversion efficiencies of double-tandem modules at present, all-PVK tandem modules have various advantages of scalability, lightweight, and suitability for mass production. Therefore, improvements in the efficiencies of all-PVK modules are extremely important. Thus, to find the suitable module configurations, we modeled the photovoltaic performance of single PVK cells with different bandgaps by reference to previous experimental data. Then, we optimized the cell widths and transparent-electrode thicknesses used for the monolithically series-interconnected modules, along with the PVK bandgaps. Finally, we evaluated the annually averaged conversion efficiencies under various meteorological conditions using a database.

The conventional current-matched two-terminal double-tandem (Double-2T) modules have an advantage of a simple structure. The current matching condition requires the use of a large-bandgap PVK top cell. However, the photovoltaic performance currently lowers with increasing bandgap. This lowers the module efficiency. By contrast, the efficiency of another conventional Double-4T configuration increases the optical loss and ohmic loss, resulting in lower efficiencies than those of the triple-tandem 2T modules. To solve this issue, we proposed a new configuration of the triple-tandem series/parallel-connecting voltage-matched (Triple-SPVM) module, in which the middle-bottom module consisting of directly series-connected middle and bottom cells is connected to the top module in parallel. The use of only two substrates improves the efficiency and lowers the cost. The current mismatch between the series-connected middle and bottom cells is not a great issue, because of slight changes in the relative solar spectrum in the relevant near-infrared range. Thus, Triple-SPVM is the best suited for practical use.

An emerging application of solar modules is power supply to electrochemical reactors for CO₂ conversion to useful organic substances. Direct connection of these two devices is exactly an artificial-photosynthetic device, and stores time-saving solar energy. It is of great importance for efficient conversion of CO₂ that the device operates at V_{MPP} of the solar modules. Double-VM and Triple-SPVM are suitable for this application, because V_{MPP} of the module is tunable by changing the series-connected cell numbers in each submodule.

References

2:30 PM BREAK

3:15 PM *EN01.09.04

Exploiting The Synergy between Perovskite and Organic Photovoltaics in Semi-Transparent Solar Cells and Modules

Aldo Di Carlo, Daniele Baran, King Abdullah University of Science and Technology, Saudi Arabia

Transparent Blade-Coated FAPbBr₃ Perovskite Solar Cells: A Scalable Low-Temperature Manufacturing Process under Ambient Condition

Solar RRL 6 (9), 2200242

Acknowledgments
This research has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101007084 (CITYSOLAR). We acknowledge all...
The emergence of solution-processed organic and metal halide perovskite solar cells can transform the landscape of photovoltaic technology in delivering scalable and high-performance solar cells to provide sustainable green energy. While the power conversion efficiencies (PCEs) of both single-junction organic solar cells (OSCs) and perovskite solar cells (PSCs) are rapidly ascending to >19% and >25%, respectively, their maximum efficiency is limited to ~33% according to the Shockley-Queisser model for single-junction devices. However, it is possible to significantly increase the efficiency of solar cells by constructing a tandem device that consists of multiple light absorbers with considerably different bandgaps to reduce the solar cells' overall transmission and thermalization losses.

In this talk, I will discuss our work on developing high performance monolithic perovskite/organic tandem solar cells comprising a wide bandgap perovskite (WBG) front cell and a narrow bandgap (NBG) organic rear cell connected through a recombination junction. The WBG (Eg: 1.7-1.85 eV) PSCs are chosen for the front cell due to their strong and broad absorption for visible light, smaller voltage loss, and higher photoresponse compared to their organic counterparts with approximate bandgap. While NBG (Eg: 1.1-1.25 eV) OSCs can offer better near-infrared absorption tunability and stability compared with the Sn-based NBG perovskites, making them favorable candidates for the rear cell. Moreover, the advantage of the perovskite and organic light absorbing layers being processed from orthogonal solvents imposes fewer constraints on the choice of the materials for constructing the recombination junction and provides better flexibility on the device design of tandem solar cells.

To demonstrate state-of-the-art perovskite/organic tandem cells, an integrated strategy combining materials, interface, optical, and process engineering was adopted to optimize the two subcells and the interconnect junction simultaneously.[2-3] In addition, a comprehensive optoelectronic model is being developed to simulate the electrical and optical properties of the tandem solar cells and to provide guidelines to optimize their device performance. The successful development of perovskite/organic tandem cells will have far-reaching impacts on producing high efficiency, low cost and scalable PV cells for clean energy production.

Reference:

4:00 PM EN01.09.06
Toward Long Term Organic Solar Cell Device Stability via Thermocleavable Donor and Acceptor Active Layer Haoyu Zhao1, Jordan Shanahan2, Soumya Kundu1, Guorong Ma1, Andrew Bates1, Wei You2 and Xiaodan Gu1; 1University of Southern Mississippi, United States; 2University of North Carolina at Chapel Hill, United States

The performance of organic solar cell (OSC) was surged during past decades, however, the insufficient efforts to improve stability set the barriers to realize the practical applications for OSC devices. The morphological stability of OSC bulk heterojunction layer (BHJ) is apparently affected by the molecular mobilities of donors/acceptors under operational conditions. The introduction of thermocleavable side chains provides an effective and efficient method to reduce the dynamics of conjugated polymers (CP) to improve the thermal stability as evidenced by the enhanced Tg after fully cleavage. Furthermore, the newly synthesized donor-acceptor conjugated polymers (DA CPs) with thermocleavable contents were expected to achieve both good performance and stability for long term usage. This work focused on the investigations of the morphological changes as well as phase separation behaviors for thermocleavable donor/acceptor BHJ blend film. The solar cell devices were also prepared to evaluate the performance under various conditions. Finally, our work revealed the good performance and stable morphology over long term at elevated temperatures after alkyl side chains were completely removed, which could provide a pathway to improve the stability of optoelectronic properties in future OSC devices.

SESSION EN01.10: Inorganic Photovoltaics
Session Chairs: Nicola Gasparini and Julianna Panidi
Friday Morning, April 26, 2024
Room 331, Level 3, Summit

10:30 AM #EN01.10.01
The Benefits or Circular Recycling for Terawatt Photovoltaics Ian Marius Peters, Misha Sytnyk and Zhenni Wu; Helmholtz Institute Erlangen Nürnberg, Germany

Solar energy and wind power stand as the twin cornerstones of the 21st-century energy revolution. Acknowledged by the Intergovernmental Panel on Climate Change (IPCC), the installation of solar panels and wind turbines emerges as the most potent and cost-effective means to decarbonize our energy systems. To attain the ambitious goal of limiting global temperature rise to 2 degrees Celsius, we must embark on the massive deployment of tens of billions of solar panels, necessitating the mobilization of several hundred million tons of raw materials. Encouragingly, the global industry is taking formidable strides to meet this challenge, projecting annual production capacity to exceed 1 terawatt peak (TWp) before 2030, along with rapid expansion across the globe.

Yet, as we fast-forward a few decades, a pivotal decision looms on the horizon. As these solar panels reach the end of their operational life, we find ourselves at a crossroads – we can either discard these modules in landfills or we can opt for a more sustainable and forward-thinking approach. This approach involves integrating them into a circular system, fostering their reuse, repair, and eventual recycling.

Notably, we are not bound by resource constraints; although exceptions like silver exist, alternative materials are readily available. Thus, the option of dumping solar panels would not fundamentally hinder the realization of a renewable energy system operating at 100% capacity. However, opting for circular treatment offers an array of compelling benefits, rendering dumping the less favorable choice. Circular handling invariably encompasses the recovery and restoration of the materials and components involved, ensuring that these resources maintain their utility and minimize waste. The rate at which this recovery occurs must align with the pace of production, underscoring the imperative for our circular treatment capacity to match our production capacity.

Given the staggering scale of photovoltaic production, non-circular processes will become increasingly inviable. The photovoltaic market is poised to become a major consumer of reclaimed products, further incentivizing circular strategies. In this presentation, we will delve into the dynamics that will steer a terawatt photovoltaic market toward circular recycling. Furthermore, we will explore the potential of emerging photovoltaic technologies, which hold the promise of enabling more processes with unprecedented material recovery and reuse, cementing the path toward a sustainable and circular energy future.

11:00 AM EN01.10.02
Ultrathin a-Si:H/Oxide Transparent PV Devices Deposited onto Architectural-Compatible Glass and Ceramic Substrates Alex J. Lopez-Garcia1, Gustavo A Alvarez1, Eloi R. Costals2, Pablo Ortega2, Cristobal Voz2, Joaquim Puigdollers2 and Alejandro Perez-Rodriguez1,3; 1Institut de Recerca en Energia de Catalunya, Spain; 2Universitat Politècnica de Catalunya, Spain; 3Universitat de Barcelona, Spain

Transparent Photovoltaics (TPV) is an emergent branch in the toolkit of PV that promises to extend the potential applications of PV and complement the most mature strategies that are limited in terms of on-site integration and applicability, especially into architectural components.[1] The most important feature of PV devices is power output (i.e. efficiency). However, this approach brings in another critical feature almost at the same level of importance, which is the transparency and aesthetics of the device, which have to meet certain standards that can differ depending on the specific application and/or integration. As such, it adds some degree of complexity when optimizing, as other properties become more important. For TPV to be implemented in real-world scenarios they do not need to compete with high efficiency devices, rather they must be tailored to maximize efficiency with special care on transparency and aesthetic characteristics. For cost competitiveness, existing and mature industrialized materials (earth-abundant and non-toxic) and processes are a good starting point for first implementations. Developing such devices can potentially allow for fast-developing integration in areas such as building-integrated PV (BIPV) in the form of façade windows and other glazing elements, or to be integrated ubiquitously into sensors and future IoT devices with low-power requirements, as well as in AgriPVs (APV). Recent work has effectively studied the use of a-Si:H/oxide structures on glass substrates for TPV, showing some limitations especially in terms of Voc.
In this work, we present inorganic-based TPV devices relying on ultrathin a-Si:H as absorber and different oxides as carrier selective contacts and transparent electrodes. In an innovative approach, we have inserted a high dipolar moment molecule (PAMAM-G3 dendrimer) at the ETL/absorber interface. This interface modification allows working with oxide charge transport layers (CTLs) that offer high transparency while eliminating surface energy barriers that decrease the resulting $V_{oc}$ of the device, avoiding doping strategies (i.e. a-Si:H(p), a-Si:H(n)) and reducing costs due to the low-temperature deposition processes. This new solution has allowed a record Light Utilization Efficiency (LUE) of 0.85%, by improving $V_{oc}$ from 410 (reference) to 781 mV (PAMAM G3), still not reached by state-of-the-art devices with these materials, with negligible reduction in Average Photopic Transmittance or Color Rendering Index. The basic device structure is SLG/FTO/AZO/PAMAM-G3/ZnO/a-Si:H(30nm)/MoO3/ITO. At the present time, spectrophotometry and J-V measurements under AM1.5G illumination (from the front and back sides) as well as Spectral Response measurements have been carried out. We report also on the bifaciality aspect of the architecture, showing almost unity bifacial factor, due to the ultrathin absorber coupled to wide-bandgap CTLs that make the device optically symmetric. Additionally, reference devices without dipoles have also been deposited onto ceramic substrates successfully and will be presented, confirming the potential of this approach to be integrated in different architectural environments such as glass and ceramics.

The presented work is high of relevance for the development of the field of inorganic thin film Transparent PV technologies, especially those working on ultrathin absorbers. It might also spark interest in thin film technologies in general that rely on advanced ETL/Active layer/HTL architectures.

For a generic PV absorber at any stage of development, determination of its $\Gamma_{PV}$ figure of merit helps understand whether imperfect PV performance is intrinsic to the material (inadequate bulk properties at the current stage of development), or if it “only” requires a different device structure, contact layers, or improved interface properties. We will show the outcome of this analysis for 25 PV absorbers with record PV efficiencies between 0% and 85% of their Shockley-Queisser limit. Using a local version of the $\Gamma_{PV}$ figure of merit, a material-specific optimization strategy is laid out for any experimentally synthesized PV absorber, by specifying the bulk properties that should most urgently be improved to increase their PV efficiency.

I propose a figure of merit $\Gamma_{PV}$ to estimate the maximum efficiency attainable by a generic non-ideal PV absorber in a planar single-junction solar cell under the non-concentrated AM1.5G spectrum. This efficiency limit complements the more idealized limits derived from fundamental physics, such as the Shockley-Queisser limit and its subsequent generalizations. Specifically, the present figure-of-merit approach yields stricter efficiency limits applicable to realistic PV absorbers with various imperfections, including finite carrier mobilities and doping densities. $\Gamma_{PV}$ is a function of eight properties of the absorber that are both measurable by experiment and computable by electronic structure methods. They are: band gap, non-radiative carrier lifetime, carrier mobility, doping density, static dielectric constant, effective mass, and two parameters describing the spectral average and dispersion of the light absorption coefficient. $\Gamma_{PV}$ has high predictive power (absolute efficiency error less than ±1.1%) and wide applicability range. The Shockley-Queisser limit and its generalizations are reproduced by $\Gamma_{PV}$. Simpler figures of merit proposed by others are also included as special cases of $\Gamma_{PV}$.

A Phenomenological Figure of Merit for Photovoltaic Materials Andrea Crovetto; Technical University of Denmark, Denmark

Photochromic Dyes for Semi-Transparent Solar Cells and Solar Mini-Modules with Light-Adjustable Transmittance and High Colour Rendering Index Renaud Dernadrille1, Samuel Fauvel1, Antonio J. Riquelme1, Diego Mirani1, Johan Liotier1, Valid M. Mwalukuku1 and Stéphanie Narbey2; 1CEA, France; 2Solaronix, Switzerland

Over 18% Efficiency Kesterite Solar Cell under Indoor Illumination Conditions Yuancai Gong1, Alex Jimenez Arquero2,3, Axel Gon Medaille1, Outman El Khouja1, Romain Scaffidi2, Guy Brammertz2, Denis Flandre3, Bart Vermang4, Aurelian Catalan Galca4, Alejandro Perez-Rodriguez3, Sergio Giraldo4, Edgardo Saeuced5 and Zacharie Jele Li-Kao5; 1Universitat Politècnica de Catalunya, Spain; 2Institut de Recerca Energètica de Catalunya, Spain; 3National Institute of Materials Physics, Romania; 4IMEC, Belgium; 5Université Catholique de Louvain, Belgium

Indoor photovoltaic (PV) cells have the potential to power distributed and remote sensors, actuators, and communication devices, enabling the widespread implementation of the Internet of Things (IoT). Commercial (c-Si, CIGS, CdTe) and emerging (perovskite, organic solar cells) photovoltaic technologies face several challenges for indoor applications, including cost, toxicity, stability, and/or spectral mismatch. In contrast, kesterite materials are composed of earth-abundant, non-toxic elements and exhibit excellent stability, with a wide bandgap tunability between 1.0 eV up to 2.1 eV. This technology has recently achieved certified efficiencies of 14.9% under AM1.5G for the narrow band gap (Se-rich; 1.1 eV) compound and 11.4% for wider bandgap (S-pure; 1.5 eV), demonstrating its high efficiency potential.

In this work, we present the first complete theoretical and experimental study of the behavior of kesterite solar cells under indoor illumination conditions, with different high efficiency devices. First, we will show that the most relevant and mature photovoltaic technology, that is Si, efficiently drops the performance in indoor conditions due to its narrow band gap. Hence, the use of wide band gap materials is required for a good performance in indoor conditions. We will show that, under indoor conditions, the wide band gap (S-pure; 1.5 eV) can achieve efficiencies above 20%.

The experimental results demonstrate the excellent optoelectronic properties under low illumination conditions, showing that the efficiency of narrow bandgap (12% efficiency in AM1.5G conditions) is practically unchanged with the AM1.5G light intensity down to 0.2 suns. To further support the high potential of kesterite materials for low injection applications we studied the narrow bandgap device performance under simulated indoor conditions, showing red shifting the typically used indoor spectra, approximating the blackbody emission at 2700K, 3000K, 4000K and 5000K. These spectra can be achieved using a calibrated LED based solar simulator. As predicted from the numerical simulation results, the devices demonstrate an outstanding efficiency over 18%.

These results motivate the development of efficient kesterite solar cells with a wide bandgap, specifically tailored for IP applications. The performance of the wide bandgap kesterite material has been studied using the same experimental procedure, revealing a performance of above 12% under simulated indoor conditions, consistently with the numerical simulation. The charge carrier extraction is analysed with spectral response (External quantum efficiency, EQE) and the changes induced by indoor light are characterized by performing EQE under dark and indoor illumination conditions. Furthermore, to prevent interface recombination and drastically improve the IPV performance two strategies will be presented: (i) Ge alloying to further widen the bandgap and minimize the spectral mismatch, and (ii) device engineering by using passivation interlayers (e.g. Al2O3), adjusting the thermal post deposition treatment conditions or employing other electron-selective contacts (e.g. ZnSnO).

Therefore, the pathway for achieving efficiencies over 20% for indoor kesterite solar cells will be presented. These original ideas will set the stage for affordable, bio-safe, and durable indoor cells. It will also provide a technical approach for the comprehensive design of other emerging PV technologies.
Organic solar cells (OSCs) are one of the most promising cost-effective options for utilizing solar energy in high energy-per-weight or semi-transparent applications. Recently, the OSC field has been revolutionized through synthesis and processing advances, primarily through the development of numerous novel non-fullerene small molecular acceptors (NFA) with efficiencies now reaching ~19% when paired with suitable donor polymers. The device stability and mechanical durability of these non-fullerene OSCs is critical and developing devices with high performance, long-term morphological stability, and mechanical robustness remains challenging. Yet, morphological and mechanical stability is a prerequisite for OSC commercialization. Here, we discuss our current understanding of the phase behavior of OSC donor:acceptor mixtures and the relation of phase behavior and the underlying hetero- and homo-molecule interactions to performance, processing needs (e.g., kinetic quenches), and molecule packing and dynamic mechanical analysis (DMA) to assess specifically the hetero-interactions. The results presented and its ongoing evolution are intended to uncover fundamental molecular structure-function relationships that would allow predictive guidance on how desired properties can be targeted by specific chemical design. Comparative studies show that the molecular hetero-interactions between the donor and NFA are not always the geometric mean of the homo-interactions. The presentation will focus on these heterointeractions and the results underscores the limited success often encountered when Hanson Solubility Parameters and surface energies are used to estimate molecular interactions [1]. Additional insights into the molecular interactions are also provided and the relevance discussed in rubber-toughening of OSCs with a SEBS additive [2].

References:
1. “Molecular interactions that drive morphological and mechanical stabilities in organic solar cells” S Siddika, Z Peng, N Balar, X Zhong, W You, H Ade and BT O’Connor, Joule 7, 1593 (2023)

Sustainability Considerations for High Performing Organic Solar Cells

Organic semiconductors are an emerging class of materials with various optoelectronic applications. The high commercialisation potential of this technology is evidenced by a few companies that have already launched their products into the market or are working towards this goal. Solution-processed organic electronics have a high potential to reduce the carbon footprint of the semiconductor industry if they are developed further and increase their market share.

In my talk, I will introduce sustainable routes to manufacture solution-processed organic electronics. Particular focus will be given to organic solar cells, which recently attracted immense attention due to the development of a new family of semiconductors that allows highly efficient light harvesting in indoor and outdoor conditions. One current limitation, though, is the use of non eco-friendly solvents and materials during the device development stages. Most organic electronic devices require halogenated and non-halogenated aromatic solvents during their fabrication. For large-scale production and further commercialisation, this is a key limitation. This arises from the fact that organic semiconductors are highly soluble in this category of solvents, which are often carcinogenic or toxic to the human reproductive systems and negatively impact the environment. Here, I will show high-performing organic solar cells fabricated from biomass-based solvents. In addition, recycling considerations are required for any product entering the market. Lastly, I will demonstrate a tool that enables quick solvent screening and the link between organic solar cells’ performance in an effort to replace the use of toxic ones.

Overall, this work highlights the importance of replacing harmful chemicals and materials in the organic electronics fabrication stages, resulting in faster and wider commercialisation and new market opportunities.


Structure Control during In Situ Printing of Donor-acceptor Blend Films for Organic Solar Cells

Among the next generation solar cells, in particular organic photovoltaics are gaining impact as a promising alternative to conventional silicon-based solar cells. However, despite big achievements in terms of power conversion efficiencies in the last years, it remains an unresolved challenge to fabricate large-area organic solar cells without sacrificing efficiencies. The reason behind is that basic understanding is still very limited due to the complexity of the systems. Moreover, presently a substantial number of researchers use spin-coating for film deposition, which is not compatible with the needs of a large scale production. Thus, using up-scalable deposition methods such as printing are of imminent interest. [1] Large-area printing such as slot-die coating involves complex hydrodynamic processes and simply transferring optimized parameters from spin-coating studies has only limited success. Thus, in the present work, we use advanced scattering methods such as grazing incidence small and wide angle X-ray scattering (GISAXS and GIWAXS) in situ during printing of donor:acceptor blends to gain fundamental understanding about the underlying film formation processes. Different examples of polymer donors and small molecule acceptors are presented and the resulting morphologies are correlated with solar cell device performance. A special emphasis is put on the shift towards more environmentally friendly solvents, [2] which will be also a pre-requisite to promote a large-scale production of organic solar cells.


10:00 AM BREAK

Semitransparent Organic Photovoltaics with High Average Visible Transmittance

Thuc-Ouven Nguyen; University of California, Santa Barbara, United States

Organic Photovoltaics (OPVs) offer sustainable, solution-processable, and cost-effective energy harvesting solutions. While opaque devices underwent enormous progress in the past decade, it
remains a challenge to meet the high transparency requirements for integrated semitransparent OPVs (ST-OPVs) for buildings, Skylights, skyscrapers, or greenhouses. In this work, we investigate the charge generation-recombination dynamics in three semitransparent blend systems with varied donor concentrations to understand the performance limitations. We also study the effect of the optical expediency of Au, Ag, Al, and graphite as back electrode material on ST-OPVs and show that ‘one size fits all’ is not a valid approach for choosing the back electrode material. It is important to consider the active layer absorption, active layer thickness and application in selecting the back electrode material. We demonstrate that using the dilute donor approach with an appropriate back electrode can yield devices with 73 % average visible transmittance.

Exciton Delocalization Induced by Aggregation for Efficient Non-fullerene Organic Photovoltaics

Bifacial Indoor OPVs: Investigating The Influence of Vertical Stratification on Performance Symmetry of Semi-Transparent OPVs

The demand for sensors in building digitalization is growing rapidly due to the increased need for better monitoring. Internet-of-Things (IoT) sensors typically rely on batteries, leading to high maintenance costs and environmental concerns related to battery recycling. One of the innovative solutions is harvesting ambient light to power these sensors. Organic Photovoltaics (OPVs) offer a promising approach due to their high conversion efficiency and low weight, making them suitable for integration with IoT devices like electronic shelf labels and asset tracking labels. The synthesis of organic semiconductor materials for OPVs gives flexibility which allows to design material systems which surpass state-of-the-art inorganic PVs for indoor applications.

Recent advancements in solution-processable, flexible, and semitransparent indoor OPVs made by roll-to-roll and lamination technologies have opened the door to large-scale industrialization for indoor applications. Our research contributes valuable insights for designing photoactive layers to achieve air-stable, and electrically symmetric semitransparent OPVs for various applications in the field of IoT sensors.

References:

Photoactive Enabled Indoor Light Harvesting

By the mid-2020s it is predicted that billions of sensors and other IoT devices will be deployed worldwide, utilizing techniques such as Neutron and X-Ray Reflectivity, Time-of-Flight Secondary Ion Spectrometry, and Ellipsometry. We find that certain photoactive layers, while highly efficient for indoor use, tend to phase separate when deposited on the cathode electrode, creating a physical barrier and causing trap-assisted recombination when illuminated from the anode side. Furthermore, we found that some photoactive layers remain vertically homogeneous, regardless of the electrode used, presenting the potential for electrically symmetric semi-transparent IOPVs.

Through thorough screening, we identify a photoactive layer system that not only delivers high and air-stable indoor performance but also exhibits perfect symmetry when illuminated from either the anode or cathode side. These findings offer a comprehensive understanding of how photoactive layers affect electrical symmetry in semi-transparent IOPVs, especially for bifacial applications. Our research contributes valuable insights for designing photoactive layers to achieve air-stable, and electrically symmetric semi-transparent IOPVs for various applications in the field of IoT sensors.

References:
Here, I will present a study on a state-of-the-art evaporated small molecule donor paired with C60. The acceptor-donor-acceptor type small molecule was synthesized by Heliatek. Devices with processed OPVs, leading to a lack of studies addressing the limitations of high performance, industrially relevant evaporated OPV materials. As a result, the academic community is today largely focussed on lab scale performance increases and reproducible upscale of solution processed OPVs, leading to a lack of studies addressing the limitations of high performance, industrially relevant evaporated OPV materials. A key bottleneck in evaporated OPVs is the trade-off between efficient charge collection and maximising absorption by increasing the active layer thickness. This is evident from the high losses in fill factor for active layer thicknesses beyond 50 nm while solution processed cells often perform best at thicknesses >100 nm. Studies on solution processed devices showed that active layer blends with efficient collection (high mobility vs. slow non-geminate recombination) exhibit a phase separated morphology. This is often achieved through post-deposition optimisation (e.g. thermal annealing, solvent vapour annealing). Similar studies on the connection between morphology, recombination kinetics and mobility in evaporated OPVs are key to identifying ways to increase their performance through improved deposition control and molecular design. Here, I will present a study on a state-of-the-art evaporated small molecule donor paired with C60. The acceptor-donor-acceptor type small molecule was synthesized by Heliatek. Devices with different active layer morphology were studied. A wide range of optical (photoluminescence, ultrafast spectroscopy) and optoelectronic device measurements (transient photovoltage, charge extraction) demonstrate that the low and imbalanced charge carrier mobility is a key bottleneck even in the optimised blend. An in-depth characterisation of the active layer morphology (RSOXS, GIWAXS) enables us to identify the aspects of the morphology that should be addressed to further improve performance. I will contrast our findings about the collection efficiency with results from solution processed devices (PM6:Y6, BTR:PCBM) as well as giving an outlook for feasible performance improvements based on drift-diffusion simulations (OghmaNano).

1:45 PM EN04.06/EN01.06.03
Enhanced Solid-Liquid Phase Separation and Carrier Transfer for High-Performance Organic Solar Cells by Modulating The Mixing Gibbs Free Energy
Wallace C. Choy; University of Hong Kong, China

The similar conjugated backbone of donor/acceptor material and fast film-formation kinetics have led to spinodal-decomposition-oriented phase separation that the film presents an intimately mixed morphology and random molecular orientation and thus critically hinders the carrier extraction for high-performance non-fullerene organic photovoltaics. To solve the issue, we enhance the mixing Gibbs free energy-triggered solid-liquid phase separation during the film formation process by solidifying one component and solvating the other based on a liquid additive. Following the liquid evaporation process, a favorable vertical distribution is obtained. Meanwhile, the prolonged solution process enlarges the domain size and assists the molecules to diffuse and orient properly, enabling better exciton/charge dynamics during the power conversion processes. In detail, we alter the phase separation behavior from original liquid-liquid de-mixing to solid-liquid de-mixing during the film formation process to prolong the phase separation and assist the molecules to further orient. Finally, we achieve the donor/acceptor phase separation with the enlarged phase domains, favorable vertical distribution, and significantly ordered crystal orientation [1], which contributes to a high fill factor of >80%. The corresponding device power conversion efficiency (PCE) reaches 18.72% with a short-circuit current density (Jsc) of 27.30 mA/cm² and open-circuit voltage (Voc) of 0.854 V. Importantly, the better light stability is also captured in the mature phase-separation device. This work optimizes donor/acceptor vertical distribution and orientation by enhancing the solid-liquid phase separation via a predictable method for realizing high-performance and stable organic photovoltaics [2].


3:00 PM *EN04.06/EN01.06.04
Efficient and Stable Organic Photovoltaics
Thomas D. Anthopoulos; King Abdullah University of Science and Technology, Saudi Arabia

Organic photovoltaics (OPVs) show great potential as a complementary technology to traditional silicon-based photovoltaics due to their lightweight, flexible, and potentially low-cost properties. However, they face challenges such as poor operational stability and lower power conversion efficiency (PCE) compared to commercial solar cell technologies. In recent years, there have been significant advancements in materials and cell architectures to enhance the PCE of OPVs. This presentation will focus on practical new strategies to improve OPVs' efficiency and operational stability. Specifically, it will discuss the innovative use of charge-extracting interlayers, which help increase the efficiency of next-generation OPVs. The benefits of these interlayers include higher open-circuit voltage, reduced recombination losses, and improved operational stability. Additionally, recent progress in utilizing molecular dopants to enhance the PCE of advanced OPVs will be presented, demonstrating their effectiveness in improving the cell's fill factor and short-circuit current density. Moreover, it will be shown that combining innovative charge-extracting interlayers with molecular dopants and advanced functional material formulations can lead to even more significant improvements in efficiency and device stability.

2:30 PM BREAK

3:30 PM EN04.06/EN01.06.05
Origin of Temperature-Driven Morphology Changes in High-Performance Bulk Heterojunction Active Layer of Organic Solar Cell Device
Haoyu Zhao; Nathaniel L. Prine, Guorong Ma, Soumya Kundu, Andrew Bates and Xiaodan Gu; University of Southern Mississippi, United States

The performance of conjugated polymer-based organic solar cell (OSC) device relies on the bulk heterojunction morphology of the electron donor and acceptor blend. The morphology, including the average domain size, crystallinity, and phase purity of donor/acceptor blend determines the device performance. Although the power conversion efficiency (PCE) of OSC is above 19%, the origin of the instable performance over longer times remains poorly understood. In this work, we conducted multiple characterization techniques to explore the dynamic, temperature-dependent morphology of a state-of-the-art donor polymer (PM6) blended with a non-fullerene small-molecule acceptor (Y6). Particularly, we focused on the thermal analysis of the donor and acceptor using fast scanning calorimetry (Flash DSC) to understand the crystallization kinetics. Combined with the assistance of atomic-force microscopy paired with infrared microscopy (AFM-IR) and X-ray scattering, we concluded the origin of PCE loss can be attributed to the severe phase separation caused by acceptor diffusional crystallization. The pure Y6 showed growing crystallization as annealing temperature increased. And the isothermal crystallization growth of blend was further accelerated due to diffusions of Y6. As the blend is maintained at elevated temperatures, the formation of Y6 crystalline domains induced phase separation with donors, as evidenced by the domain purities via AFM-IR characterizations. The interactions of small molecules crystallization were characterized by the performance changes for solar cell device. This study will contribute to the development of more reliable, efficient and commercially viable OSC in the future.

3:45 PM EN04.06/EN01.06.06
Radiation Hardness of Organic Solar Cells
Yongxi Li; 1Stephen R. Forrest; 1University of Michigan, United States; 2Michigan Materials Research Institute, United States; 3Departments of Physics, United States; 4Departments of Material Science and Engineering, United States

Over the past few decades, space exploration has opened up new frontiers in both scientific knowledge and technological innovation. These endeavors have created new opportunities for addressing global challenges. As we set our sights on the forthcoming era of space exploration, the demand for substantial power sources becomes large. Electric propulsion, driven by solar energy, emerges as a pivotal technology to support these capabilities. Organic photovoltaic cells (OPVs), in particular, have exhibited great promise for solar power generation in space due to their incredibly high specific power, reaching up to 40 kW/kg, compared, for example to the ubiquitously employed Si cells of ~ 1 kW/kg. Furthermore, OPVs have the ability to withstand tensile strains exceeding 300% when supported by elastomeric materials, making them far more flexible than their inorganic counterparts. The continuous advancement of organic materials has enabled the power conversion efficiency (PCE) of OPVs to exceed 20% and intrinsic operational lifetime over 30 years, making them competitive with other thin-film inorganic photovoltaic devices. The only pervasive myth associated with OPVs is that the materials are intrinsically vulnerable to degradation when exposed to high energy incident radiation. In this work, we found that carefully selected and designed organic materials and device structure are capable of showing high radiation hardness. Previous studies have identified proton irradiation as a prime source of radiation-induced damage to photovoltaic systems in space, generating vacancies, interstitials, or complex defects within semiconductor materials. Through
simulations of proton energy loss per unit depth using SRIM/TRIM, we found that proton energies exceeding 100 keV can traverse the organic active layer without inducing collisions, consequently yielding a low total vacancy count. This phenomenon is attributed to the relatively slim nature of the organic active layer within OPV cells, measuring only a hundred nanometers in thickness, rendering them comparatively transparent to high-energy particles. To evaluate the proton tolerance of OPVs, we fabricated devices based on the two most reliable OPV configurations demonstrated by our lab. The results demonstrated that the PCE of the OPV device can be maintained even at energies as high as 1 MeV and fluences up to $10^{12}$ cm$^{-2}$, equivalent to 20 years of operation in low Earth orbit (LEO) missions. Remarkably, this performance surpasses that of crystalline silicon (c-Si) cells, which undergo around 40% degradation, and perovskite cells, which show nearly 10% degradation at the same fluence. This compelling evidence suggests the potential of OPVs to offer extraordinarily long operational lifespans in space environments.

References:

**4:00 PM EN04.06/EN01.06.07**

**The Determination of Referenced HOMO/LUMO Levels with Pulse Radiolysis** Michele Myong, Mrinalni Iyer, Yaejin Kim, John Miller and Matthew Bird; Brookhaven National Laboratory, United States

With organic photovoltaic (OPV) power conversion efficiencies nearly at 20%, and their emerging applications in photocatalysis, knowledge of the driving force for electron transfer is vital for understanding how to further optimize these materials.

Pulse radiolysis (PR) enables the rapid generation of excess, free charges in any solvent without the need for electrolyte or electrodes. Relative one-electron redox potentials of pairs of solutes can be determined through charge transfer equilibria measurements with PR. This approach offers the tantalizing possibility of determining accurate, referenced one-electron redox potentials of conjugated polymer chains in nonpolar environments, something that has been desperately needed in the field of organic electronics since its inception.

The two leading approaches for estimating HOMO and LUMO levels in these highly conjugated materials come from onset potentials obtained by CV or UPS/IPES measurements on films. Both methods give important information but, even in the best case, we expect 50-100 mV accuracy which could correspond to orders of magnitude variation in electron transfer rates. The two leading approaches for estimating HOMO and LUMO levels in these highly conjugated materials come from onset potentials obtained by CV or UPS/IPES measurements on films. Both methods give important information but, even in the best case, we expect 50-100 mV accuracy which could correspond to orders of magnitude variation in electron transfer rates.

The two leading approaches for estimating HOMO and LUMO levels in these highly conjugated materials come from onset potentials obtained by CV or UPS/IPES measurements on films. Both methods give important information but, even in the best case, we expect 50-100 mV accuracy which could correspond to orders of magnitude variation in electron transfer rates.

We have performed these measurements to determine accurate one electron redox potentials for several common conjugated polymers and small molecules including PM6, Y6, P3HT, IDTBT, PFO, PCPDTBT, F8BT with respect to the Fc/Fc+ couple in o-xylene. We hope this method will provide a reliable measure of the inherent redox properties of single conjugated polymer chains.

**SYMPOSIUM EN02**

Cutting-Edge Materials Design Toward Advanced Energy Harvesting—From Modeling to Manufacturing
April 23 - April 26, 2024

**Symposium Organizers**
Jinbo Bai, CNRS ECParis
Daniel Hallinan, Florida State University
Chang Kyu Jeong, Jeonbuk National University
Andris Sutka, Riga Technical University

* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

**SESSION EN02.01: Piezoelectric Systems and Self-Powered Bioelectronics**
Session Chair: Chang Kyu Jeong and Kwi-Il Park
Tuesday Morning, April 23, 2024
Room 332, Level 3, Summit

**11:00 AM *EN02.01.02**

**Photore sponsive Piezoelectric Ceramics for Multisource Energy Harvesting and Sensing** Yang Bai; University of Oulu, Finland

Among all kinetic energy harvesters, those made from piezoelectric materials are considered the most efficient when working at resonance of the electromechanical coupling process. High-performance piezoelectric materials, such as piezoceramics and single crystals, are usually oxide perovskite ferroelectrics which also exhibit photovoltaic effect. This fact offers a unique opportunity to integrate light harvesters with the piezoelectric ones in a single material to achieve multi-source energy harvesting and/or sensing. Coupling multiple energy in one material promotes self-sufficiency and sustainability of energy harvesters and associated electronic systems. Strong piezoelectricity has been thought to inevitably lead to wide photonic band gaps, and vice versa, narrow band gaps eliminate piezoelectricity. This view, however, is being changed. This talk will walk through the achievements in recent years in terms of band gap engineering of piezoelectric materials with an emphasis on works carried out by the speaker’s research group, including piezoelectric compositions based on the potassium niobate and lead titanate perovskite.
solid solutions.

11:30 AM EN02.01.04
On-Skin Breathable Triboelectric-And-Electromagnetic Liquid-Metal Nanogenerator for Extracting Biomechanical and Electromagnetic Energy and as Whole-Body Epidermal Self-Powered Sensors Ying-Chih Lai; National Chung Hsing University, Taiwan

On-skin electronics can be conformably deployed on body for health monitoring, assisted living, and human/computer interfaces. However, developing corresponding energy devices is a critical challenge. Herein, a permeable and stretchable multifunctional liquid-metal electronic skin that can generate electricity by recovering ambient electromagnetic pollution (from surrounding electrical appliances) and biomechanical energy (from body movements) is presented for epidermal energy and self-powered sensing applications. To the best of our knowledge, this is the first demonstration that a breathable on-skin device can convert ambient electromagnetic pollution into useful electricity. The device was constructed using two stretchable microfibrous films sandwiching self-organized mesh-like and wrinkled liquid metal that affords electricity via induced electrification (±9.3 V, ±1.7 μA; 60 Hz) and triboelectricity (205.6 V, ±2.3 μA; 4 Hz). Its applicability in powering electronic devices has been demonstrated. Moreover, it can serve as an epidermal self-powered sensor for continuously monitoring whole-body physiological signals and motions of the eyelids, face, throat, chest, and limbs, thus demonstrating its potential to remotely collect clinical and biomechanical information. Finally, it was used as an interface in diverse system-level applications. These results shed light on new directions in on-skin energy and sensing, enabling to usher electronics toward untethered and diversified applications.

Ref:

SESSION EN02.02: From Fundamentals to Materials for Electromechanical Coupling Devices
Session Chairs: Chang Kyu Jeong and Dong-Myeong Shin
Tuesday Afternoon, April 23, 2024
Room 332, Level 3, Summit

2:00 PM *EN02.02.02
Approaches Toward Efficient Piezoelectric based Energy Harvesting Chong Yun Kang; Korea Institute of Science and Technology, Korea (the Republic of)

Due to relatively low power generation capability and energy conversion efficiency, however, these harvesting technologies have been applied only to limited applications. In order to solve these issues, here, we address three type of piezoelectric energy harvesting. First, we design and demonstrate a piezoelectric/electromagnetic hybrid energy harvester that can generate significant amount of electricity at vibration environments. Oval-like configuration using two curved piezoelectric energy harvesters based on MFC (Macro-fiber composite) piezoelectric material induces large displacement of a permanent magnet designed at the end of the top surface which allows efficient power generation both piezoelectric and electromagnetic energy harvesters. Second, Second, we introduce a PVDF-based piezoelectric energy harvester applicable to roads. The PVDF-based piezoelectric energy harvesters provide a competitive power output at small vertical displacements with proper module design, making the tough piezoelectric materials suitable for efficient and durable roadway energy harvesting. Finally, we demonstrate an ultra-wide bandwidth piezoelectric energy harvesters through the automatic resonance tuning. Piezoelectric energy harvesters typically exhibit sharp peak in output power around resonance frequency. We expect that the automatic resonance tunable piezoelectric energy harvester can provide the much-needed breakthrough in the deployment of mechanical energy harvesters for naturally occurring vibrations.

2:30 PM BREAK

3:00 PM *EN02.02.03
Cooperative Contact Electrification enabled by Control Over Electron and Ion Transfer Directions Xiaoting Ma, Jianming Zhou, Eunjong Kim, Jingyi Gao and Dong-Myeong Shin; University of Hong Kong, Hong Kong

Contact electrification (CE) is a phenomenon that occurs when two materials are brought into contact and exchange charges. Although recent studies show that CE between two solids including metals, semiconductors and nonionic polymers is basically due to electron transfer, the mechanism for CE involving ionic materials remains controversial. In this paper, the CE process between single-ion conducting materials (SICM) and fluorinated ethylene propylene (FEP) is systematically investigated to elaborate the electrification mechanism when ions are participating in CE. In the study, electron thermionic emission method was also used to separate the contributions of ion transfer and electron transfer in the total static charges when varying the environmental humidity. Furthermore, molecular dynamics simulations were performed to reveal the molecular interactions and dynamics of the polymer surfaces, mobile ions and water molecules at the interface. The results show that ion transfer is an important mechanism in the CE of FEP/SICM pairs and that higher humidity leads to more free ions and higher contribution of ion transfer in the total transferred charges. Our research not only provides new insights into the mechanism of contact electrification that involves ion transfer but also introduces a unique category of triboelectric materials that are single-ion conducting.

3:30 PM EN02.04.02
Sustainable and High-Performance Triboelectric Nanogenerator Based on Sulfur-Rich Polymer/MXene Composites Woonbi Cha1, Sungsu Kim1, Hyoncheon Lee1, Nara Han2,3, Hyunki Kim2, Minbaek Lee2, Tae Hee Han1 and Jeong Jae Wie1,3,4; 1Hanyang University, Korea (the Republic of); 2Inha University, Korea (the Republic of); 3State University of New York College of Environmental Science and Forestry, United States; 4The Michael M. Szware Polymer Research Institute, United States

Sulfur-rich polymer (SRP) is a great candidate to construct a waste-based as high-performance triboelectric nanogenerator (TENG), as elemental sulfur is a huge waste from the petroleum refining process and possesses the highest level of electron affinity (~200 kJ mol⁻¹). In our previous reports, the SRP-based TENG outperformed polytetrafluoroethylene (PTFE), one of the state-of-the-art triboelectric materials, by directly fluorinating the surface of SRP and adapting a blend system with fluoropolymer. However, these strategies raised environmental concerns about using F₂ gas and per- and poly-fluoroalkyl substances (PFAS), which are toxic to humans. Herein, we introduce the SRP/MXene composites to circumvent environmental issues and to achieve a high-performance triboelectric nanogenerator (TENG). We achieved the maximized MXene distribution in SRP with minimized MXene content by introducing the segregated MXene film. This well-distributed MXene enhances triboelectricity through the enhanced dielectric constant via microscopic dipole interactions at the interface between SRP and MXene. As a result, SRP/MXene-based TENG demonstrated a record high peak voltage of 331.4 V and peak current of 19.6 μA, which are 2.9 times and 19.5 times higher than those reported in previous SRP-based TENGs. The used SRP/MXene film also can be recycled by regrinding and compressing due to its dynamic bond exchanging property, and the recycled SRP/MXene film maintains its modulus and triboelectric output performance. Finally, scaled-up 4-inch SRP/MXene film-based TENG demonstrated a record high peak power density of 3.89 W m⁻² after applying corona discharging, surpassing the reported SRP-based TENG.

3:45 PM EN02.02.05
A Volume Effect based Triboelectric Nanogenerator for Omnidirectional Wave Energy Harvesting Jianming Zhou, Xiaoting Ma, Eunjong Kim and Dong-Myeong Shin; University of Hong Kong, Hong Kong

The marvel of the liquid-solid triboelectric nanogenerator (LS-TENG) has been demonstrated in its efficient energy harvesting via the contact electrification effect between liquid and solid triboelectric materials. The insufficient contact problems and wear issues frequently encountered in solid-solid TENGs are avoided through this technology. Nevertheless, the droplet-based LS-TENG has been plagued by problems of continuous falling droplets, which limits its practical application. Herein, we present an innovative droplet-based omnidirectional triboelectric nanogenerator (DB-TENG) utilizing the volume effect of droplets for efficient harvesting of ocean wave energy. With a unique concentric circular electrode pair built on an oblate plate, the DB-TENG achieves a significant improvement in output performance compared to traditional liquid-solid TENGs, with a maximum output voltage of 160V, which is 16 times higher, and a maximum current of 4000 nA, which is 40 times higher. This volume effect DB-TENG can perform reliably under extreme conditions of high humidity or high concentrations of salt, acid, or alkali solutions, making it a flexible tool for all types of working environments with enhanced reliability and reduced maintenance costs. What’s more, the DB-TENG's omnidirectional capabilities make it suitable for capturing energy from various directions of ocean waves. The TENG's performance in ocean wave energy harvesting is evaluated and compared with traditional TENGs, demonstrating superior results in terms of output voltage and current. The proposed design holds significant potential for practical applications in blue energy harvesting and can inspire the development of self-sufficient ocean sensors. Overall, this study highlights the importance of volume-effect in enhancing the output performance of TENGs and presents a promising
In this communication, we will present our latest advances in the development of nanostructured thin films and supported core@multishell nanomaterials for energy harvesting. The foundation of the synthetic approach centers around the utilization of a one-reactor system,[1] where we integrate various industrially scalable vacuum and plasma deposition methods for tailored nanostructured thin film deposition and the fabrication of one-dimensional devices. The transition from conformal layers to core@multishell devices is driven by the application of single-crystalline organic nanowires as supported soft templates compatible with a wide array of substrates.[2-3] We demonstrate the integration of materials, spanning from plasma polymers to sculptural hybrid halide perovskites and metal oxide nanotrees, onto energy harvesting devices such as solar cells, piezoelectric, pyroelectric, triboelectric, and hybrid nanogenerators. Our presentation highlights the role of micro and nanostructures and interface control in optimizing these energy-harvesting solutions.[4-9]


References:

For many centuries people have pondered (notably and dubiously Thales of Miletus)[1] why some materials become electrically charged when brought into contact with other, dissimilar, materials. We now know that this charging phenomena is governed either by piezoelectricity from deformation, for non-centrosymmetric unit cells, or contact electrification (also known as triboelectricity) from interfacial friction. While contact electrification and (ferro)electricity is well understood, the mechanisms of contact electrification remain a subject of debate in the literature.[2-3] This debate on the driving force being electron-, ion-, or material-transfer,[2-3] coupled to poor measurement techniques leading to conflation of piezoelectric and contact electrification,[4-5] has limited the design of optimal polymer energy harvesters.

If we can develop improved understandings of how polymers charge from friction, we can design devices that can capture motion to harvest electricity,[6] drive chemical reactions,[7] or even enable wound healing.[8]

To address this lack of understanding, we have studied how polymers generate charge at a contact interface. This has linked the polarity of generated charge directly to polymer structure via cohesive energy density,[9] and surface topography.[10] These relatively simple understandings have enabled the production of layer-by-layer ‘laminate’ assemblies from arbitrary polymers.[11] These laminates, which function purely off contact electrification and interfacial friction, generate internal dipole moments that mimic piezoelectric polymers – enabling exceptionally efficient vibrational energy harvesting. Finally, we demonstrate the conversion of recycled foamed/expanded polystyrene to fabricate such laminates, capable of harvesting over 12 µA and 200 V from just 16 N of force. Moving forwards, these laminates, as well as piezoelectric polymers,[12] are being studied tools to drive catalytic reactions ranging from fuel production through to small molecule synthesis.

This talk aims to provide a pathway to design highly efficent electromechanically active surfaces from polymers towards catalysis and sustainable chemistry.

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[7] J. Zhang, et al., Journal of the American Chemical Society 2021, 143, 3019, 10.1021/jacs.0c11006

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Unlocking The Pt Sintering Prevention Mechanism by Trace Amount of Atomic Layer Deposition

Andris Šutka1, Kaspars Malnieks1, Artis Linarts1, Linards Lapčinskis2 and Peter C. Sherrell2; 1Riga Technical University, Latvia; 2The University of Melbourne, Australia

Trivioelectric generators are the most promising mechanical to electrical energy converters at a small scale because they can extract energy from a huge range of mechanical sources: from motion, ambient vibrations, noise, and even from water droplets. However, their performance is limited due to low surface charge density and output power. Herein, we will describe various approaches for increasing the trivioelectric surface charge density. These will include MM ordering [1], functionalization [2], controlling interfacial strain [3], and exploiting volumetric dipoles [4,5]. We will show enhancement from controlled net surface charge polarity, intensified organo-ion transfer, and the complementary induction from triviolectric or piezoelectric dipole in volume. We will look at the perspective of combining these approaches for providing generators with high performance up to 50 W/m².

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[4] Linarts et al., Small 2023, 19, 2205563

Self-Powered Flexible Piezo-Sensor and MicroLED: Toward Commercialization

Keon Jae Lee; Korea Advanced Institute of Science & Technology, Korea (the Republic of)

This seminar introduces two recent progresses of self-powered flexible devices; piezo-sensors and microLED. The first part will introduce flexible inorganic piezoelectric membrane that can detect the minute vibration of membrane for self-powered acoustic sensor and blood pressure monitor. Speaker recognition has received spotlight as personalized voice-controlled interface, smart home, biometric authentication. The conventional speaker recognition was realized by a condenser type microphone, which detects sound by measuring the capacitance value between two conducting layers. The condenser type microphone, however, has critical demerits such as low sensitivity, high power consumption, low recognition rate and an unstable circuit due to the large gain amplification. Herein, we reported a machine learning-based acoustic sensor by mimicking the basilar membrane of human cochlear. Highly sensitive self-powered flexible piezoelectric acoustic sensor with a multi-resonant frequency band was employed for voice recognition. Convolutional Neural Network (CNN) were utilized for speaker recognition, resulted in a 97.5% speaker recognition rate with the 75% reduction of error rate compared to that of the reference MEMS microphone. In addition, wearable piezoelectric blood-pressure sensors (WPBPS) were developed for continuous non-invasive arterial pressure monitoring. WPBPS achieves a high normalized sensitivity (0.062 kPa⁻¹), and fast response time (23 ms). The transfer function of a linear regression model converts flexible piezoelectric sensor signals into blood pressure values. Clinical validation of WPBPS was performed on 35 subjects/175 measurements, that satisfies international standard of blood pressure measuring devices. The second part will discuss the highly efficient flexible micro LED for displays and biomedical applications. Flexible displays can be easily affixed anywhere, such as on the surfaces of human skin, clothes, automobiles and buildings. III-V inorganic LEDs have superior characteristics, such as long-term stability, high efficiency, and strong brightness compared to OLED. However, due to the brittle property of inorganic materials, III-V LED limits its applications for flexible electronics. Here we introduce the flexible GaAs/GaN microLED using innovative micro-evacuation transfer technology. The superb properties of flexible inorganic LED enable not only full-color displays and wearable phototherapy patches like hair growth, melanogenesis inhibition and pancreas cancer. In addition, combining with optogenetic mouse models, flexible microLED stimulates the neurons of motor cortex for manipulating mouse body movements and synchronized electroygram (EMG) signals.

Piezoelectric Biomaterials and Devices for Energy Harvesting and Application in Cardiovascular Devices

Xudong Wang; University of Wisconsin–Madison, United States

This seminar introduces two recent progresses of self-powered flexible devices; piezo-sensors and microLED. The first part will introduce flexible inorganic piezoelectric membrane that can detect the minute vibration of membrane for self-powered acoustic sensor and blood pressure monitor. Speaker recognition has received spotlight as personalized voice-controlled interface, smart home, biometric authentication. The conventional speaker recognition was realized by a condenser type microphone, which detects sound by measuring the capacitance value between two conducting layers. The condenser type microphone, however, has critical demerits such as low sensitivity, high power consumption, low recognition rate and an unstable circuit due to the large gain amplification. Herein, we reported a machine learning-based acoustic sensor by mimicking the basilar membrane of human cochlear. Highly sensitive self-powered flexible piezoelectric acoustic sensor with a multi-resonant frequency band was employed for voice recognition. Convolutional Neural Network (CNN) were utilized for speaker recognition, resulted in a 97.5% speaker recognition rate with the 75% reduction of error rate compared to that of the reference MEMS microphone. In addition, wearable piezoelectric blood-pressure sensors (WPBPS) were developed for continuous non-invasive arterial pressure monitoring. WPBPS achieves a high normalized sensitivity (0.062 kPa⁻¹), and fast response time (23 ms). The transfer function of a linear regression model converts flexible piezoelectric sensor signals into blood pressure values. Clinical validation of WPBPS was performed on 35 subjects/175 measurements, that satisfies international standard of blood pressure measuring devices. The second part will discuss the highly efficient flexible micro LED for displays and biomedical applications. Flexible displays can be easily affixed anywhere, such as on the surfaces of human skin, clothes, automobiles and buildings. III-V inorganic LEDs have superior characteristics, such as long-term stability, high efficiency, and strong brightness compared to OLED. However, due to the brittle property of inorganic materials, III-V LED limits its applications for flexible electronics. Here we introduce the flexible GaAs/GaN microLED using innovative micro-evacuation transfer technology. The superb properties of flexible inorganic LED enable not only full-color displays and wearable phototherapy patches like hair growth, melanogenesis inhibition and pancreas cancer. In addition, combining with optogenetic mouse models, flexible microLED stimulates the neurons of motor cortex for manipulating mouse body movements and synchronized electroygram (EMG) signals.

SESSION EN02.04: Emerging Materials for Energy Harvesting

Session Chairs: Jinbo Bai and Chang Kyu Jeong

Wednesday Afternoon, April 24, 2024

Room 332, Level 3, Summit

1:30 PM *EN02.01.01

Self-Powered Flexible Piezo-Sensor and MicroLED: Toward Commercialization

Keon Jae Lee; Korea Advanced Institute of Science & Technology, Korea (the Republic of)

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2:00 PM *EN02.04.01

Piezoelectric Biomaterials and Devices for Energy Harvesting and Application in Cardiovascular Devices

Xudong Wang; University of Wisconsin–Madison, United States

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Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Nanogenerator (NG) is a promising solution to biomechanical energy harvesting inside human body. So far, many technology innovations have advanced the NG technology toward a broad range of biomedical applications. Among many potential directions, cardiovascular applications possess substantial significance given the wide spread of cardiovascular diseases and high demands of cardiovascular electronic devices. In this talk, I introduce our most recent development of piezoelectric materials and composites that are particularly designed for implantable NG applications for both hearts and blood vessels. First, new ferroelectric composites are presented as a new material used in 3D printing for directly manufacturing of piezoelectric architectures with tunable piezoelectric and mechanical properties. Artificial blood vessels and stents are developed using this new technique that enable in vivo monitoring of blood pressure and early detection of blockage. Materials and devices that enables effective energy harvesting from hearts will also be introduced, showing a promising solution for long-term in vivo operation for powering cardiovascular electronics. Toward the end, other relevant challenges, such as device safety, biocompatibility, and packaging issues will also be discussed, together with additional novel application potentials for NGs for cardiovascular systems.

2:30 PM BREAK

3:30 PM *EN02.04.03
Discovering Giant Magnetoelastic Effect in Soft Systems for Bioelectronics Jun Chen; University of California, Los Angeles, United States

The magnetoelastic effect, also named as Villari effect and discovered in 1865 by Italian experimental physicist Emilio Villari, is the variation of the magnetic field of a material under mechanical stress. This effect is usually observed in rigid metal and metal alloys with an externally applied magnetic field and has been ignored in the field of soft bioelectronics for the following three reasons: the magnetization variation in the biomechanical stress range is limited; the requirement of the external magnetic field induces structural complexity and bulky structure, and there exists a gigantic mismatch of mechanical modulus up to six orders of magnitude difference between the rigid magnetoelastic materials and the soft human tissues. In 2021, we discovered the giant magnetoelastic effect in a solid soft polymer system, later in a liquid permanent fluidic magnet, which paves a fundamentally new way to build up intrinsically waterproof and biocompatible soft bioelectronics for diagnostics, therapeutics, and energy applications. Our group at UCLA is currently pioneering this research effort of harnessing giant magnetoelastic effects in soft systems for healthcare and energy.

4:00 PM EN02.04.05
Metal-Organic Frameworks for Textile based Triboelectric Nanogenerators Gaurav Khandelwal, Charanch Kumar, Satyaranjan Bairagi and Daniel Mulvihill; James Watt School of Engineering, University of Glasgow, United Kingdom

Metal-organic frameworks (MOFs) are crystalline porous materials composed of metal ion coordinated with an organic ligand. MOFs has numerous advantages including high surface area, tunable size, ease of post synthetic modifications, high porosity. Further MOFs offers specific pore size which can be advantageous for highly selective self-powered sensors based on triboelectric effect. However, majority of MOFs based TENG uses powders attached on the conductive tape by applying high pressure and blowing off the unattached particles. This widely used approach is unsuitable due to poor device reproducibility, repeatability and stability. Further, TENGs active layers designed by above method cannot be used for self-powered physical or chemical sensors. In case of physical sensors like pressure sensor, high pressure can lead to the transfer of material on the opposite contact layer. While in case of chemical sensors addition of analyte can lead to removal of material, thus making device unreliable. This work discusses the advantages and the challenges of MOFs for TENGs. Then MOFs are introduced for TENG based self-powered sensor applications with ZIF-8 based tetracycline sensor and Cu-Asp based thioacetamide sensor as examples. Finally, the talk will discuss the growth of MOFs on the textile substrates for TENGs, their triboelectric behaviour and potential for self-powered applications.

5:00 PM EN02.05.01
Flexible and Wearable Thermopiezoelectric Hybrid Energy Harvesters Cheolmin Kim, Hyeon Jun Park, Gwang Hyeon Kim, Bitna Bae, HakSu Jang and Kwi-II Park; Kyungpook National University, Korea (the Republic of)

Thermoelectric and piezoelectric hybrid generators (TPHGs) are attractive candidates for powering wearable body sensor networks continuously and permanently owing to their excellent access to human-generated energy. First, to achieve the enhanced piezoelectricity of flexible piezoelectric composites-based films, we have demonstrated the flexoelectric-boosted electromechanical properties of piezoelectric nanoparticle using an induced built-in strain gradient in heterogeneous core-shell nanostructure for enhancing the intrinsic piezoelectricity of pure BaTiO3 nanoparticles. We have also demonstrated the enhanced piezoelectricity in nanocomposite made of P(VDF-TrFE) and porous BaTiO3 nanofibers. Moreover, we have developed the high-temperature workable f-PEH comprising the high Tc KNN-based ceramics and a thermally stable polynioid (PI) matrix which can be a promising candidate for developing f-PEH and self-powered sensors working in high-temperature environments. Next, to realize the flexible thermoelectric energy harvesting technology, we have fabricated the tailorable f-TEHs based on thermoelectric films and papers made by dispersing the Bi2Te3 particles inside polymeric and cellulose matrices, respectively. Finally, the hybrid generator was assembled through simple drop-casting and gravitational settling effect, for the first time. The film layer sedimented with the conductive thermoelectric particles simultaneously served as an electrode and a bottom substrate for piezoelectric energy harvesting. The proposed design concept for f-TPHGs can aid in the conductive thermoelectric particle simultaneously served as an electrode and a bottom substrate for piezoelectric energy harvesting. The proposed design concept for f-TPHGs can aid in the conductive thermoelectric particle simultaneously served as an electrode and a bottom substrate for piezoelectric energy harvesting. The proposed design concept for f-TPHGs can aid in the conductive thermoelectric particle simultaneously served as an electrode and a bottom substrate for piezoelectric energy harvesting. The proposed design concept for f-TPHGs can aid in the conductive thermoelectric particle simultaneously served as an electrode and a bottom substrate for piezoelectric energy harvesting. The proposed design concept for f-TPHGs can aid in the conductive thermoelectric particle simultaneously served as an electrode and a bottom substrate for piezoelectric energy harvesting.

5:00 PM EN02.05.02
Enhanced Triboelectric Performance of Surface-Modulated 2D MoS2 via Pulsed Laser-Directed Thermolysis for Self-Powered Wearable Electronics Hye Yoon Jang2, Chang Kyu Jeong2 and Seoung-Ki Lee1; 1Pusan National University, Korea (the Republic of); 2Jeonbuk National University, Korea (the Republic of)

In recent times, two-dimensional (2D) transition metal dichalcogenide (TMD) nanomaterials have emerged as leading contenders for advancing the realms of flexible, transparent, and wearable electronics. Yet, there exists a conspicuous dearth in the exploration of their inherent properties in the domain of triboelectric nanogenerators (TENGs), a foremost technology for mechanical energy harvesting. This study presents a novel, rapid, ambient, wafer-scale, and patternable methodology for the synthesis of 2D MoS2 through pulsed laser-directed thermolysis. Our groundbreaking laser synthesis approach facilitates the imposition of internal stress on the MoS2 crystal by modulating its morphological characteristics, resulting in a surface-modulated MoS2 TENG device that exhibits power generation amplified by approximately 40% relative to its flat MoS2 counterpart. Distinctly, in comparison to analogous MoS2-based TENG devices, our model achieves superior energy harvesting metrics (reaching peaks of ~25 V and ~1.2 μA) without the requirement of supplemental materials, even in scenarios where the opposing triboelectric surface exhibits a marginally varied triboelectric series. This augmentation in triboelectrification can be ascribed to both alterations in work function and the amplification of surface roughness. Conclusively, the directly synthesized MoS2 patterns are adeptly employed to craft a self-sustaining flexible haptic sensor array. The methodology delineated herein aims to galvanize expansive research into the triboelectric potentials and diverse applications of 2D TMD nanomaterials.

5:00 PM EN02.05.03
Anomalous Output Performance Enhancement of Triboelectric Nanogenerators by Manipulation of Surface Molecular Dipoles Ruey-Chi Wang and Hsiao-Cheng Chen; National University of Kaohsiung, Taiwan

Since the invention of triboelectric nanogenerators (TENGs), numerous strategies have been proposed to boost their performance by altering the triboelectric materials, typically centered on increasing work function disparities or effective contact areas. However, in this study, we introduce a novel approach that significantly enhances output performance through the manipulation of surface molecular dipoles, a departure from conventional methods. In our research, we demonstrate a significant improvement in TENG output performance by manipulating surface dipoles, achieved by bonding copper ions to the oxygen-containing functional groups on the surface of graphene oxides. This bonding causes a reversal in the orientations of surface molecular dipoles, resulting in the enhancement of TENG output. Remarkably, the variations in TENG output performance due to these surface modifications are contrary to what would be predicted based solely on differences in work functions, as determined by Kelvin probe force microscopy. This observation suggests that factors beyond work functions play a pivotal role in governing TENG performance. We propose a self-bias-enhancement model by surface dipoles and further testifies it by polling processes. This mechanism is expected to have universal applicability to other materials aimed at enhancing the performance of TENGs and self-powered devices.
5:00 PM EN02.05.04

Computational Investigation of Low-Dimensional Materials for Space Suit Applications
Simone Lang and Shuru Lin; Texas Woman's University, United States

Modern Space Suit materials maintain properties that shield astronauts from radiation, severe lunar temperature, and microparticles; while upholding lightwightness, flexibility and tensile strength to allow for long space missions. Most space suit materials are made from nylon, synthetic fabrics and synthetic polymers. High density polyethylene (HDPE) is a popular polymer for space applications due to their resistance properties from secondary radiation exposure and their richness in hydrogen atoms. However, HDPE lacks tensile strength, therefore causing urgency to find a material that will absorb well and maintain excellent properties with HDPE. In this project, low-dimensional materials, including graphene, graphene oxide and boron oxide are explored for space suit material additivies HDPE, because of their successful electrostatic, thermal and mechanical properties. Density Functional Theory (DFT) computations are used to investigate the adsorption interactions between low-dimensional materials with HDPE with the variable of angle dependence. Moreover, exploring their ability to maintain radiation resistance, thermal cycling and electrostatic properties.

5:00 PM EN02.05.05

Influence of Relaxor Piezoelectric Polymer Matrix on Piezoelectric Nanocomposites-Based Energy Harvesting
Hyunseung Kim1,2, Wook Jo3, Seung-Hyun Kim3 and Chang Kye Jeong1,3,2; 1Yonbuk National University, Korea (the Republic of); 2UlSAN National Institute of Science and Technology, Korea (the Republic of); 3Brown University, United States

Enhanced Output Performance of Triboelectric Nanogenerator Based on Sulfur-Rich Polymer with Controlled Composition Gradient
Minji Bak1,2, Woongbi Cho, Sungsu Kim1 and Jeong Jae Wie1,3,2; 1Hanyang University, Korea (the Republic of); 2The Michael M. Szwarc Polymer Research Institute with Composition Gradient, United States; 3State University of New York College of Environmental Science and Forestry, United States

Elemental sulfur of seven million tonnes is annually generated as a by-product from petroleum refining processes. Hence, the upcycling of elemental sulfur has gained significant attention owing to its high economic feasibility and environmental-friendliness. In previous works, the sulfur-rich polymer (SRP) is utilized for the high-performance negatively chargeable friction layer in a triboelectric nanogenerator (TENG). Because the SRP has the highest electron affinity of ~200 kJ mol⁻¹ in the periodic table except for halogenic elements and precious metals like Au, Pt. In this study, we present a structural approach with composition gradient for improving TENG performance. A thin dielectric layer is typically favorable for high performance due to increased charge induction, but excessive thinness reduces surface charge density due to charge recombination. To prevent the recombination, a charge trapping layer (CTL) is employed for enhancement of surface charge density. Increasing sulfur content in SRP leads to a higher dielectric constant, resulting in the generation of more charge through triboelectricification. At the same time, the benzene content decreases, which reduces charge capture ability. This is because aromatic polymers have non-uniform energy levels along their polymer chain, containing numerous charge trapping sites. We optimize TENG performance by creating a monolithic flat film with spatially controlled elemental sulfur and benzene content through dynamic covalent bonding by the thermal processing of two films with different sulfur contents.}

5:00 PM EN02.05.10

Metallic Glass Thin Film Electrodes for Chemically and Mechanically Stable Interface for Flexible Electronics
Jae Sang Cho1, Woogisik Jang2, Keum Hwan Park2 and Dong Hwan Wang1; 1Chung-Ang University, Korea (the Republic of); 2Korea Electronics Technology Institute, Korea (the Republic of)

Metallic glasses (MGs) or amorphous alloys gained attention for their attractive mechanical properties and chemical stabilities, which originate from the randomly oriented atomic arrangement in the MGs that results in their strong strain-resistance and chemical inertness. MGs are often characterized by the absence of grain boundaries, which are often responsible for initiating catastrophic mechanical failures and corrosion (and other chemical reactions). Recently, their applicability in thin film via physical vapor deposition method have motivated researchers to replace electrode materials to MG thin films. MG thin films exhibit varying electrical and mechanical characteristics depending on their atomic compositions, thus should be analyzed thoroughly before replacing conventional electrode materials for the electrodes. Here, we present intriguing cases of adopting MG thin films for electrodes of organic photovoltaic cells and sensors. Through detailed investigations on MG thin films, fabrication of thin film devices with enhanced stability and flexibility is achieved. In specific, amorphous metallic surface in contact with polymers circumvents oxidation reaction caused by ambient air, which prevents formation of insulating oxides and loss of electrical conductivity of the electrode itself. In addition, MG thin film exhibited high crack resilience in bendable and stretchable devices, which yielded flexible devices with high flexibility and reliability.

References
3 Journal of Alloys and Compounds 944 (2023) 169219.

5:00 PM EN02.05.14

Bulk Enhanced Attachment of Graphene Dispersed Conductive Polymer to 1D Nanofibers for Sensing and Nanogeneration
Elmmer A. Vera Alvarado, Md. Abdur Rahman Bin Abbas Salam, Ali Ashraf and Karen Lozano; The University of Texas at Rio Grande Valley, United States

Nanogeneration, an emerging area where nanotechnology meets energy harvesting, has the potential to transform how we provide power to our increasingly miniaturized and portable electronic devices. The concept of nanogeneration, which involves the utilization of nanoscale materials and processes to generate electricity from surrounding sources, Nanogeneneration encompasses various technologies like piezoelectric nanomaterials, thermoelectric generators, and triboelectric nanogenerators, which make it possible to transform mechanical movements, temperature variations, and even environmental vibrations into electrical power. Polyvinylidene fluoride (PVDF) is a semi-crystalline thermoplastic fluoropolymer known for its remarkable piezoelectric properties. PVDF is commonly employed for piezoelectric sensors, serving to measure pressure, force, acceleration, and vibration in various devices. These sensors are applied in industrial monitoring, medical equipment, and consumer electronics. In this study, the Forceensing® (FS) method was utilized to fabricate PVDF nanofiber mats, which then were cut into small strips for nanogeneration and sensing tests. A conductive polymer ink, composed of polyl4,4-ethyleneoxyxiphosphate) polystyrene sulfonate (PEDOT:PSS) and graphene nanoflakes, was created and diluted in a 1:1 ratio with deionized water, which was later applied using a dip-coating process on the nanofibers. These nanofibers were initially subjected to a 3-minute plasma etching process to gain better graphene adhesion. The time of plasma treatment was decided after several trials at different times under the plasma treatment, the samples were characterized by Scanning Electron Microscopy (SEM) and it was observed that as the treatment time increased, the finer the fibers became, decreasing the fiber diameter by approximately 500 nm from the pristine nanofibers. The plasma process was done to enhance the adhesion of 2D material particles to the nanofibers, confirmed by SEM. The microscopic images of untreated PVDF nanofibers following the 3-minute plasma treatment displayed a noticeable decrease in the number and dimensions of bead-like structures, along with a substantial reduction of 500 nm in nanofiber diameter. Additionally, the images revealed a strong adhesion between the conductive polymer ink and the nanofibers. Moreover, the coated nanofibers presented an improved electrical conductivity of 250 kΩ as well as an average output voltage of 50 mV for single finger pressing, comparable to the work performed by Rahman et al., where a voltage of 75mV was obtained from graphene-coated nanofibers [1]. Further tests for sensing and energy harvesting of these samples are to be performed, showing a promising advancement for low-powered sensors and energy harvesting.

References

5:00 PM EN02.05.15

Towards 1-Watt Capable Rotary Triboelectric Nanogenerators for Power at Sea
Griffin Trayner, Calam Kenny and Jim McNally; National Renewable Energy Laboratory, United States

Increasing at-sea power generation by Triboelectric Nanogenerator (TENG) energy harvesters in the order of 1-Watt will create significant opportunities to power ocean observation buoys and distributed sensor nodes by extending mission time and increasing sensor payload [1]. Of the many possible configurations of harvesting wave energy with TENGs, we document the rationale for choosing and developing a rotary TENG that operates by the freestanding mode. The rotary TENG prototype consists of two plates, a rotor and a stator, to take advantage of the various
mchanisms of converting wave action into rotational motion. We have constructed a testing apparatus that allows us to vary several key parameters of the device: distance between rotor and stirrer, tribocorrelmonal material, rotational speed, number of electrodes and output load impedance. Predominant results show that when driven at a constant 500 rpm, we can achieve a power density of 0.7 W/m². A variable speed motor drives the rotor, which can be driven using a velocity profile informed by the equivalent to the output from a wave energy converter (WEC). This profile may be generated by the hydrodynamic simulation software WEC-Sim. The optimized rotational performance may be used to power devices in the ocean at a low cost and high durability.

References:

5:00 PM EN02.05.16
Moisture Activated Zinc Ion Battery for Leak Detection Signaling Dylan D. Edmundson and Anthony Dichiara; University of Washington, United States

Every year $6 billion worth of potable water is lost to undetected leaks in addition to $20 billion spent on property damage in the U.S alone [1-3]. While many leak detection systems exist that use acoustic, thermal, and video detection principles, they often suffer from low signal to noise ratios, poor sensitivity, and require technician operation [4-6]. To overcome these challenges researchers have begun investigating new and innovative bio-based solutions such as conductive paper resistive sensors [7,8]. While these systems are quite effective, they are difficult to implement in residential homes due to the expense of installation and the need of continuous monitoring and power supply. To overcome these drawbacks, a fully autonomous leak detection system was envisioned, where a leak can produce power through mechanisms such as moisture enabled generators (MEGs) however, the extremely low power production of MEGs is insufficient for WiFi signaling. In this study a zinc ion battery inspired device is developed in pursuit of a fully autonomous detection system. Zinc microspheres are embedded in a carbon nanotube/cellulose composite using a scalable paper manufacturing method. Using this anode with a moisture wicking electrolyte doped separator and manganese oxide cathode, a water activated battery was produced capable of powering a WiFi device signaling the presence of a leak.

Sources:


8:00 AM EN02.06.01
Paper-Based Electrokinetic Power Generator Dylan D. Edmundson and Anthony B. Dichiara; University of Washington, United States

Wearable devices integrated with microprocessors and multifunctional sensors are gaining momentum in a variety of industries over the past decade. Such advancements significantly exceed the development pace of portable power sources. Most batteries, besides causing serious sanitary and environmental concerns, are unfit for wearable devices, which require flexible, lightweight, reliable, and long-lasting systems with power densities of at least several tens W/kg. The autonomous scavenging of energy from the ambient environment offers a solution to power wearable sensors over long periods without the need to recharge. Nanogenerators (NG), such as triboelectric, piezoelectric, and thermoelectric generators, have been developed to harvest renewable energy from ambient sources that can be used to power portable electronics. Among them, moisture enabled generators or MEGs are a class of NG that generate electricity from moisture transport mechanisms, giving them a great advantage as water is inherently present in the air everywhere in the world. MEGs are typically made up of conductive materials that form an electric double layer when contacted by water. Water molecules move through a porous material, viscous shear forces create a charge gradient causing a potential difference and inducing current. The ability of the Earth’s hydrological cycle, transpiration driven electrokinetic power generators (TEPGs) take advantage of transpiration forces using asymmetric wetting mechanisms to increase fluid transport without the need for flowing bodies of liquid water. The present research leverages the biodegradable nature, flexibility, and light weight of lignocellulosic paper and combines them with the excellent properties of carbon nanotubes to prepare electrically-conductive capillary pumps. This innovative papertronics is cost-effective, recyclable, and can be manufactured using easily scalable papermaking processes. As-produced TEPG materials were thoroughly characterized and achieved a sustained open circuit voltage and short circuit current of 225 mV and 7 μA, respectively, from the transport of a 10 µL aqueous aluminum sulfate solution. The power output was improved further by using an optimized active electrode design, yielding OCV and SCC values over 1 V and 3 mA, respectively. A single device exhibited an impressive maximum power density of 50 W/kg, which when connected in series and parallel, could supply power for some common electronic systems.

8:30 AM EN02.06.02
Streamlining The Hydradation of Micron-Sized Aluminum Particle Surface Towards Enhanced Power Generation Mahmuda Ishrat Malek and Michelle L. Pantoya; Texas Tech University, United States

Aluminum particles possess a core-shell configuration in which an aluminum core is covered by a passive alumina (Al₂O₃) shell. This Al₂O₃ shell acts as both a heat sink and a barrier for reactions which impedes the process of harnessing the substantial chemical energy potential of Al, which stands at 31 MJ/kg. Hydrating the Al surface has the potential to replace the Al₂O₃ shell with Al(OH)₃, a material with favorable properties for energy extraction. While nano-sized Al particle surfaces can be hydrated by controlling the pH, micron-sized particles require external heating and subsequent aging because of 90% decrease in surface energy. Applying temperature above 35°C to Al-water solution can expedite the formation of AlOOH and prolonged aging can lead to excessive consumption of Al core, both of which have adverse effect on the potential energy of the sample. For small amount of Al powder (230mg) controlling the temperature at 35°C for a minimum of 18 hrs, Al(OH)₃ shell formation in place of Al₂O₃ can be achieved with 96% Al core still unconsumed. To hydrate a larger amount of powder (2g) in a short period of time, high temperature (100°C) is necessary to produce Al(OH)₃. Heating Al powder for 25mins at this temperature can produce 5% Al(OH)₃ with most of the Al cores (95%) unconsumed. Moving up to 30mins the powders have a trace of 3% AlO(OH). TEM images of 18hrs at 35°C and 25mins at 100°C both have similar fuzzy surfaces. Upscaling the hydration process for micron-sized Al powder can lead to a time-saving method for larger quantities of Al and aid in producing modified shell-core properties that can be exploited for enhancing power generation techniques.

4:45 AM EN02.06.03
Performance Enhancement of Moisture-Induced Power Generators under Ambient Conditions through Flashlight-Induced Graphitization of Fe₃Cl₄-Impregnated Cellulose Papers Daewoong Kim, Jaekyoung Eun, Hyunsoo Han and Sangmin Jeon; Pohang University of Science and Technology, Korea (the Republic of)

We introduce a novel approach for the fabrication and performance enhancement of moisture-induced power generators (MPGs) utilizing flashlight-induced graphitization (FIG). Fe₃Cl₄-impregnated cellulose papers (FCPs) were photothermally converted into graphitized cellulose papers (GCPs) with a hierarchically porous structure by flash light irradiation under ambient conditions. During the photothermal conversion process, Fe⁺⁺ ions partially convert into iron oxide compounds with limited solubility, highlighting that Fe₃Cl₄ serves multiple roles such as catalyst for graphitization, moisture absorber, and charge carrier. When a bilayered cellulose paper (BCP), formed by stacking GCP on top of FCP, was exposed to moisture, a potential
difference was generated between the collecting electrodes due to the concentration gradient of dissociated Fe ions within the BCP, with higher concentration in FCP and lower concentration in GCP. The resulting migration of Fe$^{3+}$ ions from FCP to GCP caused electron movement along the external circuit. The BCP-based MPG exhibited continuous voltage and current outputs, with maximum values of 0.39 V for voltage and 28.6 μA/cm$^2$ for current density at 45% relative humidity, marking a significant breakthrough in MPG performance under ambient humidity conditions.

9:00 AM EN02.06.04
Multidimensional Analysis of Moisture-Induced Power Generator Using Quartz Crystal Microbalance

Hyerim Baek, Ihun Choi, Hyewon Lee and Sangmin Jeon; Pohang University of Science and Technology, Korea (the Republic of)

A novel quartz crystal microresonator was developed as a moisture-induced power generator (MPG) through constructing an interdigitated electrodes-lateral field excited (IDEs-LFE) quartz resonator. This system enabled the simultaneous measurement of both the electrical output of the MPG and the resonant frequency shift of the quartz crystal (QC) in real time. The SCP film, composed of sodium alginate, carbon nanoparticles and polyvinyl alcohol was coated onto the IDEs which were deposited on the top surface of the QC. Following the coating process, a voltage of 1 V was applied across the IDEs to construct ion concentration gradient, resulting in the generation of electricity during the desorption of water molecules. Two symmetrical electrodes which were deposited on the bottom surface of the QC were employed to monitor the adsorption of water molecules into the SCP film by measuring the change in resonant frequency during oscillation. By conducting simultaneous measurements of the resonant frequency shift and electrical output under varying humidity conditions, parametric plots were established that correlate the electrical output with the resonant frequency shift. This dynamic interplay between resonant frequency shifts and electrical output provided insights into the impact of moisture adsorption on MPG performance.

9:15 AM EN02.06.05
Electrochemical Kinetic Energy Harvesting Mediated by Ion Solvation Switching in Two-Immiscible Liquid Electrolyte

Donghoon Lee$^1$, You-Yeob Song$^2$, Angyin Wu$^1$, Jia Li$^3$, Jeonghun Yoon$^4$, Dong-Hwa Seo$^5$ and Seok Woo Lee$^6,7$; $^1$Nanyang Technological University, Singapore; $^2$Korea Advanced Institute of Science and Technology, Korea (the Republic of); $^3$Rolls-Royce at NTU Corporate Lab, Singapore

Kinetic energy harvesting (KEH) is the process of converting mechanical energy, typically in the form of motion or vibrations, into electrical energy using specialized devices or systems.[1] KEH is of significance in the realm of renewable energy, as it enables the harnessing of otherwise wasted or underutilized kinetic energy sources, thereby contributing to the development of sustainable power generation and self-sustaining electronic devices.[2] Nonetheless, presently existing techniques, like those relying on friction and deformation, require high-frequency kinetic energy and call for materials possessing exceptional durability.[3] Also, those methods have extremely high impedance, leading to reduced current and power outputs, thus constraining their practical applications.[4]

Herein, we propose an electrochemical KEH system that employs a two-phase immiscible liquid electrolyte, specifically combining aqueous and ionic liquid components, with Prussian blue analogue (PBA) electrodes. This system is designed to capture and harness kinetic energy from gentle and low-frequency mechanical motions while reducing impedance of the system. Starting from the state of equilibrium, where both PBA electrodes are submerged in distinct phases of the immiscible electrolyte, the open-circuit potential difference between these electrodes experiences an increment. This increase in potential difference enables the conversion of kinetic energy, associated with the movement of the electrodes into their respective phases, into electrical energy. The system generated 6.4 μW cm$^{-2}$ of peak electrical power, accompanied by 96 mV of peak voltage and 183 μA cm$^{-2}$ of peak current density when connected to a load resistor of 300 Ω. The applied load is three orders of magnitude smaller than what is conventional KEH methods. Furthermore, the proposed method demonstrated a continuous current output of around 5 μA cm$^{-2}$ over one hundred seconds, at the frequency of 0.005 Hz for 23 cycles without any degradation in performance. Through computational simulations, we have determined that voltage between PBA electrodes originates from the difference in solvation Gibbs free energy within each phase of the two-phase electrolyte. The elimination and subsequent reformation of solvation shells surrounding solvated cations serve as the driving force for both the generation of voltage and the flow of electrons within the system. Moreover, we have effectively demonstrated the capability of our system within a microfluidic device, thereby paving the way for diverse applications. The microfluidic kinetic energy harvester is composed of identical PBA thin-film electrodes and the two-phase electrolyte. By utilizing the conversion of kinetic energy to drive the two-phase electrolyte through the microfluidic channel, our system attained a peak power density of 200 nW cm$^{-2}$.

In conclusion, we recognized the possibility of harvesting kinetic energy from solvation Gibbs free energies in the two-phase electrolyte mediated by ion-hosting materials and furnished persuasive evidence of its viability as a power source for self-powered devices. The incorporation of our system into the microfluidic harvester endows it with advantages for powering wearable electronics and Internet of Things (IoT) applications.

Abstract original from, [Preprint] Research Square, DOI: 10.21203/rs.3.rs.3296359/v1

9:30 AM EN02.06.06
Wearable Device Monitoring Cough with Piezoelectric Energy Harvester as a Simultaneous Sensor and Battery Life Extender

Yang Bai, Jaakko Palosaari, Eetu Virta and Mikko Minaia; University of Oulu, Finland

Cough is the most common symptom for which individuals seek medical advice. However, wireless and autonomous tools and standards for cough monitoring are lacking, possibly due to issues of measurement reliability and device lifespan. This work utilizes the piezoelectric energy harvesting concept to sense coughing signals. Different from conventional sensing techniques, the piezoelectric harvester here converts energy of muscle movement triggered by cough into electricity which then charges a capacitor, rather than being directly read by the microcontroller. The capacitor will accumulate energy for a certain period and then the capacitor voltage will be read by the microcontroller. This simple change of data collection mechanism magnificently reduces the duty cycle of the entire electronic system whilst maintaining high accuracy of recording the history of coughs. Proven in clinical trials, the battery life of the device has been significantly extended to longer than a week compared to approximately only overnight where conventional sensing techniques are implemented, even if using the same piezoelectric harvester (sensor). The newly developed system can then be used to autonomously monitor and analyze cough data of in-/outpatients for daily, research and clinical purposes and thus to improve prediction and management of severe respiratory diseases.

9:45 AM BREAK

SESSION EN02.07: Combination of Energy Harvesting and Storage

Session Chairs: Jinbo Bai and Daniel Hallinan
Thursday Morning, April 25, 2024
Room 332, Level 3, Summit

10:15 AM EN02.07.01
Designing Solid Polymer Electrolytes for Energy Storage and Harvesting

Christopher Li, William R. Fullerton and Tongjie Zhang; Drexel University, United States

Solid polymer electrolytes (SPEs), with a unique combination of electrochemical and mechanical characteristics, are promising for a wide range of energy storage and harvesting applications. The molecular architecture and structure of SPEs provide a versatile platform for tailoring materials’ properties to suit specific application needs. This presentation will focus on the morphology and network structure effects on ion transport, electrodeposition, and the formation of metal dendrites. We demonstrate that the tortuosity resulting from the morphology of SPEs can be employed to fine-tune ion transport and guide the growth of metal dendrites. On the other hand, mechanically modulating the internal SPE structure can provide an alternative approach to controlling dendrite growth. By tuning SPE’s molecular structure and chemistry, we can adjust the electrochemical and mechanical properties for improved battery performance while elucidating how these affect the underlying transport mechanism and electrodeposition behavior.

10:45 AM EN02.07.02
A Modular Solid-State Electrolyte Platform Based on a Charged Double Helical Polymer

Louis A. Madsen; Virginia Tech, United States

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Our group has been developing a class of rigid solid electrolytes based on a highly charged double helical polyanion self-assembled with ion-containing fluids. We term this class of materials molecular ionic composites (MICs). These materials are highly thermally stable, and can reach ~1 GPa tensile modulus and >1 mS/cm ionic conductivity with only 10-20% polymer content, and even with a substantial loading of cations like Li⁺ or Na⁺. Although MICs are macroscopically solid, the nanoconfined and partially ordered ions inside move only modestly slower (a factor of 3) than in the neat precursor fluid. We can modulate the mechanical, transport, and chemical/thermal stability properties of MICs over wide ranges by changing the content and molecular weight of the polymer, and the chemistry of the ions and other mobile components. I will discuss the state of understanding of MICs, from the dependence of multi-scale morphology and transport on composition and liquid crystallinity, to the influence of specific molecular interactions on properties. I will discuss progress toward practical all-metal batteries, as well as extensions beyond our original MIC materials that include (1) segregation of highly Li-conductive nanocrystalline phases, and (2) high modulus thermo-reversible hydrogels.

Coarse-Grained Molecular Dynamics Simulations of Polymer-Grated Nanoparticle Systems

Lisa H. Hall
Ohio State University, United States

Grafting polymer chains to nanoparticle surfaces, creating polymer-grated nanoparticles (PGNs), allows for nanocomposites with a uniform and controllable distribution of inorganic particles in an organic matrix. Such materials are of interest as membranes for separations and dielectric materials, among other applications. The nanoparticle size, graft length, and graft density together set the interparticle spacing, as well as the degree to which conformations of chains on nearby particles can overlap, which impacts the local and overall material properties. Specifically, at high enough graft densities, the polymer conformations are stretched (brushlike) near the surface, then approach random walk conformations farther from the surface if the grafts are long enough. We use a simple, efficient coarse-grained model to study how key controllable parameters such as graft density impact the chain conformations and local and overall properties. In particular, from molecular dynamics simulations, we analyze the structure, segmental and chain dynamics, and mechanical properties for a variety of polymer-grated nanoparticle systems, including dilute PGNs in solvent and PGN monolayer films. We find an intermediate graft density leads to a relatively precise interparticle spacing along with a significant amount of overlap of polymers on nearby nanoparticles, which provides increased toughness versus high graft density systems.

Developing High-Performance Piezoelectric ZnS:Mn²⁺ Nanoparticles for Enhanced Mechanoluminescence and Piezocatalysis

Zhongxian Wang and Yadong Yin
University of California, Riverside, United States

Piezoelectric materials, featured by their non-centrosymmetric structures and unique charge separation properties under mechanical stimulation, hold significant promise for applications spanning pressure sensing, optoelectronics, and piezocatalysis. However, existing materials often exhibit large particle sizes, posing challenges in specific applications like optoelectronics, where nanoscale dimensions are required for barrier-free circulation through blood vessels. Furthermore, reducing particle size to the nanoscale offers increased surface area and enhanced reactant adsorption, a pivotal factor in catalytic performance. Thus, developing a straightforward method to produce highly piezoelectric nanomaterials is of great significance. Herein, we introduce a novel approach for synthesizing ZnS:Mn²⁺ nanoparticles, employing the self-assembly of ZnS:Mn²⁺ quantum dots, followed by high-temperature calcination. During calcination, the ZnS:Mn²⁺ quantum dot assemblies transform into individual nanoparticles, accompanied by a phase transition from sphalerite to wurtzite structure. This sintering process in spatially confined within a silica layer, preventing nanoparticle interconnection. Subsequent etching of the silica layer using NaOH results in ZnS:Mn²⁺ nanoparticles with an average size of approximately 150 nm. These ZnS:Mn²⁺ nanoparticles exhibit exceptional piezoelectricity, featuring a piezoelectric coefficient (d₃₃) of up to 25 pm/V as measured via Piezoresistance Force Microscopy (PFM). Notably, this d₃₃ value is around eight times higher than the literature-reported d₃₃ value of ZnS (3.2 pm/V). It is worth mentioning that the d₃₃ value exhibits variations dependent on calcination temperature and duration. Furthermore, the ZnS:Mn²⁺ nanoparticles display robust mechanoluminescence, both when dispersed in a PDMS film and an aqueous solution under focused ultrasound excitation. This mechanoluminescence emission from the nanoparticles has potential applications in controlling neural stem cell activities. Moreover, the piezoelectric ZnS:Mn²⁺ nanoparticles demonstrate excellent performances in piezocatalytic dye degradation, effectively decomposing organic dyes like rhodamine B and methylene blue. The degradation process is attributed to the generation of reactive oxygen species from the combination of charge carriers and OH⁻. In the solution, a mechanism supported by Electron Spin Resonance (ESR) measurements. The introduction of h²⁺, hydroxyl radical, and superoxide radical scavengers into the reaction system significantly reduces the degradation rate, further substantiating the catalytic mechanism. Compared to undoped ZnS nanoparticles synthesized in a similar manner, ZnS:Mn²⁺ nanoparticles exhibit superior piezocatalytic performance due to defect-induced polarization. Intriguingly, both mechanoluminescence and piezocatalysis are contingent on the non-centrosymmetric wurtzite structure of ZnS and its associated defect-induced polarization, each showcasing different optimal dopant concentrations and operating under distinct ultrasound frequencies.

SESSION EN02.08: Thermal Energy Harvesting

Session Chairs: Yang Bai and Andris Sutka
Thursday, April 25, 2024
Room 332, Level 3, Summit

1:30 PM EN02.08.01
Soft-Matter Engineering for Thermoelectric Wearables with Unprecedented Power Generation
Younghoo Han and Mohammad H. Malakooti
University of Washington, United States

Stretchable thermoelectric generators (S-TEGs) have recently drawn attention since they can compliantly be attached to complex surfaces to induce temperature change or harvest electricity from waste heat. Unlike conventional thermoelectric modules that are rigid and brittle, flexible thermoelectric devices commonly comprise elastic polymers with encapsulated semiconductor pellets. This stretchable device architecture also provides conformal contact with curved surfaces such as the human body. We have designed multifunctional elastomer composites to enhance the heat management and deformability of these emerging TEGs. Our approach involves dispersing liquid metal droplets within elastomers to create liquid metal elastomer composites (LMECs). LMECs with microdroplets exhibit high thermal conductivity while remaining electrically insulating, serving as thermal interface materials in the devices. Additionally, we have embedded hollow thermoplastic microspheres in the base elastomer to synthesize soft matter with low thermal conductivity, which separates the top and bottom thermal interface layers and encapsulates the semiconductor pellets. The difference between the conductivity of the two elastomer composites facilitates a larger heat flux in thermoelectric semiconductors, leading to improved device performance. In this talk, we will begin with a brief overview of TEGs that utilize liquid metals and bismuth telluride semiconductors. Following this introduction, we will present our new findings on the design rationale of S-TEG, focusing on the improvement of energy harvesting performance at low-temperature gradients, along with enhancing mechanical resilience and stretchability. In particular, we will highlight the essential role of device structure in thermoelectric energy conversion, utilizing both numerical simulations and experimental analyses to illustrate our findings. The resulting S-TEG design is optimized for efficient thermal management, resulting in a notable power harvesting performance increase, exceeding baseline levels by more than sixfold. The electromechanical and energy harvesting characterization of this engineered S-TEG will be presented to showcase its full potential for a range of emerging applications. To conclude, we will explore the practical applications of these thermoelectric generators across various use cases.

1:45 PM EN02.08.02
Nanocomposite Ceramics Materials for Energy Harvesting and Heat Management
Zouhair Hanani, Brigita Rozic, Daoud Mezzane, Mimoun El Marsse3, Anna Morozovska, Serhiy Ivanchenko, Hana Uršič, Matjaz Spreitzer and Zdravko Kutnjak
University of Picardie Jules Verne, France; National Academy of Sciences of Ukraine, Ukraine


2:00 PM EN02.08.03
Soft Caloric Materials for Green Cooling Technologies
Dejvid Cresnar, Matic Morgan, Bostjan Zalar, Samo Kralj, Zdravko Kutnjak, Gregor Skacej and Brigita Rozic
1Jozef Stefan Institute, Slovenia; 2University Cadi Ayyad, Morocco; 3University of Picardie Jules Verne, France; 4National Academy of Sciences of Ukraine, Ukraine


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We are developing a wearable textile-based system that bypasses the intermediate electrical conversion step by directly converting heat harvested from the body to pneumatic energy using a low-boiling-point fluid (LBPF). Our system consists of two pouches—a “warm” and “cool” pouch, thermally insulated from one another—where heat emitted from the body vaporizes a LBPF in the warm pouch to drive pneumatic actuation. After that, the vapor phase of the LBPF is recovered via condensation in the cool pouch, which is exposed to the lower temperature of the ambient compared to that of the body. Following eventual depletion of the LBPF in the warm pouch after a number of actuation cycles, the device can be flipped, placing the now-fluid-filled cool pouch in contact with the user to continue to vaporize the LBPF in a repeatable manner.

To address these energy conversion limitations, mitigate portability concerns caused by tethers to external power sources, and appeal to a larger percentage of those with physical disabilities, we developed a wearable textile-based system that directly converts heat harvested from the body to pneumatic energy using a low-boiling-point fluid (LBPF). Our system consists of two pouches—a “warm” and “cool” pouch, thermally insulated from one another—where heat emitted from the body vaporizes a LBPF in the warm pouch to drive pneumatic actuation. After that, the vapor phase of the LBPF is recovered via condensation in the cool pouch, which is exposed to the lower temperature of the ambient compared to that of the body. Following eventual depletion of the LBPF in the warm pouch after a number of actuation cycles, the device can be flipped, placing the now-fluid-filled cool pouch in contact with the user to continue to vaporize the LBPF in a repeatable manner.

We characterized the system performance by modeling the transient pressure response, power output, efficiency, and life cycle of the device and compared modeling results with experiments, as well as with comparable thermal-to-electronic energy harvesting devices used in wearables in prior work. Our model uses fundamental thermodynamic and heat transfer principles to show how the frequency of operation and geometry of the device affect the overall system performance. We also demonstrated the practicality of this system with a user applying the device to pneumatically actuate an assistive actuator for grasping. This work enables the use of body heat as a viable power source for pneumatically actuated assistive devices that can be used to enhance mobility assistance.


Printed Triboelectric Nanogenerator Incorporating MXene-Enhanced PVBVA for Skin-Interactive Devices and Touch-Sensing Arrays 

In this work, we introduce a novel triboelectric nanogenerator (TENG) technology that utilizes poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVBVA) in combination with Ti3C2 MXenes, two-dimensional transition metal carbides etched from the Ti3AlC2 MAX phase ceramics. Inks from these materials are formulated for microdispense printing and printed onto aluminum substrates using a Hyrel extrusion printer. This combination significantly enhances the triboelectric properties of the manufactured TENG device.

Our findings show that the PVBVA layer alone yields a triboelectric output of approximately 110 V. However, with the introduction of MXene at a concentration of 2.75 mg/ml, the output escalates to 150 V, and further increases to 250 V at a concentration of 5.5 mg/ml, demonstrating a substantial enhancement in performance. Beyond energy harvesting, we leveraged this TENG technology in a water energy harvesting system, effectively extracting energy from sources such as raindrops. Additionally, we developed a 2 x 2 touch sensor array utilizing this technology. This sensor array can generate charge through the triboelectric effect and dynamically map the output voltage values in response to touch, showcasing its potential for human-machine interaction and touch-sensitive interfaces.

In summary, our research introduces a groundbreaking approach to TENG fabrication by combining 3D printing technology with a PVBVA-MXene composite. This leads to TENGs with markedly improved triboelectric performance. The versatility of these TENGs not only enables efficient energy harvesting from environmental sources like rain but also holds significant promise for applications in touch-sensitive devices. This makes them a valuable asset for developing self-powered devices and interactive interfaces in fields such as healthcare and robotics.


Solvothermal Synthesis of Ferrite Nanocrystals for Use as Magnetic Energy Storage Materials

In this work, we introduce a novel technique for synthesizing ferrite nanocrystals for use as magnetic energy storage materials. These materials are characterized by their ability to store and release electrical energy, making them ideal for a wide range of applications in the field of energy storage.

Electrochemical impedance spectroscopy (EIS) was used to investigate the electrical properties of the synthesized ferrite nanocrystals. The results indicate that these materials exhibit a high degree of reversibility and stability, making them suitable for repeated charging and discharging cycles.

Furthermore, we fabricated a prototype energy storage device using the synthesized ferrite nanocrystals. The device was tested under various conditions to evaluate its performance and durability. The results demonstrate that the device has a high energy density and good cycle life, making it a promising candidate for future energy storage applications.

Overall, the research presented in this study paves the way for the development of advanced magnetic energy storage materials with improved performance and lower environmental impact.
inside. Compared with inorganic dielectrics, polymer dielectrics from synthetic resins exhibit stable dielectric performance over a wide range of frequencies, superior high voltage endurance, excellent flexibility and processing properties. High-temperature resistance ability of polymer dielectrics is extremely important for the harsh operating environment with high temperature requirements. Nevertheless, most polymer dielectrics are more vulnerable to high temperatures due to their low glass transition temperature ($T_g$). The capacitive performance of polymer dielectrics degrades rapidly at high temperatures and electric fields, which is mainly attributed to the exponential increase of conduction loss. The increased leakage current further leads to an undesirable temperature rise inside the polymer dielectrics and consequently accelerates the thermal runaway of capacitors. Therefore, inhibiting the conduction loss of polymer dielectrics is extremely important for high-temperature capacitive performance.

The bulk-limited conduction and electrode-limited conduction are the two main mechanisms inside the polymer dielectrics. With increasing the electric field and temperature, more trapped charge carriers are thermally activated to overcome the potential barrier of traps, even though the carrier energy is lower than the maximum energy of the potential barrier, and participate in the electrical conduction. Therefore, the conduction loss inside polymer dielectrics displays an exponential growth with temperature under high electric field. Introducing more deep charge traps is beneficial to suppress the bulk-limited conduction. Incorporating a small amount of wide bandgap inorganic fillers or small organic molecules with strong electronegativity into the high-temperature resistant polymer dielectrics is an effective method to increase the density of deep traps and trap depth. These fillers can act as trap centers to immobilize the charge carriers and constrain their mobility inside polymer composites, accordingly leading to the reduction in conduction loss. As for the electrode-limited conduction loss, charge carriers from the electrode can gain sufficient energy provided by thermal activation to overcome the energy barrier at metal-dielectric interface and increase the conduction loss. Increasing the barrier height at the electrode/polymer interface is helpful for the suppression of electrode-limited conduction loss. Inserting a charge-blocking layer such as highly insulated inorganic and organic layers between the electrode and polymer dielectric can significantly increase the barrier height for the charge injection from the electrode.

From this, we unify the bulk and electrode-limited conduction losses and simultaneously suppress these two types of conduction loss through the surface engineering of polymer composites dielectrics. As the leakage current at high temperatures and electric fields is significantly inhibited, and the breakdown strength is greatly improved compared with the unmodified polymer dielectrics. Accordingly, the polymer composites dielectrics exhibit superior capacitive performance with high discharged energy density and discharge-charge efficiency at high temperatures.

5:00 PM EN02.09.05
Ultra-High Durability and Performance of a Proton Composite Membrane containing long-Chain Amino Sulfonated Poly(arylene ether) and Cerium Oxide-Titanium Carbide over 1000 Hours for Hydrogen Fuel Cells
Ae R. Kim, Milan B. Poudel and Ivypann Arunkumar; Jeonbuk National University, Korea (the Republic of)

As a key component of proton exchange membrane fuel cells (PEMFCs), the durability of the proton exchange membranes (PEMs) directly determines the service life of the PEMFCs. In this study, poly(arylene ether) containing amino and trifluoromethyl units (AFPAE) was synthesized by nucleophilic aromatic polycondensation followed by nucleophilic substitution to obtain butyl sulfonated poly(arylene)(SAFPAE). CeO2-TiC prepared by the hydrothermal process were incorporated into the SAFPAE matrix and the content of the CeO2-TiC was optimized. The morphological, physicochemical, and electrochemical investigation of the prepared membranes demonstrated that the random dispersion of the CeO2-TiC in the SAFPAE matrix improves the thermal and mechanical stability as well as water adsorption, ion exchange capacity and proton conductivity. Particularly, the optimized SAFPAE/CeO2-TiC exhibited high current output and power output at 20% relative humidity and 60 °C outperforming commercial membranes. Most importantly, the SAFPAE/CeO2-TiC composite membrane demonstrated MEA durability over 1100 h under low humidity 20% RH operating conditions and was about 4.4 times more stable than pristine SAFPAE. SAFPAE with a special structure of hydrophile backbone containing trifluoromethyl group and long aliphatic sulfonic acid group to create nano-sized proton conduction channels whereas, TiC provides mechanical support and CeO2 improves the durability of PEM by scavenging free radicals. Therefore, the SAFPAE/CeO2-TiC composite membrane reported in this study is a potential candidate for high-performance and durable PEMFC, suggesting its applicability in future large-scale PEMFC.

5:00 PM EN02.09.06
Synthesis Characterization and Electrochemical Evaluation of Quanternized Poly(2,6-dimethyl-1,4-phenylene oxide)/Ionic Liquid Composite Membrane for Anion Exchange Membrane Fuel Cell Application
Ramasamy Gokula priyam, Beom Ho Kim, Hyo Bin Kwak and Dong J. Yoo; Jeonbuk National University, Korea (the Republic of)

Quanternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO) serves as a polymer electrolyte membrane facilitating hydroxide ion conduction, whereas with limited hydroxide conductivity and certain physicochemical drawbacks. To address this, modifications are necessary to enhance its overall performance. Composite membranes of QPPO and an ionic liquid were fabricated using the solvent casting technique. The ionic liquid, which contains quaternized imidazole groups, enhances hydroxide transport pathways within the QPPO membrane. Varying weight % of the ionic liquid were incorporated into the QPPO membrane fabrication. The role of the ionic liquid in the QPPO membrane is to increase the bound water content and develop a hydrogen bonding network with the hydroxide ion transport channels, thereby increasing the hydroxide ion conductivity. Remarkably, the optimized 9%-8% composite membrane exhibits superior hydroxide ion conductivity compared to the QPPO membrane, achieving 135 mS cm⁻¹ at 90 °C, while the QPPO membrane reached 56 mS cm⁻¹ at the same temperature. Additionally, the QPPO/ionic liquid composite membranes exhibit appreciable water uptake, swelling ratio, thermal, and mechanical properties. In single-cell tests, the QL%-8% composite membrane achieves a maximum power density of 328 mW cm⁻² at 60 °C, under conditions of 70% humidity on the anode side, 100% humidity on the cathode side, and an H₂/O₂ flow rate of 100/200 ml min⁻¹. Overall, this study illustrates the enhancement of QPPO membrane performance through the incorporation of synthesized ionic liquids.

5:00 PM EN02.09.08
Machine Alignment Methods for Precision Roll-Forming of A5052 Aluminum Sheets: Achieving Smooth Finishes and Microstructure Evaluation
Krishna S. Bhandari; Jeju National University, Korea (the Republic of)

The roll-forming process stands as a crucial technique in shaping metal sheets across diverse industries, ranging from jewelry and aerospace to the automobile sector. Ongoing research endeavors center on achieving precision in shaping and minimizing defects, with a particular focus on challenges like spring-back—the tendency of a metal sheet to revert to its original shape post-formation. This scientific investigation has a dedicated purpose: to enhance the alignment of roll-forming machines, thereby ensuring the production of precise and smooth profiles. The study places special emphasis on a5052 aluminum sheets, a material prevalent in various industrial applications. Delving into the specifics, the research scrutinizes the intricacies of roll-forming a5052 aluminum sheets, providing a comprehensive examination of the associated challenges and opportunities. Beyond this, the study explores the integration of cutting-edge technologies to optimize the alignment and formability of roll-forming machines. These technologies encompass laser alignment, real-time feedback sensors, CNC systems for precise control, machine learning algorithms for adaptive processes, and finite element analysis for comprehensive simulation. The overarching objective is clear: to optimize both the alignment and formability of the roll-forming process, which will be used in sensor-making technology to additive manufacturing and nanomaterials. Through this, the research aims to contribute to the advancement of manufacturing techniques, ensuring the production of high-quality and accurately shaped metal profiles and materials across various industrial applications.

5:00 PM EN02.09.10
A Skin-Wearable Triboelectric Nanogenerator for Self-Powered Motion Monitoring and Energy Harvesting
Asha A. Jun, Seungbeom Kim, Jinhyung Kim, Sangeeop Lee, Uyeon Kim and Seok Kim; Pohang University of Science and Technology, Korea (the Republic of)

Self-powered and wearable pressure sensors based on triboelectric nanogenerators (TENGs) have gained attention as promising candidates for tactile sensing and energy harvesting because of their design capability and ability to operate at low frequencies. Much research work has focused on enhancing tribo-negative materials for flexible TENGs, the limited choices for tribo-positive materials have been a limiting factor. A crucial challenge in the development of wearable sensors is achieving biocompatibility without compromising broad-range sensitivity and energy-harvesting capabilities. Here we report a TENG based skin-wearable and self-powered pressure sensor by a simple fabrication using layer by layer deposition method. The flexible layered triboelectric nanogenerator (L-TENG) features a dielectric-to-dielectric configuration, with polytetrafluoroethylene (PTFE) and polymethyl methacrylate (PMMA) films serving as negative and positive triboelectric layers, respectively. These layers are sandwiched within a flexible and biocompatible polydimethylsiloxane (PDMS) matrix. A nanostructured PDMS surface obtained by oxygen plasma served as the structural backbone for the bottom indium tin oxide-copper electrode and overlying tribo-positive PMMA layer. The self-powered L-TENG sensor exhibited a broad bandwidth of 7.287 mV/pa for low pressure and 0.063 mV/Pa for high pressure. Additionally, the L-TENG sensor adeptly detected physiological motions such as wrist extension and flexion, and finger bending angles while efficiently harvesting wasted energy from routine physical activities like walking and jogging. Notably, the maximum peak-to-peak voltages of 18.3 V and 57.4 V were measured during these motions. The L-TENG holds vast potential in wearable technology, spanning applications in healthcare, human-machine interfaces, and the powering of microelectronics from physical activities.

Keywords: skin-wearable, self-powered, wearable pressure sensing, triboelectric nanogenerator (TENG), energy harvesting, human motion monitoring

5:00 PM EN02.09.11
Tribovoltaic Devices based on Sliding Contact TiO2 Films
Andris Sutka; Kaspars Malnicks; Peter C. Sherrell and Osvalds Verners; Riga Technical University, Latvia; 2 RMIT University, Australia
Surface Charge Effects: An Advantage for Enhancing The Piezoelectric Conversion Efficiency in GaN NWs

Nanotechnologies, France; 2Group of Electrical Engineering of Paris, France

atmosphere to coalesce crystallites and to selectively orient texture in the (00l) direction, improving the quality of devices. Additionally, different doping strategies have been investigated to
amines/diamines, followed by spin-coating and a short hot-plate annealing at 300 C. Then, different post-deposition treatments have been explored using a tubular furnace under chalcogen
results for Cu2ZnSnS4 and BaZrS3, but there is still little information regarding van der Waals materials with low-dimensionality.4,5
particular, thiol-amine solvent systems have recently demonstrated great potential to synthesize chalcogenide compounds (typically poorly soluble in polar solvents), producing promising
Molecular precursor ink deposition is an excellent approach for thin film synthesis, being a low-energy, low-cost and versatile method, allowing various compositional analysis by modifying
their possible post-treatment for modulating their surface trap density, to the fabrication and testing of piezoelectric nanogenerators, passing through the characterization of single NWs using nano-characterization tools based on atomic force microscope equipped with electrical modules. We experimentally highlight that the electromechanical coupling coefficient of GaN NWs is strongly affected by the expression of the SC. By finely adjusting the NW dimensions, we demonstrate that the SC effects can be advantageous for strongly improving the electromechanical conversion efficiency of GaN NWs up to 43%. We also establish that the piezoelectric response of the GaN NWs is sensitive to their direct environment. We confirm experimentally that the SC are useful for improving the piezo-conversion, and evidence that by properly engineering the GaN NWs surfaces, the piezoelectric response of the GaN NW-based nanogenerators can be enhanced. Finally, by architecting the nanogenerator design with regard to the deformation mode (direct compression or vibration) and the targeted application, we demonstrated generated power density in the µW−mW/cm² range in response to mechanical inputs miming the environmental ones (equivalent forces of few Newton in the 1-200 Hz frequency range).

8:30 AM *EN02.10.01
Surface Charge Effects: An Advantage for Enhancing The Piezoelectric Conversion Efficiency in GaN NWs

Noelle Gogneau 1, Pascal Chretien 2, Amaury Chevillard 1, Tanbir Kaur Sodhi 1,2, Szu-wei Chen 1, Laurent Couraud 1, Laurent Travers 1, Jean-Christophe Harmand 1, Francois Julien 1, Maria Tchemnycheva 1 and Frederic Houze 2; 1Group of Electrical Engineering of Paris, France, 2Center for Nanosciences and Nanotechnologies, France;

For powering micro-devices with strong dimension constraints (smaller than 1 cm² or 1 cm³), it is crucial to develop ultra-compact piezoelectric nanogenerators characterized with a high conversion efficiency per surface/volume unit. To reach this objective, we must both improve the electromechanical conversion efficiency of the active material and optimize the generator design to maximize the piezoelectric system performances in response to the environmental mechanical and vibration inputs. 1D-nanodevices have emerged as system of interest for developing ultra-compact piezoelectric generators. This interest lies in their quasi-lattice perfection and large surface-to-volume ratio, which confer to NWs larger degree of elastic deformation without mechanical deterioration and higher sensitivity to applied forces in comparison with their 2D-film counterparts and conventional bulk piezoelectric materials. In addition, sub-100 nm-wide NWs present the particularity to exhibit specific properties that can lead to a strong modulation of their characteristics. Among these “new properties”, we can cite the exfoliation of the piezoelectric materials, the formation of nano-contact at the NW/electrode interface allowing an enhanced energy harvesting, or the modulation of the free carrier concentration due to the surface charge (SC) effects. Regarding this last property, simulations have recently established that these SC effects can be advantageous for improving the piezoelectric response of the NWs, since they can limit, in given conditions, the screening by the free carriers of the piezoelectric charges. Since the expression of the SC effects depends on the NW dimensions and on the NW environment (in other terms of the soft matrix embedding them into nanogenerator devices), the in-depth understanding of the relationship between the SC effects and the piezoelectric conversion capacities of the NWs is now a prerequisite for further improving the device performances and thus approaching a future technological transfer.

To investigate the SC effects in sub-100 nm-wide GaN NWs, we use a system-wide multi-scale analysis going from the growth of the GaN NWs by plasma-assisted Molecular beam epitaxy and their possible post-treatment for modulating their surface trap density, to the fabrication and testing of piezoelectric nanogenerators, passing through the characterization of single NWs using nano-characterization tools based on atomic force microscope equipped with electrical modules. We experimentally highlight that the electromechanical coupling coefficient of GaN NWs is strongly affected by the expression of the SC. By finely adjusting the NW dimensions, we demonstrate that the SC effects can be advantageous for strongly improving the electromechanical conversion efficiency of GaN NWs up to 43%. We also establish that the piezoelectric response of the GaN NWs is sensitive to their direct environment. We confirm experimentally that the SC are useful for improving the piezo-conversion, and evidence that by properly engineering the GaN NWs surfaces, the piezoelectric response of the GaN NW-based nanogenerators can be enhanced. Finally, by architecting the nanogenerator design with regard to the deformation mode (direct compression or vibration) and the targeted application, we demonstrated generated power density in the µW−mW/cm² range in response to mechanical inputs miming the environmental ones (equivalent forces of few Newton in the 1-200 Hz frequency range).

9:00 AM *EN02.10.02
Versatile Thiol-Amine Chemistry for The Synthesis of Complex Chalcogenides and Chalcohalides: New Opportunities to Develop Earth-Abundant Materials for Energy Applications

Ivan Caño Prades 1, David Rovira Ferrer 1, Maykel Jimenez Guerra 2, Jonathan Turnley 2, Marcel Placidí 1, Joaquim Puigdollers 1, Rakesh Agrawal 2 and Edgardo Saucedo 1;
1Universitat Politècnica de Catalunya, Spain; 2Purdue University, United States

Earth-abundant chalcogenides and chalcohalides are garnering substantial attention as innovative semiconductors compatible with solar energy harvesting, thermoelectric, pyroelectric applications and other optoelectronic technologies.1 Among them, van der Waals materials possess an anisotropic crystal structure resulting from covalently-bonded ribbons along one crystallographic direction, which leads to unique electrical properties (e.g enhanced carrier transport) when the material is correctly oriented. Among recent successes Sb2(S,Se)3 solar cells have achieved efficiencies above 10%, and SbSX (X=I,Br) micro-scale devices have been synthesized for the first time showing excellent optoelectronic properties2. However, although the synthesis techniques used so far have enabled significant progress, it is necessary to explore manufacturing routes that are more cost-effective, scalable and versatile in terms of composition and chemical doping.

Molecular precursor ink deposition is an excellent approach for thin film synthesis, being a low-energy, low-cost and versatile method, allowing various compositional analysis by modifying the stoichiometry of the precursor solutions, its integration into distinctive scalable deposition methods (including roll-to-roll coating), and deposition on flexible and non-planar substrates. In particular, thiol-amine solvent systems have recently demonstrated great potential to synthesize chalcogenide compounds (typically poorly soluble in polar solvents), producing promising results for Cu2ZnSnS4 and BaZrS3, but there is still little information regarding van der Waals materials with low-dimensionality.3,4

In this work, Sb2Se3, Sb2S3 and Sb(S,Se)3 thin films have been synthesized by dissolving either the chalcogenide itself or the constituent elements into different mixtures of ethanediol and amines/amines, followed by spin-coating and a short hot-plate annealing at 300 C. Then, different post-deposition treatments have been explored using a tubular furnace under chalcogen atmosphere to coalesce crystallites and to selectively orient texture in the (00l) direction, improving the quality of devices. Additionally, different doping strategies have been investigated to tune the conductive type and carrier concentration. For n-type doping, Sb2Se3 samples have been prepared incorporating NH4Cl and SbCl3 to the precursor solution (Cl-doping). On the other hand, p-type doping strategies have been investigated through Sn-doping and synthesis of Se-rich samples, resulting in an increase of the Voc of photovoltaic devices. Structural, compositional and electronic characterization have been performed by X-ray diffraction, microscopy, X-ray and UV photoelectron spectroscopy (determination of valence band and Fermi level), Seebeck coefficient and JV measurements.

Additionally, the universality of the thiol-amine solvent for chalcogenides will be discussed, presenting its successful implementation for synthesis on other systems, including emerging chalcohalide materials (e.g. SnS,SnSe) and Ag-based anti-perovskites (Ag2S). The latter has a cubic structure analogous to standard perovskite (switching anions by cations and vice-versa), bandgap around 1 eV, and shows superior behavior above room temperature. Overall, this work demonstrates the viability of thiol-amine solvents to synthesize a broad range of cutting-edge complex chalcogenide materials, allowing composition and doping control, and opening the door to explore new properties for energy harvesting applications.

9:15 AM *EN02.10.03
Self-Assemblies of Piezoelectric Metabolites and Their Energy Harvesting Applications

Rusen Yang; Xi’an University, China

Piezoelectric metabolite materials have received increasing attention in recent years owing to their inherent biological nature and efficient energy conversion capability, and piezoelectric
The triboelectric effect is as old as the hills, and the first reported effects of electrification date back to Thales of Millet in 600 BC. However, it was only in the 17th century that experimental evidence of triboelectricity was found, and in the next century that electrostatic generators began to appear, their benefits not being exploited until much later. Triboelectric generators for energy harvesting are a very recent development, not even 15 years old. The advent of these generators and their popularity stem from the work of Prof. Zhong Lin Wang and his team at the Georgia Institute of Technology. They develop triboelectric nanogenerators (TENGs). Paying attention with the ‘nanogenerator’ term, which should not be taken to mean a nanometer-sized generator, but a generator that generally includes nanomaterials within it. More generally today, TENG is the established term for triboelectric generators dedicated to energy harvesting, even if nanomaterials are not present. While the basic concept of triboelectricity is well established, with positive and negative charges separating when two materials rub or make contact, many questions remain. This separation of charges is not necessarily two-sided (i.e. negative charges on one material and positive charges on the other), and research has shown the co-presence of positive and negative charges on the same surface after contact. Generally, electron transfer is involved, but sometimes also ion transfer, as well as material transfer when surfaces come into contact: in some situations, it’s a point of debate. Likewise, the development of nanocomposites raises another question regarding the ranking of these new materials in the classification of the triboelectric series. Some studies show that preconditioning of materials can promote or conversely reduce triboelectricity: is there a sound strategy for implementing this route? As far as the basic operating modes for developing TENGs are concerned, there are several approaches: vertical contact-separation, sliding, free-standing, single electrode… Should one mode be favored over another in terms of expected performance if application requirements do not dictate it? How is performance in terms of energy harvested or produced truly calculated or estimated, and how can performance be easily compared between TENGs?

Through an abundant panorama of works from the literature on TENGs and their approaches, we will attempt to shed light on some of these questions, and to highlight the advantages, difficulties and cautions to be taken in the announced promises in the actual use of these generators for energy harvesting. We will also present our research work on TENGs through the development of a test bench dedicated to the precise characterization of these materials in sliding mode, as well as a consolidated theoretical study enabling us to evaluate performance on resistive or capacitive loads. This theoretical study also led to a proposal for optimal TENG operation, which we then validated experimentally.
Organic Solar Cells: Concepts towards The Single Junction Limit and Beyond

11:00 AM *EN04.01.04
Degradation Mechanisms in Highly Efficient Organic Solar Cells Based on Non-Fullerene Acceptors Klaus Meerholz, Univ of Cologne, Germany

During recent years, organic solar cells composed of different donor-acceptor-type polymers and non-fullerene acceptors (NFA) have approached and even exceeded the 20% hurdle. However, still questions remain regarding their long-term stability, i.e. the degradation processes involved.

Here, we present a comprehensive study on ca. 10 different NFAs and try to derive structure/property relations regarding their chemical stability / degradation mechanism, respectively. Experiments include the 1) analysis of the chemical stability of the NFAs themselves by mass spectrometry, 2) electrochemical stability tests of the radical anions ("electrons"), 3) solar cell devices based on PCE-12 and the NFAs, respectively, as prepared ones as well as aged by accelerated life-time testing, and 4) chemical analysis of the degradation products.

11:30 AM *EN04.08.02
Interfacial Engineering in Organic Solar Cells Huajiong Zhou, National Center for Nanoscience and Technology, China

Solution-processed organic solar cells (OSCs) have attracted much attention due to their low cost, flexibility and high transparency. Recently, the power conversion efficiency (PCE) of OSCs is approaching 20%. However, the unsatisfied interface issues limit further improvement in PCEs and stability of OSCs, through affecting the physical processes such as exciton separation and/or charge transport/extraction/recombination in the device. Our recent study on interface engineering in OSCs has shown that the introduction of new electron transporting materials could enhance the PCE and suppress the photodegradation at the cathode interface, achieving over 10000 hours of storage and thermal stability in OSCs. An original strategy for selecting an optimal interfacial layer based on the surface energy has been proposed, to optimize the morphology of the active layers by regulating the surface energy and its microscopic distribution of the interface layer. At the end, we have constructed semi-transparent devices by utilizing optical microcavities, achieving high uniformity of device transmission and controllable adjustment of reflection color, which offers a viable design strategy for semi-transparent OSCs toward applications in next-generation smart photovoltaic windows.

2:00 PM *EN04.02.02
Critically Assessing The Potential and Challenges of Machine Learning for Designing Organic Photovoltaic Devices Martin Seifried, North Carolina State University, United States

Due to the complexity of designing organic semiconducting materials (OSCs) and devices, researchers have long used computational tools to screen candidate molecular structures and gain further insight into physical processes. Machine learning (ML) is emerging as a powerful tool for accelerating this even further. While processing conditions are known to play a significant role in determining PCE, ML has so far only been used to predict the power conversion efficiency (PCE) of organic photovoltaics (OPV) from molecular structure alone.

In this talk, I will discuss how we can integrate device fabrication data into ML models, as well as best practices of ML for OPV. One of the key challenges of gathering such datasets is the difficulty of extracting data from the literature. We have created the first dataset containing both molecular structure and device processing conditions. We find sobering evidence of the low quality of such data, which is particularly important if we seek to use ML to accelerate the development of OPVs and OSCs. Many are aware of the widespread problem of the low quality of literature data, which affects numerous fields and is not discussed openly enough. The question for the future of ML and meta-analyses based on datasets derived from the literature becomes: what do we do going forward?
Delocalisation in Device-Scale Drift-Diffusion Models

In organic semiconductors, even small amounts of delocalisation can considerably enhance charge and exciton transport as well as charge separation. We recently developed delocalised kinetic Monte Carlo (dKMC), the first computational method able to describe the motion of partially delocalised charges [1] and excitons [2] in organic semiconductors on mesoscopic time and length scales, while considering the critical influence of energetic disorder, quantum-mechanical couplings, and polaron formation. dKMC has revealed new, basic physics of transport in organic semiconductors and can explain why mobilities predicted by traditional kinetic Monte Carlo are usually too low, showing that delocalisation over just a few molecules can increase mobilities by orders of magnitude [1,2]. Similarly, applying dKMC to the two-body problem of charge separation reveals a decisive enhancement of internal quantum efficiency (IQE) from a small amount of delocalisation [3,4].

In this talk, I will show that the benefits of delocalisation—first identified on the mesoscopic scale—also improve performance on the macroscopic, device scale. To do so, we have parametrised drift-diffusion models using dKMC to arrive at the first delocalisation-aware device models.

Our parametrisation relies on several new computational approaches. The first is jumping kinetic Monte Carlo (jKMC), a model that approaches the accuracy of dKMC, but with a computational cost comparable to conventional KMC [5,6]. Rates entering jKMC are simple modifications of ordinary Marcus hopping and can be used to include delocalisation effects in any existing KMC code. The low computational cost of jKMC also allows us to carry out the first calculations of all remaining parameters necessary for drift-diffusion models, which could not be computed by full quantum techniques. These include steady-state mobilities, generation rates, and carrier recombination rates, processes that we show are also significantly affected by even modest delocalisation.

Putting all the ingredients together, our delocalised drift-diffusion code [7] can compute JV curves while faithfully capturing charge and exciton delocalisation. The results confirm the importance of delocalisation in device performance and help explain recent high-performance blends that defy explanation using classical models.

Diodes (LEDs). Many of these applications require low-temperature deposition of ITO thin film. But it remains a challenge to achieve satisfactory electrical conductivity and optical

Indium tin oxide (ITO) has been widely used as a transparent electrode in various applications including solar cells, liquid crystal displays, plasma displays, smart windows, and light emitting
devices (LEDs). ITO is a two-dimensional (2D) material with a direct bandgap of approximately 3.6 eV. It is a promising material for optoelectronic devices due to its high carrier mobility, good optical
transparency, and stability. However, the synthesis of high-quality ITO thin films is a challenging task because of the high temperature required for the deposition process, which can lead to the oxidation of the ITO layer, resulting in a decrease in transparency and a shift in the optical bandgap.

The recent successes of emerging photovoltaics are largely driven by innovations in material science. However, closing the gap to commercialization still requires significant innovation to match contradicting requirements such as performance, longevity and recyclability. In this contribution, we suggest a layout of a Digital Twin for PV materials able to provide the necessary acceleration of innovation.

The rationale of the Digital Twin is to bridge the gap between first principles calculations, currently not able to predict the crucial solid state properties for emerging PV materials, and high
throughput experimentation, currently not able to provide datasets of the necessary scale needed to train generative artificial intelligence (AI) models. The crucial aspect of our layout is feature extraction, that is, identifying and retaining only the relevant and non-redundant information present in a dataset. This allows designing fast proxy experiments and surrogate models across all relevant scales. We will learn more from faster and simpler experiments, and the resulting massive (but cheaply acquired) dataset will allow building better approximate models for solid state structure from chemical structure, closing the gap for molecular inverse design, that is, from a set of desired properties all the way back to molecular structure.

Our proposed layout of the Digital Twin combines machine learning approaches, as performed in materials acceleration platforms (MAPs), with physical models and digital twin concepts used in engineering. This layout will allow using high-throughput (HT) experimentation in MAPs to improve the parameterization of quantum chemical and solid-state models. In turn, the improved and generalized models can be used to obtain the crucial structural parameters. HT experimentation will thus yield a detailed understanding of generally valid structure-property relationships. Most importantly, and different from black-box AI approaches, our physics-aware approach can benefit from human abstract thinking, increasing the chance for breakthrough innovation.

Building a Digital Twin in PV materials is viable. We show that some of the necessary building blocks are already available, doing useful work today. Finally, we identify promising approaches for the open challenges such as fast scale-bridging surrogate models and large scale optimization under uncertainty.

The Photocurrent in Organic Solar Cells does not Vanish at Open-Circuit

Our results imply that OPVs are truly far-from-equilibrium systems, which opens realistic prospects to mitigate the thermalisation losses and eventually beat the near-equilibrium thermodynamic limit [2]. In fact, the results presented show that even regular OPVs are Hot-Carrier Solar Cells in the sense that excess energy contributes to output power. The question of whether charge transport in operational organic solar cells (OSC) occurs far-from-equilibrium or not is of significant practical and fundamental importance. While the equilibrium picture of the OSC assumes that the photogenerated charge carriers quickly lose their energy and attain lattice temperature, kinetic Monte Carlo (kMC) simulations of OSC have consistently shown that photogenerated charge carriers are extracted before reaching thermal equilibrium energy: the population thermalizes, albeit to an effective temperature that exceeds that of the lattice [1].

Probing the distribution of photogenerated charges possessing this excess energy has proven to be notoriously hard. In this work, we use Johnson thermometry to measure the temperature of the photogenerated carriers carried out by cross-correlated current noise spectroscopy. Two representative material systems, P3HT:PCBM and PM6:Y6, are tested against their inorganic counterparts, silicon. The experiments univocally prove, in stark contrast to silicon photovoltaics, that charges in operational OSC are not thermalised and are almost twice as hot as the lattice.

The experimental findings are confirmed by kMC simulations. The simulations show that the energetic disorder in organic semiconductors is not only the reason for slow thermalisation but also due to incomplete relaxation in a disordered density of states—provide better agreement, yet with at times uncommon ramifications: here, we will show that a non-negligible photogenerated current under open-circuit conditions is a general feature of OSCs.

In more detail, we have investigated the internal quantum efficiency of photogenerated charges in non-fullerene acceptor OSCs in the steady state. Therefore, we have first measured their external quantum efficiency spectrum under different experimental conditions, including a constant background illumination. Utilizing a small signal light source, modulated at low frequencies, and varying the working conditions from reverse (collection) to forward (injection regime) fields, allowed us to determine how efficient photogenerated charges can be extracted at any point on the current-voltage-curve. We find that while the yield decreases towards open-circuit, it does not vanish completely and some 10–20% of the short circuit yield remains; therefore, the resulting photocurrent has to be compensated by charge injection in order to reach zero net current. In a subsequent step, we were able to reproduce these experimental findings with kinetic Monte-Carlo device simulations involving non-equilibrium dynamics with decoupled photo- and injection currents.

How ‘Hot’ are the Charges in OPV? Privata M. Vitis, Constantin Tormann, Clemens Goeehler, Dorothea Scheunemann and Martijn Kemеринк; Universität Heidelberg, Germany


Effects of Deposition Angle on The Thin Film Quality of Indium Tin Oxide Grown by Magnetron Sputtering

Indium tin oxide (ITO) has been widely used as a transparent electrode in various applications including solar cells, liquid crystal displays, plasma displays, smart windows, and light emitting diodes (LEDs). Many of these applications require low-temperature deposition of ITO thin film. But it remains a challenge to achieve satisfactory electrical conductivity and optical transmittance at low deposition temperatures. This work proves that the sputtering deposition angle has significant effects on the ITO film microstructure and properties. The ITO thin films are grown by a unique single beam ion source enhanced magnetron sputtering. The sputtering and ion beam directions relative to the substrate surface are varied from 30 to 90 degrees and the film

References


SESSION EN04.04: Poster Session
Session Chair: Oskar Sandberg
Tuesday Afternoon, April 23, 2024
Flex Hall C, Level 2, Summit

Effets of Deposition Angle on The Thin Film Quality of Indium Tin Oxide Grown by Magnetron Sputtering Tabitha Amoled1,2 and Qi H. Fan1; 1Michigan State University, United States; 2Egerton University, Kenya

Indium tin oxide (ITO) has been widely used as a transparent electrode in various applications including solar cells, liquid crystal displays, plasma displays, smart windows, and light emitting diodes (LEDs). Many of these applications require low-temperature deposition of ITO thin film. But it remains a challenge to achieve satisfactory electrical conductivity and optical transmittance at low deposition temperatures. This work proves that the sputtering deposition angle has significant effects on the ITO film microstructure and properties. The ITO thin films are grown by a unique single beam ion source enhanced magnetron sputtering. The sputtering and ion beam directions relative to the substrate surface are varied from 30 to 90 degrees and the film

References


Polymer solar cells (PSCs) employing a bulk heterojunction structure exhibit a significant potential as energy sources for advanced portable electronic devices due to their low weight, scalable roll-to-roll (R2R) processing, and cost-effectiveness. Recent advances in the design of high-performance photoactive materials and device optimization, have resulted in a remarkable increase in the power conversion efficiency (PCE) of PSCs, surpassing 19%. Recently, the P6M copolymer has been widely used in the photoactive layers of PSCs due to its high crystallinity, superior hole mobility, and strong pre-aggregation behavior. However, achieving high-performance PSCs based on the P6M polymer normally requires the use of halogenated solvents such as chloroform and chlorobenzene. Unfortunately, the use of these halogenated solvents is limited in mass production because of environmental toxicity concerns. Furthermore, due to the strong temperature-dependence aggregation property of the P6M polymer, PM6-based large-area PSCs fabricated using large-scale coating methods exhibit a significant reduction in PCE. For example, PM6-based small-area (0.12 cm²) PSCs exhibit a PCE of 15.1%. However, the PCE of PM6-based large-area (54.5 cm²) PSC submodules can be significantly reduced to 8.73%. This decrease in performance of PM6-based large-area PSCs in nonhalogenated systems can be attributed to the oversized domains and nonuniformity in the photoactive layer, leading to an increased cell-to-module (CTM) loss. The undesirable morphology of the PM6-based photoactive layer can be controlled using a high-temperature (HT) process such as a hot solution or preheated substrates. However, such a complicated process is unsuitable for the production of cost-effective and highly reproducible R2K PSC modules. Therefore, it is necessary to develop new p-type polymers for high-performance large-area PSC modules based on simple processes and minimize the CTM loss in nonhalogenated systems. Terpolymers composed of three different monomers have recently attracted attention as promising p-type polymer. Terpolymers can accurately control photophysical properties, such as frontier energy levels, light harvesting ability, pre-aggregation behavior, miscibility, and crystallinity, by introducing a third component directly into the donor-acceptor (D-A) copolymer backbone. 

Herein, we synthesize a new series of 1D/2R terpolymers for fabricating room-temperature (RT) and nonhalogenated solvent processed high-performance PSC submodules. The terpolymers are composed of three components: benzo[1,2-b:4,5-b']dithiophene (BDT-F), thiieno[3,4-c]pyrrole-4,6(S)-dione (TPT-D), and benzo[1,2-c:4,5-c']dithiophene-4,8-dione (BDI). Three PBTPTBD terpolymers (i.e. PBTPTBD-25, PBTPTBD-50, and PBTPTBD-75) are synthesized using different ratios TPT-D to BDI compositions, corresponding to TPT-D contents of 25%, 50%, and 75%, respectively. The composition ratio of TPT-D to BDI and TDD components can be used to control the light harvesting ability, energy level, molecular ordering, and charge transport properties of the PBTPTBD polymers. A grazing incidence wide-angle X-ray scattering and contact angle analysis shows that the PBTPTBD-75:BTP-C11 blended film exhibits a promotion dominant face-on orientation with good miscibility. The RT and nonhalogenated solvent processed PBTPTBD-75:BTP-C11 PSC exhibit a high PCE of 15.55%. Furthermore, PBTPTBD-75:BTP-C11-based PSC submodules, processed with o-xylene under RT conditions, achieve a notable PCE of 11.57% over a 55 cm² active area. This PCE value is among the highest reported in single-junction PSC submodules processed with nonhalogenated solvent.
OSC
t with the inverted n-p structure are considered more suitable for commercialization compared to those with conventional p-i-n structure, due to the superior stability of the materials used. However, the highest efficiencies (above 17% to 20%) are currently achieved exclusively using the conventional structure. In fact, efficiencies above 17% from OSCs with the inverted structure are scarcely reported, mainly due to the low values of fill factor (FF) which characterize devices in this configuration. Electron and hole transport layers play a crucial role in determining the performance of OSCs. Therefore, a proper selection of them is essential to achieve higher efficiency in OSCs with inverted structure and to close the gap with devices with conventional structure.

Transparent conductive oxides are usually employed as electron transport layers (ETLs) in OSCs with inverted structure. Among them, zinc oxide (ZnO) is the most studied and adopted, since it provides a good band alignment with the organic semiconductors and it can be easily deposited from solution. Tin oxide (SnO2) represents a valid alternative to ZnO as ETL, offering superior transparency to the visible light and higher electron mobility. Moreover, unlike ZnO, SnO2 is reported to have an excellent ambient stability and to not cause any photocatalytic degradation of the organic materials [1].

A broad use of SnO2 as ETL in OSCs is currently hindered by the difficulty in fabricating films of the material with low defect density. SnO2 films for OSCs are often obtained from solution processing, starting from nanoparticle colloidal dispersions, with the result of a high defect density, especially on the surface. Moreover, organic ligands, used to stabilize the nanoparticle dispersions, often leave residuals in the deposited film, which can compromise the interface with the active layer. As a result, the overall performance of OSCs with SnO2 as ETL is often poor, with in particular low values of FF [2].

In this work, highly efficient OSCs with inverted structure are demonstrated by using as ETL SnO2 deposited by atomic layer deposition (ALD). ALD is an industrial grade technique which can be applied at the wafer level and also in a roll-to-roll configuration. ALD allows obtaining compact layers of SnO2 with exceptional quality and low defect density. SnO2 fabricated by ALD already attracted attention in the research field of photovoltaics, for perovskite [3] and tandem solar cells [4]. Nonetheless, its use in OSCs is scarcely reported and its potential not yet fully exploited. By using ALD to deposit the SnO2 ETL, we fabricated OSCs with PM6:LB-BO active layer, reaching a champion efficiency of 17.26% and a record FF of 79%. The devices fabricated outperform not only solar cells using SnO2 nanoparticles casted from solution (PCE 16.03%, FF 74%) but also those utilizing the more common ZnO (PCE 16.84%, FF 77%).

Furthermore, the OSCs with ALD SnO2 show a higher stability under illumination in comparison with those utilizing ZnO. The outstanding results achieved are demonstrated to arise from a superior quality of the interface between the ALD SnO2 film and the active layer and, thus, from a reduced charge carrier recombination [5].


5:00 PM EN04.04.09
Anisotropic Nature of Vibronic Coupling, Singlet Fission and Triple Transport of Single Crystalline Acenes (n=4-6) Yi Rao; Department of Chemistry and Biochemistry, Utah State University, United States

The escalating global energy predicament implores for a revolutionary resolution—one that converts sunlight into electricity—holding the key to supreme conversion efficiency. We embark on the exploration of the principle of generating multiple excitons per absorbed photon, a captivating concept that possesses the potential to redefine the fundamental confines of conversion efficiency, albeit its application remains limited in photovoltaic devices. At the nucleus of this phenomenon are two principal processes: multiple exciton generation (MEG) within quantum-confined environments, and singlet fission (SF) inside molecular crystals. The process of SF, characterized by the cleavage of a single photogenerated singlet exciton into two triplet excitons, holds promise to potentially amplify photon-to-electron conversion efficiency twofold, thereby laying the groundwork to challenge the detailed balance limit of solar cell efficiency. Our discourse primarily dissects the complex nature of SF in crystalline organic semiconductors, laying special emphasis on the anisotropic behavior of SF and the diffusion of the subsequent triplet excitons in single-crystalline polycrystalline organic semiconductors. We initiate this journey of discovery by elucidating the principles of MEG and SF, tracing their historical genesis, and scrutinizing the anisotropy of SF and the impact of quantum decoherence within the purview of functional mode electron transfer theory. We present an overview of prominent techniques deployed in investigating anisotropic SF in organic semiconductors, including femtosecond transient absorption microscopy and imaging as well as stimulated Raman scattering microscopies, and highlight recent breakthroughs linked with the anisotropic dimensions of Davydov splitting, Herzberg-Teller effects, SF, and triplet transport operations in single-crystalline polycyanines. Through this comprehensive analysis, our objective is to interweave the fundamental principles of anisotropic SF and triplet transport with the current frontiers of scientific discovery, providing inspiration and facilitating future ventures to harness the anisotropic attributes of organic semiconductor crystals in the design of pioneering photovoltaic and photonic devices.

5:00 PM EN04.04.10
Probing Nanomorphology of Guest Component in Ternary OPVs Tanner M. Melody, Acacia Patterson and Brian A. Collins; Washington State University, United States

Recent advancements in organic photovoltaics (OPV) solar technology show that with the inclusion of a third guest component to the traditional binary devices, efficiencies can surpass 20% which are comparable or even above competing technologies. The addition of ternary components contribute to increasingly complex nanomorphologies that most characterization techniques cannot determine. Our objective is to identify these key nanostructures that maximize the ternary advantage. First, we characterize the thermodynamic mixing of donor and acceptor molecules in phase-separated equilibrium states via surface energy measurements combined with the blend demixing experiments we have previously demonstrated using spectral X-ray microscopy. We then determine the dominant paradigm ternary morphology that enhances performance using traditional GIWAXS in conjunction with chemical sensitive nanoprobes such as spectrally resolved RSoXS analysis and STXM directly on high performance active layers. Uncovering the morphological pathways that these ternary components provoke will allow us to inflect the fabrication process of these devices to maximize the ternary advantage for commercially viable, high-performance OPVs.

SESSION EN04.07: Device Physics II—Exciton and Charge Carrier Dynamics
Session Chairs: Tayebeh Ameri and Thomas Anthopoulos
Thursday Morning, April 25, 2024
Room 328, Level 3, Summit

8:30 AM *EN04.07.01
Charge Generation in Neat Non-Fullerene Acceptor Domains Kaila Yallum and Natalie Hanriot; University of Bern, Switzerland

Non-fullerene acceptors (NFAs) are exciting molecules allowing high efficiency in organic photovoltaic (OPV) blends with conjugated polymers. Interestingly, changes can also be generated by neat NFA films without additional donor. To understand the origins of exciton dissociation in neat NFAs, we have looked at the impact of aggregation, external electric field end non-linear effects. We used solvatochromism in order to gain insight on charge redistribution after excitation in isolated NFAs. We found that aggregated NFAs feature a more dipolar excited state, owing to their low charge carrier mobilities, the competition between extraction and recombination of photogenerated charge carriers is an important factor limiting the performance of organic solar cells. This competition is further complicated by the inevitable presence of contact-induced dark carriers in the device. In this work, we clarify the effect of contact-induced dark charge carriers on photovoltaic device performance through theoretical device simulations. We find that first-order recombination between photogenerated carriers and contact-induced dark carriers is the dominant bimolecular recombination channel limiting charge collection in state-of-the-art organic solar cells. Furthermore, analytical models for the current-voltage characteristics are
The performance of organic solar cells has made large strides with power conversion efficiencies exceeding 19%, and the milestone of 20% well within sight. The emergence of non-fullerene acceptors has been critical for the process of free charge generation and the origin of performance limiting loss pathways has been a subject of debate. More specifically, the critical role of low energetic offsets in non-fullerene based OPVs does not lead to any increase in activation energy barriers for charge transport in the CT state across multiple polymer/non-fullerene acceptor blends and understanding the uniqueness of the Y6 acceptor due to its large dipole moment change upon photoexcitation.

10:00 AM BREAK

10:30 AM EN04.07.05

Elucidating The Performance Impeding Role of Exciton Dissociation in Low Offset Nonfullerene Acceptor-Based Solar Cells Angshuk Dhara,1 Manasi Pranav1, Bowen Sun,2 Rong Wang2, Larry Lüer2, Christoph J. Brabec2, Naoyuki Ishii3,4 and Dieter Neher1; 1University of Potsdam, Germany; 2Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

The performance of organic solar cells has made large strides with power conversion efficiencies exceeding 19%, and the milestone of 20% well within sight. The emergence of non-fullerene acceptors (NFAs) has played a vital role in these advancements. Particularly, organic blends comprising of NFAs with polymeric donors (D) have low energetic offset between the ionization energies ($\Delta I_D$) of the two components have demonstrated excellent photovoltaic performance with superior charge generation yields in conjunction with reduced voltage losses. However, the process of free charge generation and the origin of performance limiting loss pathways has been a subject of debate. More specifically, the critical role of low $\Delta I_D$ on the voltage losses and charge-generation efficiencies ask for a more detailed analysis. In this work, we systematically explore the role of energetic offset through methodical assessment of free charge generation process in a sample set of Y-series acceptors (Y6 and Y5) with well known polymeric donor, PM6. Herein, the PM6:Y5 material system is found to have a relatively lower energetic offset as compared to high performing system PM6:Y6. Our sample set uses the NFAs Y5 and Y6 blended with different molecular weights of the polymer donor PM6, spanning a large PCE range from 15% to 10%. This poor photovoltaic performance is further accompanied with pronounced field-dependence of free charge generation as demonstrated via time delayed collection field (TDCF) measurements. Using transient absorption spectroscopy (TAS), we find that the poor performing PM6:Y5 material system suffers from inefficient charge transfer at the interface, ultimately limiting the overall photovoltaic performance of Y5 based blends. We highlight the significance of driving force through field-dependent TAS measurements by demonstrating concomitant increment in free charge generation and exciton dissociation yields under the application of external electric field. These results supported with bias-dependent steady-state and transient photoluminescence studies provides a holistic view of the overall process and propounds that poor exciton dissociation is one of the main performance limiting channel in materials systems with diminishing energetic offset.

References.

10:45 AM EN04.07.06

Activationless Charge Transfer Governs Photocurrent Generation in Organic Photovoltaic Blends Yifan Dong,1 Deqing Qian,2 Helen Bristow3, Tack Ho Lee4, Hyojung Cha5 and James Durrant1,6; 1Imperial College London, United Kingdom; 2Fudan University, Shanghai, China; 3King Abdullah University of Science and Technology, Saudi Arabia; 4Pusan National University, Korea (the Republic of); 5Kyungpook National University, Korea (the Republic of); 6Swansea University, United Kingdom

Organic photovoltaics (OPVs) have recently shown substantive progress in device efficiency, driven in particular by advances in non-fullerene acceptor design and suppression of energy offsets between exciton (S1) and charge-transfer (CT) states. Ultrafast charge transfer (< 200 fs) from polymer donors to fullerene acceptors has often been observed and attributed to the origin of efficient photocurrent generation in polymer/fullerene blends. While efficient charge photogeneration has also been observed in polymer:non-fullerene OPVs, several studies have reported much slower CT rates on the order of tens of ps. As suggested in Marcus theory, higher activation energy barriers could be the origin of slower CT rates. However, it remains unclear whether the suppressed S1-CT offset and/or the hybridisation/thermal equilibrium between S1 and CT states would lead to higher barriers for charge generation and hinder charge transfer in such small-offset OPV blend systems. Herein, utilizing temperature-dependent transient absorption spectroscopy for a range of polymer:non-fullerene and polymer:fullerene OPV blends, we elucidate that the activation energy for charge generation is below 15 meV, implying that activationless charge generation pathway governs photocurrent generation in archetypal polymer based OPVs including the highly efficient low-offset PM6:Y6 blend. Suppression of the energy offsets in non-fullerene based OPVs does not lead to any increase in activation energy barriers for charge separation. While activation is chargeless, bimolecular recombination of charges proceeds with a high activation barrier of several hundreds of meV. Efficient charge photogeneration is universal among the blends studied herein and is not a limiting factor for device performance, while the geminate and/or non-geminate recombination losses appear to be the limiting factors.

11:00 AM EN04.07.07

Origin of Electric Field Dependence of Charge Generation in Organic Photovoltaics with Planar and Bulk Heterojunctions Kwohee Nakano, Yumiko Kaji and Keisuke Tajima; RIKEN CEMS, Japan
Efficient, electric-field independent charge generation in the photo-electron conversion process in organic photovoltaics (OPVs) leads to high short-circuit current ($J_{sc}$) and fill factor (FF).

However, the origin of the electric-field dependent charge generation in OPVs is still unclear. In this study, we fabricated bulk- and planar-heterojunction (BHJ and PHJ) type OPVs with the same donor (PM6) and acceptor (Y6) materials and investigated their charge generation process. The state energies of the singlet excited ($S_1$) and charge transfer (CT) states were experimentally quantified. In addition, the molecular orientation was determined by variable angle spectroscopic ellipsometry (VASE).

The charge generation process in the BHJ is electric-field independent, while that in the PHJ is strongly electric-field dependent. The state energy offset between $S_1$ and CT states in the PHJ is 70 meV smaller than that in the BHJ, indicating that insufficient energy offset is one of the origins of the electric-field dependent charge generation in the PHJ. We also fabricated the PHJ with acceptors exhibiting different molecular orientations to figure out the effect of the relative molecular orientation between the acceptor and the donor domain on the charge generation process. We observed that the acceptor with face-on orientation to the donor domain showed field-dependent generation, whereas that with end-on (the direction of the end edge of the molecular long axis) oriented one had field-independent generation. The results suggest that the energy difference between $S_1$ and CT states and the molecular orientation in the BHJ film must be considered to realize high-performance OPV devices.

11:15 AM *EN04.07.08

Triplet Excitons in Organic Solar Cells

Alexander Gillett; University Of Cambridge, United Kingdom

Driven by the development of non-fullerene electron acceptor materials, the performance of organic solar cells (OSCs) has recently shown a remarkable improvement, with power conversion efficiencies nearly doubling from 11% to 19% in less than 10 years. However, the efficiency of OSCs is still lower than inorganic technologies, where efficiencies of >20% are commonplace. This is primarily due to excessive non-radiative recombination in OSCs, which reduces the open circuit voltage from the radiative limit.

In our work, we have identified recombination via low energy triplet excitons as a key factor responsible for the large non-radiative losses in OSCs. In state-of-the-art systems, such as ‘PM6:Y6’, up to 90% of the charge carrier recombination proceeds via triplet exciton states; this reduces the open circuit voltage by up to 60 mV. To address this issue, we propose two viable strategies. First, through the identification of systems where recombination via triplet excitons is suppressed, we demonstrate that significant hybridisation of the molecular triplet exciton and triplet charge transfer state can disfavour terminal recombination into the former. Second, we show that triplet-triplet annihilation has the potential to mitigate against triplet exciton losses by recycling up to half of these states back formed into singlet excitons, providing an opportunity for radiative recombination to occur. For this, our findings provide a framework to alleviate non-radiative losses via triplet excitons in OSCs, which could push efficiencies towards and beyond the 20% milestone.
Metal-oxide transport layers have become an essential building block for fabricating thin-film solar cells. In particular, the robustness, inert nature, easy processability from solution, and high-specific NiOX structural surface defects that are limiting the charge extraction, and we propose a passivation strategy using carbazole-based self-assembly monolayers (SAMs). We demonstrate organic solar cells1,2. Nevertheless, the inherent formation of surface traps during the fabrication process, originating either from structural defects or from ligand residuals, can influence the stability to maintain up to approx. 30% of the Rainbow multi-junction further up.

Here, we study the charge generation and voltage loss characteristics of a series of well-defined PHJs (including IT-4F/PM6 and Y6/PM6) produced by a polymer film transfer method4 as well as high photocurrents through tuning the acceptor layer to the exciton diffusion length.


**4:30 PM EN04.08.08**

A Modified NiOx Layer for Robust and Photostable Organic Solar Cells

David Garcia Romero, Lorenzo Di Mario, Feng Yan, Carolina M. Ibarra Barreiro, Suhas Mutalik, Loredana Protesescu, Petra Rudolf and Maria Antonietta Loi; University of Groningen, Netherlands

Metal-oxide transport layers have become an essential building block for fabricating thin-film solar cells. In particular, the robustness, inert nature, easy processability from solution, and high-carrier mobilities offered by several both n-type, such as SnO₂ or ZnO, and p-type, like NiOx or MoO₃, have made them promising candidates for improving performance and scaling up organic solar cells1,2. Nevertheless, the inherent formation of surface traps during the fabrication process, originating either from structural defects or from ligand residuals, can influence negatively the solar cell characteristics and device stability, and ultimately make them fail to become a standard transport layer.

Here, we have studied independently two different systems: firstly an n-p-i structure using SnO₂ as the bottom n-type layer and, secondly, a p-i-n structure with a bottom NiOₓ as the p-type layer. In both cases, commercially available well-known colloidal inks were employed. For the first case, s-shaped 3-V curves and poor device stability evidenced the suboptimal interface quality with SnO₂. We identified the presence of potassium ions as stabilizing ligands, staying on the film surface as trap sites. By removing them with a simple washing with deionized water, we remove the s-shape and improve the device efficiency from 12.82% to 16.26% and the stability to maintain up to 87% after 100 hours3.

In the second case, a low VOC is found when NiOₓ is used as the hole transport layer with the same active layer. Through the combination of multiple spectroscopic methods, we pinpoint the specific NiOₓ structural surface defects that are limiting the charge extraction, and we propose a passivation strategy using carbazole-based self-assembly monolayers (SAMs). We demonstrate the passivation mechanism and we generalize it by screening out several SAMs. After all the optimization, solar cells with around 18% of power conversion efficiency are demonstrated.


**SESSION EN04.09: Active Layer Composition and Morphology**

**Session Chairs: Xinhui Lu and Tao Wang**

Friday Morning, April 26, 2024

Room 328, Level 3, Summit

8:30 AM | EN04.09.01

**Combined Dynamics and Nanostructure Analyses for Paths that Maximize NFA Solar Cell Performance**

Brian A. Collins; Washington State University, United States

Organic solar cells stand on the precipice of ≈20% efficiencies and large-scale commercialization. Unfortunately, constrictive processing options and a lack of direct connections between nanostructure, device dynamics, and performance hold back the promise of this exciting technology. I will describe our efforts in combining device-relevant loss analyses with quantitative nanostructure characterization to reveal key considerations in maximizing device performance. In particular, one barrier to scalability is runaway crystallinity of NFA solar cells where slight fluctuations in additive concentrations compromise even lab-scale devices. We find that expanding processing toward non-halogenated additives both halt runaway crystallinity and work toward less-toxic manufacturing. However, only a detailed connection between the new morphology and device dynamics can reveal the opportunities for further improvements. Applying these processing and measurement strategies will be critical to understanding and mastering new materials breakthroughs that launch the technology toward a new solar future.

9:00 AM | EN04.09.02

**Multicomponent Blend Strategy for Enhanced Performance and Longevity in Organic Photovoltaics**

Taseebh Amer1,2; 1Kiel University, Germany; 2University of Edinburgh, United Kingdom

Organic photovoltaics have made remarkable progress in recent years, achieving power conversion efficiencies of over 19% in laboratory-scale devices, marking a significant step towards their commercial viability. This advancement can be attributed to the integration of non-fullerene acceptor materials and the adoption of the multicomponent ternary blend approach within the organic photovoltaics field. However, the organic photovoltaic community, focused on enhancing the power conversion efficiency, has previously overlooked the critical aspects of lifetime and stability issues for more than a decade. Recent efforts have focused on addressing these concerns, with numerous studies conducted to comprehend the degradation mechanisms and improve the overall longevity of organic photovoltaics.

This presentation will delve into the development of the ternary blend approach, which has not only elevated the power conversion efficiency but also enhanced the open circuit voltage and fill...
Understanding The Crystalline and Amorphous Morphology of Organic Solar Cells using Grazing-Incidence X-Ray and Neutron Scattering Techniques

While (push-pull) semiconducting polymers are now displaying better device performances than ever before, their commercial uptake remains limited, in part due to challenges in terms of reproducibility. Next to consistent device fabrication, continuous material quality is of high importance to obtain optimal and reliable performance metrics. Often the assumption is made that the “drawn” chemical structure is representative of the active material used in applications such as polymer-based solar cells. It has, however, become clear that this is not always the case. In this work, we assess the structures of two top-performing organic solar cell donor polymers, PM6 and D18, both for commercial and synthesized samples.

Structurally Pure and Reproducible Polymer Materials for High-Performance Organic Solar Cells – Insights in the Chemical Structures of PM6 and D18 Sander Smeets1,2, Jochen Vandervoskikken1,2, Guan Liu1, Tyler Quill1, Sam Gielen1, Laurence Lutsen1,2, Koen Vandewal1,2 and Wouter Maes1,2; 1Hasselt University, Belgium; 2IMEC, Belgium; 3Stanford University, United States

Organic photovoltaic materials or polymers typically form semicrystalline thin films. It is widely recognized that the bulk heterojunction (BHJ) morphology of organic photovoltaic thin films, which consists of both crystalline and amorphous regions, plays a crucial role in determining the performance of devices. However, understanding the intricate three-dimensional multi-length scale morphology of these thin films remains a grand challenge.

In this talk, we present our recent progress on decoding the complex BHJ morphology of OPVs and developing strategies to control the morphology to enhance device performance. In addition to employing conventional techniques like GIXS/GIWAAXS, we will introduce two innovative methods: GTSAXS, which allows for the quantification of vertical nanomorphology, and GISANS combined with deuteration, a technique used to detect amorphous phase structures. Armed with these state-of-the-art scattering techniques, we investigated the optimal active layer morphology for OPVs, aiming at understanding the impacts of amorphous and crystalline phase structures on device performance and to advance the practical applications of these devices. Furthermore, these scattering techniques can also be applied in material science, chemistry, biology and condensed matter physics studies.

Evidence for Entropy-Driven Charge Separation in Non-Fullerene Acceptor/Polymer Bulk Heterojunction Kushal Rijal1, Neno N. Fuller2, Fatimah H. Rudayni1,2 and Wai-Lun Chan3; 1University of Kansas, United States; 2Jazan University, Saudi Arabia

Organic photovoltaics (OPVs) based on non-fullerene acceptors (NFAs) have achieved power conversion efficiencies close to 20%. These NFA OPVs can efficiently generate free carriers at the donor/acceptor (D/A) interface despite a very small energy level offset. However, why efficient charge separation can occur with a minimal energy loss is still not clear. We will present our recent time-resolved two-photon photoemission (TR-TPPE) spectroscopy measurements on exciton dynamics in a representative NFA-polymer blend, the Y6/PMe bulk heterojunction (BHJ).

We find that charge transfer (CT) excitons are formed within a few picoseconds after the photoexcitation. Subsequently, an energy uphill process occurs in which the energy of the CT exciton is increased by 0.15 eV on the 10-100 ps timescale. We attribute this energy uphill process to the conversion of bound CT excitons to free electron-hole pairs. The observed energy uphill process is rather anomalous because excited electrons typically lose their energy to the environment when no external electric field is applied. We propose that the energy uphill charge separation process is driven by entropy. The entropy-driven charge separation would be promoted by the specific nanostructure of NFA BHJs. This work is based upon work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Award No DE-SC00024525.

Evidence for Entropy-Driven Charge Separation in Non-Fullerene Acceptor/Polymer Bulk Heterojunction Session Chair: Keisuke Tajima Friday Morning, April 26, 2024 Room 328, Level 3, Summit

Study on The Network Formation Mechanism of The Photoactive Domains in Organic Photovoltaics Jingang Kim1, Yepin Zhao1 and Yang Yang1,2; 1University of California, Los Angeles, United States; 2California NanoSystems Institute, University of California, Los Angeles, United States

Organic photovoltaics (OPVs) have emerged as a promising technology for clean energy generation, characterized by their cost-effectiveness, solution processability, and high transparency. In recent years, there has been a spike in power conversion efficiency of all-polymer solar cells using blends of the common donor polymer PBD-T and PM6 with two acceptor polymers, namely P3NT-BDT and P3NT-BDF. These compounds function as macroscopic absorbers with large optical cross-sections extending to around 900 nm due to their π-extended naphthalene rings. Combining data from steady-state optical spectroscopy and time-resolved photoluminescence, transient absorption, electron spin resonance, and time-delayed collection field experiments provides not only a concise but also quantitative assessment of the losses due to limited photon absorption, geminate and non-geminate charge carrier recombination, field-dependent charge generation, and inefficient carrier extraction. Kinetic parameters obtained by pulsed laser spectroscopy are used to reproduce the experimentally-measured device W characteristics and indicate that low fill factors originate either from non-geminate recombination competing with charge extraction or from a pronounced field dependence of charge generation, depending on the donor polymer. The methodology presented here is generic and can be used to quantify the loss processes in BHJ OSCs, including both all-polymer and small-molecule NFA systems.

Interface Energy Level Offset of Organic Solar Cells Measured by UPS and IPEES and Its Correlation with Voc and CT Exciton Energy Gyuhyoon Lee1, Younghwan Kim1, Min-Jae University of Science and Technology, Saudi Arabia

For some fundamental reasons, the performance of all-polymer solar cells is behind the state-of-the-art in small molecule non-fullerene acceptor bulk heterojunction organic solar cells. This work investigates the efficiency-limiting processes in all-polymer solar cells using blends of the common donor polymer PBD-T and PM6 with two acceptor polymers, namely P3NT-BDT and P3NT-BDF. These compounds function as macroscopic absorbers with large optical cross-sections extending to around 900 nm due to their π-extended naphthalene rings. Combining data from steady-state optical spectroscopy and time-resolved photoluminescence, transient absorption, electron spin resonance, and time-delayed collection field experiments provides not only a concise but also quantitative assessment of the losses due to limited photon absorption, geminate and non-geminate charge carrier recombination, field-dependent charge generation, and inefficient carrier extraction. Kinetic parameters obtained by pulsed laser spectroscopy are used to reproduce the experimentally-measured device W characteristics and indicate that low fill factors originate either from non-geminate recombination competing with charge extraction or from a pronounced field dependence of charge generation, depending on the donor polymer. The methodology presented here is generic and can be used to quantify the loss processes in BHJ OSCs, including both all-polymer and small-molecule NFA systems.
In organic light-emitting diodes (OLEDs) and heterojunction organic solar cells (OSCs), the energy offset between HOMO and LUMO, also called the transport gap ($E_T$), is substantially different from optical gaps due to the relatively large exciton binding energies. However, the inability to independently measure the LUMO levels makes it hard to elucidate important things like electron injection barrier at the cathode in OLEDs and the voltage loss mechanisms in Voc of OSCs.

We have recently developed highly sensitive inverse photoemission spectroscopy (IPES) instrument specifically for the LUMO level measurement of organic semiconductors. In combination with the existing ultraviolet photoemission spectroscopy (UPS) we determined all the relevant transport energy levels (HOMO, LUMO, Fermi level and vacuum level) in any organic semiconductor surface and interface. In addition, combination of the electron source for IPES and the electron energy analyzer for UPS allowed us to utilize reflection electron energy loss spectroscopy (REELS) to determine the gaps. We first demonstrate that all these measurements can be performed for an identical sample as a function of thickness. We also determine the energy levels at both C60/pentacene and C60/CuPc interfaces so that the factors affecting the voltage losses that led to observed Voc value of the model planar heterojunction organic solar cells can be evaluated.

In addition, we fabricated bilayer model organic solar cells using C60/pentacene and C60/CuPc pairs. The deposition sequence of each layer was alternated resulting in four different types of devices, namely, C60/pentacene, pentacene/C60, C60/CuPc, and CuPc/C60. We confirmed that their exists interfacial energy offset difference between C60/pentacene and pentacene/C60 devices, which is also reflected in Voc values of respective devices. This is due to the difference in molecular orientation for pentacene depending on the deposition sequence in this binary system. On the other hand, we could not observe any dependence of Voc on deposition sequence of C60 and CuPc devices nor could we measure any energy offset at the interface, where the molecular orientation is expected to be independent of deposition sequence. We further investigate the charge transfer (CT) exciton energies for all the devices by using sensitive external quantum efficiency (EQE) measurement. These combined measurements led us to identify the most important parameter in determining the Voc of these model bilayer organic solar cells.

This work was supported by Korea Basic Science Institute (National Research Facilities and Equipment Center) grant funded by the Ministry of Education (2021R1A6C101A437) and National Research Foundation of Korea (NRF) BRL program grant funded by the Korean government (MSIT) (2022R1A4A3030766).

**SYMPOSIUM EN05**
Light-driven CO2 reduction into chemicals is considered as a promising way to meet carbon neutral targets. Photoelectrochemical (PEC) CO2 reduction has attracted significant attention as a prevailing way to store intermittent solar energy in fuels and chemicals as well as closing the chemical carbon cycle. Unfortunately, thermodynamically viable photocathode materials for this process favor hydrogen evolution reaction (HER), thus leading to either insufficient activity or selectivity for CO2 reduction reaction (CO2RR). Besides the thermodynamic requirement, the semiconductor/electrolyte interface also plays a pivotal role in defining the performance of photocathodes, which can directly affect light driven CO2RR efficiency and determine the product selectivity. Here, we show few examples of how light absorbent materials can be used in integrated photoelectrochemical cells or when directly interfaced with the electrolyte for CO2RR. Specifically, we show how one can improve the stability and performance of photoelectrodes for PEC CO2R in systems that use Cu2O or halide perovskite materials. In addition, we will discuss how ZnTe can enable photo-generated charge carrier transfer, but also acted as electrocatalyst for boosting carbon product selectivity and suppressing HER. Our work demonstrates that the fundamental understanding of the processes at the photoelectrode/electrolyte interface allows the systematic improvement of photoelectrode stability of CO2RR selectivity.

**Molecular-Derived Coatings Improve The Selectivity and Durability of CO2 Reduction on Chalcogenide Photocathodes**

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**Molecular-Derived Coatings Improve The Selectivity and Durability of CO2 Reduction on Chalcogenide Photocathodes**

Kevin Kan1, Nicholas Watkins1, Jonas Peters1, Theodor Agapie1, Christopher Muzzillo2 and Andriy Zakutayev2; 1California Institute of Technology, United States; 2National Renewable Energy Laboratory, United States

Direct solar-driven conversion of carbon dioxide to chemicals and fuels requires identification of efficient, durable, and selective photocathodes. Chalcogenide p-type semiconductors, exemplified by chalcopyrite Cu(In,Ga)Se2 (CIGS), have been effectively deployed as photocathodes. However, selectivity toward CO2 reduction and durability of the commonly used CdS buffer layer remain unsolved challenges. We have demonstrated that for the wide band gap CuGa3Se5 chalcopyrite absorber these challenges are well addressed by an organic coating generated in situ from a N,N′-(1,4-phenylene)bispyridinium ditriflate salt in the electrolyte. The molecular additive provides a 30-fold increase in selectivity toward CO2R products compared to the unmodified system and lowers Cd corrosion at least 10-fold. This dual functionality highlights the promise of hybrid solid-state-molecular photocathodes for enabling durable and efficient solar fuel systems. This presentation will highlight the variations in product selectivity and durability observed for different combinations of coatings derived from molecular precursors in the electrolyte with photocathodes including CuGa2S4 and Cu(In,Ga)2S4, with and without CdS buffer layers.

**References**

Defect-Passivated Perovskite Photoanode coupled with Iodide Oxidation Reaction enabling Efficient Stable Unbiased Hydrogen Production

Jiyoung Yun, Young Sun Park, Hyungsoo Lee, Wooyong Jeong, Chang-Seop Jeong, Gyuimin Jung, Chan Uk Lee, Jeongyoub Lee, Subin Moon, Soobin Lee and Jooho Moon; Yonsei University, Korea (the Republic of)

Defect-passivated perovskite photoanode coupled with iodide oxidation reaction enabling efficient stable unbiased hydrogen production

Jiyoung Yun, Young Sun Park, Hyungsoo Lee, Wooyong Jeong, Chang-Seop Jeong, Chan Uk Lee, Jeongyoub Lee, Subin Moon, Soobin Lee, Sumin Kim, Junhwan Kim, and Jooho Moon*

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The unassisted photoelectrochemical (PEC) hydrogen production is one of the promising candidates to replace the carbon-based energy sources. However, the previously reported photoanodes have suffered from low efficiency resulting from poor light absorption and limited charge separation capability. Lead halide perovskite has emerged as a promising breakthrough to overcome the limitations of conventional photoanode materials (such as BiVO₄, Fe₂O₃, Ta₃N₅, SnO₂, and WO₃) owing to its tunable bandgaps, excellent hole mobility, and long hole-diffusion length. These superior properties enable perovskite-based photoanode to achieve remarkable high-performance parameters including a photovoltage of ~1.1 V and a photocurrent density of around 200 mA/cm².
m2 cm−2. However, there are still challenges in achieving competitive hydrogen production, particularly in terms of onset potential and long-term stability. The poor onset potential can be attributed to the high thermodynamic potential (1.23 V with respect to reversible hydrogen electrode (VRHE)) required for the oxygen evolution reaction (OER) and the sluggish kinetics of OER involving a four-electron transfer process. Moreover, the charge accumulation due to interfacial defects and slow charge transfer reaction result in efficiency loss and photocathode degradation.

Herein, we report a straightforward strategy to improve the onset potential and durability of perovskite photocathode. This approach involves simple defect passivation method by decorating 4-methoxyphenethylamine on electron transport layer (ETL) effectively suppressing efficiency loss and charge accumulation at ETL/perovskite interface. Furthermore, we replace the OER with the iodide oxidation reaction (IOR) by employing an active IOR catalyst (Co0.2Ni3S2) to enhance the kinetics of charge transfer reaction. The combined effects of interface engineering and the IOR catalyst are manifested by the enhanced PEC performance and stability. The perovskite photocathode reveals a -0.2 VRHE onset potential and improved fill factor along with a high durability for 200 h. We additionally demonstrate unbiased hydrogen production consisting of single perovskite photocathode and Pt catalyst achieving the operation current of 12 mA cm−2 and stable operation for 24 h.

2:15 PM EN05.02.03
A Polymer Overlayer Generates Long-Lived Charges in PM6:Y6 Bulk-Heterojunction Photoanodes with Improved Photoelectrocatalytic Performance Tack Ho Lee; Pusan National University, Korea (the Republic of)

Photogenerating charges with long lifetimes to drive catalysis is challenging in organic semiconductors. Here, we investigate the role of a PM6 polymer overlayer on the photoexcited carrier dynamics in a PM6:Y6 bulk-heterojunction (BHJ) photoanode undergoing ascorbic acid oxidation. With the additional polymer layer, the hole lifetime is increased in the solid state BHJ film. When the photoanode is electrically coupled to a hydrogen-evolving platinum cathode, remarkably long-lived hole polarons are observed on the timescale of seconds under operational conditions. We demonstrate that these long-lived holes enable the organic photoanode with the polymer overlayer to show enhanced ascorbic acid oxidation performance, reaching ~7 mA cm−2 at 1.23 VRHE without a co-catalyst. An external quantum efficiency of 18% was observed using 850 nm excitation. We propose that the use of an organic overlayer can be an effective design strategy for generating longer charge carrier lifetimes in organic photoanodes for efficient oxidation catalysis.

2:30 PM EN05.02.04

Conversion of solar energy into hydrogen by photoelectrochemical water splitting is an emerging technology with large potential for sustainable green hydrogen generation. However, reaching the combination of high performance, stable and inexpensive photoelectrodes remains a scientific challenge. Solution-processable perovskite and organic photoactive materials have shown remarkable efficiency in solar cells, and they are extremely promising candidates for photoelectrochemical devices, but their application so far has been limited by their instability in aqueous media. In this presentation, we will show both perovskite and organic photoanodes applying NiFeOOH-functionalized self-adhesive graphite sheet, providing a simple, cost-effective approach to prevent degradation by the aqueous environment and eliminate almost all electrical losses between the photoactive layer and the water oxidation-catalyst.

The all-inorganic perovskite photoelectrodes incorporate solely Earth-abundant materials and apply a low annealing temperature carbon paste with tuned energy level CsPbBr3 photoactive layer. Controlling the perovskite phase by a facile chemical bath method allows to achieve a pure 3D CsPbBr3 layer with 8.1 mA cm−2 photocurrent density at +1.23 VRHE (close to the radiative efficiency limit of CsPbBr3) with record perovskite photocathode stability: 100% of stabilized photocurrent density maintained for more than 100 h. Devices with >1 cm2 area, and low-temperature processing will also be demonstrated.1 We will also discuss our most recent results towards reaching bias-free water splitting with these CsPbBr3 photoanodes by applying high porosity electrospun top electrode layers.

The polymer-non-fullerene acceptor containing organic (PM6:D18:L8-BO) photoanodes achieve breakthrough photocurrent densities over 25 mA cm−2 at +1.23 VRHE and remarkable, days-long operational stability. We will discuss strategies of how the continuous operation of the organic photoanode could be extended even further. Finally, polymer-polymer photoelectrodes, as well as monolithic organic tandem photoanodes (i.e., two photoactive layers integrated into one photoanode to generate high photovoltage) with exceptionally low, negative onset potential and bias-free water splitting in two-electrode setup with solar-to-hydrogen efficiency reaching 5% will also be presented.

References:

2:45 PM EN05.02.05
Organic Semiconductor-BiVO4 Tandems for Solar-Driven H2O and CO2 Splitting Celine W. Yeung,1 Virgil Andrei,1,1, Tack Ho Lee2,3, James Durrant2 and Erwin Reisner1; 1University of Cambridge, United Kingdom; 2Imperial College London, United Kingdom; 3Pusan National University, Korea (the Republic of)

Photoelectrochemical (PEC) devices offer great promise for simultaneous solar light harvesting and chemical storage, converting water and CO2 into value-added products.1 While progress has been made to improve their solar-to-fuel conversion efficiencies, most conventional inorganic prototypes face challenges in terms of insufficient photovoltage, moisture instability, high material cost or toxicity.2,3 In this work, we introduce PEC devices based on an organic n-conjugated donor acceptor bulk heterojunction, protected by a carbon-based encapsulant to produce green H2 and the platform chemical CO. By rationally combining design strategies from both organic photovoltaic and PEC fields, the photoanodes achieve long-term H2 production over 300 h, which is tenfold higher than reported systems. Further interfacing the devices with a molecular CO2 reduction catalyst allow for tunable and selective CO production under 0.1 sun. The combined light absorption of these photoanodes with BiVO4 enable their assembly into a standalone artificial leaf, demonstrating unbiased concurrent CO2 reduction and water oxidation over 96 h. This establishes a new path for organic semiconductors, as we approach the composition, function, and efficiency of natural leaves.

References:

3:00 PM BREAK

SESSION EN05.03: Oxides and Oxide Perovskites
Session Chairs: Robert Hoye and Katarzyna Sokol
Monday Afternoon, April 22, 2024
Room 335, Level 3, Summit

3:30 PM EN05.03.01
Linking Defect Chemistry to Photo- and Electrochemical Performance Ludmilla Steier; University of Oxford, United Kingdom
Doping or alloying strategies are heavily employed in the design of new catalysts for photoelectrochemical, photochemical and electrochemical conversion reactions with enhanced solar energy harvesting efficiencies and/or desired surface chemistry. In the electrochemical reduction of CO₂ for example, efforts are focused on the development of electrocatalysts with high activity and selectivity towards C₂H₄ products ideally breaking the scaling relations currently observed for metal surfaces. In photoelectrochemical and photocatalytic devices research has focused on developing catalysts with light harvesting in the visible, strong surface electric fields and long charge carrier lifetimes. In both, electro- and photocatalytic systems, perovskite oxides have been employed heavily, offering a more versatile defect chemistry platform. Here, I will showcase some of our studies on oxide perovskite materials employed in photo- and electrocatalysis discussing links between defect chemistry and catalytic performance. One example will be the visible light absorber (La,Sr)Ru,TiO₂ employed in the Z-scheme photocatalyst sheet device from Profs. Wang and Domen which led to a record 1% solar-to-hydrogen efficiency. Taking inspiration from this material, we have been investigating the performance of other dopants and compositions in photo- and electrocatalytic conversion of CO₂ leading us to look very closely into the material surface compositions and the ways of reporting of catalytic activity.


4:00 PM EN05.03.02
**Ti₃C₂Tₓ MXene as Effective Conductive Material for Enhancing the Activity of Cu-Doped TiO₂ Nanotube Photocatalysts – Application in Photooxidation and in H₂ Production**

Gilles D. Berhault, Ziba Roostaei, Frédéric Dappoza and Chantal Guillard; CNRS, France

Photocatalysis is one of the most promising approaches for photon energy conversion and environmental remediation. In this respect, TiO₂ is the most used semiconductor due to its high photocatalytic response. However, TiO₂ also presents a high propensity for electron-hole recombination. To solve this issue, several options were found to limit recombination: cationic doping, change of the semiconductor morphology or addition of C allotropes. Previous studies performed in our group have shown that 1D TiO₂ nanotubes can help in enhancing the separation of electron-hole pairs resulting in higher photooxidation while doping by copper allows increasing the response under visible light. Another option is to add a conductive material which can enhance the transport of photoelectrons from TiO₂ to Cu. Previous work performed using graphene oxide showed the validity of this approach but also the instability of this material under irradiation. An alternative solution is to use the emerging class of MXene compounds which were found to exhibit very high conductivity. The objective of this work will then be to synthesize Cu/Ti₃C₂Tₓ/TiO₂ systems in which the Ti₃C₂Tₓ MXene will be evaluated for its propensity in enhancing the transport of photoelectrons, improving in this way the separation of electron-hole pairs. Comparison will be performed between 1D TiO₂ nanotubes and a P25 reference while Cu/Ti₃C₂Tₓ/TiO₂ will be applied for both photooxidation (formic acid photodegradation) and for H₂ production.

**Materials and Methods**

Ti₃C₂Tₓ MXene layers were obtained by HF etching of Ti₃AlC₂ MAX precursors to remove Al. TiO₂ nanotubes were obtained under hydrothermal alkaline conditions. Two series of impregnation were performed: first, GO or MXene were impregnated onto P25 or TiO₂ nanotubes while Cu(NO₃)₂·3H₂O was then impregnated onto the resulting materials.

**Results and Discussion**

Systematic comparisons between P25 and nanotubes were done during the construction of various Cu/TiO₂, MXene/TiO₂ and Cu/MXene/TiO₂ configurations. Results emphasized the important role played by surface oxygen vacancies in the enhancement of the photooxidation activity. While the addition of Cu onto P25 induces the creation of new oxygen vacancies onto P25 improving its photooxidation efficiency, on TiO₂ nanotubes, copper interacts mainly through the consumption of these surface oxygen vacancies initially present on the titanium oxide surface. Beneficial effects were the observed only at low Cu loadings. Photocurrent analysis also emphasized the strong increase in conductivity resulting from the addition of Ti₃C₂Tₓ. This high conductivity enhancement leads to a substantial increase of the photocatalytic response in photooxidation with an activity of Cu/Ti₃C₂Tₓ/P25 150 % higher than for P25 and 50 % higher than for Cu/P25 while the highest activity was reached using Cu/Ti₃C₂Tₓ/TiO₂ nanotubes. In H₂ production, surface oxygen vacancies play a more indirect role since their consumption through copper addition favors a higher Cu-Ti interaction and a better transfer of electrons from TiO₂ to Cu. This leads to very active Cu/TiO₂ nanotube systems for H₂ production. Surprisingly, the addition of Ti₃C₂Tₓ leads to an apparent lower H₂ evolution activity. H₂ chemisorption analysis reveals in fact that Ti₃C₂Tₓ plays the role of an excellent trap for the hydrogen produced which is then stored inside our materials revealing in this way the ability for H₂ storage of Ti₃C₂Tₓ MXene.

**Conclusion**

The utilization of Ti₃C₂Tₓ MXenes as conductive materials enhancing the transport of photoelectrons from a semiconductor, TiO₂ to an electron acceptor, Cu has been demonstrated in photooxidation. Results also emphasized the important role played by surface oxygen vacancies while Ti₃C₂Tₓ MXene was found to present quite interesting properties as H₂ storage material.

4:15 PM EN05.03.03
**Ceria and Metal Ferrite Core-Shell Nanoparticle for Solar Thermochemical Fuel Production**

Ziyao Wu, Aniket S. Patankar, Ahmed Ghoniem, Xiaoyu Wu, Wonjae Choi and Harry Tuller; 1 Massachusetts Institute of Technology, United States; 2 University of Waterloo, Canada; 3 Ewha Womans University, Korea (the Republic of)

Two-step metal oxide-based Solar Thermochemical Hydrogen Production (STCH) is an emerging technology that directly utilizes high-temperature heat to split water and carbon dioxide, producing hydrogen and carbon monoxide, respectively. Using heat can be a more cost-effective source than electricity, particularly for high-capacity factors and continuous fuel production. However, to achieve ambitious targets like the US DOE HydrogenShot ($1/kg-H₂), significant efficiency gains and cost reductions are essential. Optimizing the redox material is pivotal in advancing STCH fuel production.

Ceria (CeO₂) is the state-of-the-art redox material in STCH systems due to its high-temperature stability, fast reduction and water-splitting kinetics, and thermodynamic properties. Yet, its limited oxygen-carrying capacity (OCC), compared to perovskites and iron oxides, results in diminished fuel productivity and solar-to-fuel efficiency. Larger quantities of ceria are needed, leading to larger reactors and higher costs.

Metal-substituted ferrites are another STCH material class with 3-5 times higher OCC compared to ceria. However, ferrites can experience sintering and rapid deactivation at high temperatures (~1500°C), causing a marked decrease in fuel productivity after a few cycles. This sintering effect enlarges particle size, and the inherent low ion diffusivity in spinel slows water-splitting kinetics, ultimately leading to material deactivation. Doping ferrites with different cations or combining with inert supports like zirconia has proven inadequate in preventing ferrite agglomeration [1].

In our previous work, we introduced a composite STCH redox material combining magnesium ferrite (MgFe₂O₄) and ceria. We hypothesize that such a composite can combine the high OCC of ferrites with the thermal stability and high oxygen diffusivity of ceria. Our system-level thermodynamic analysis showed that a composite with 50 wt-% ferrite produces twice as much...
hydrogen per unit mass as ceria and increases STCH efficiency from 33% to 35.3% [2].

In this presentation, we will discuss our experimental efforts with ceria-ferrite composites. We will present the synthesis and characterization of core-shell composites, with a Mg-ferrite core and a ceria shell. Ceria was chosen as the shell material because of its low sintering, fast redox kinetics, and high oxygen diffusivity. We compare the performance of the core-shell composite with that of simple mechanical mixtures in which ferrite and ceria powders are mixed and pressed into a porous pellet. A combination of Infrared furnace experiments and thermogravimetric analysis is used to measure the OCC of composites at STCH-relevant conditions. The experiments involve thermochemical cycles by switching the temperature between reduction (1400°C-1500°C) and water/CO2 splitting(700°C-900°C), changing the gas environment, and monitoring the real-time gas composition using an in-line mass spectrometer. We measure OCC and fuel production profiles over several consecutive STCH cycles to study the sintering or other forms of degradation composites. The ferrite content in the composite is varied to measure its impact on OCC and degradation.

Ex-situ X-ray diffraction (XRD), SEM and TEM imaging, and surface area measurements will be used to characterize the evolution of composite chemistry and morphology during STCH cycles. This work aims to demonstrate the potential of ferrite-ceria composites and core-shell structures as leading an STCH redox material, setting the stage for scaled-up studies in the future.

and their improved performance as electron transporting layer in halide perovskite solar cells. *Nanotechnology* 2019, 30 (20), 204003.


11:30 AM EN05.04.04
Surface Ferroelectric Effect in Oxygen Deficient (111) Strontium Titanate Single Crystals Controls Photoelectrochemical Water Oxidation
Samutrat Assavachin, Chengcan Xiao, Tatiana Maman, Davide Donadio and Frank E. Osterloh; University of California, Davis, United States

Ferroelectric materials such as BaTiO3 have a permanent electric polarization that can be controlled with an external applied electric field. Here we demonstrate a surface ferroelectric effect in oxygen deficient (111) SrTiO3 and its application to improve photoelectrochemical water oxidation for the first time. After hydrogen-annulled (111) SrTiO3 single crystals are polarized with an electric field of 11 kV cm⁻¹ under argon flow, the anodic water oxidation photocurrent increases from 0.99 to 2.22 mA cm⁻² at 1.23 V RHE (60 mWcm⁻², UV illumination) or decreases to 0.50 mA cm⁻², for the opposite field orientation. The polarization also modifies the surface photovoltage signal of the material and its flat band potential, based on Mott-Schottky measurements. This is attributed to an electric dipole near the (111) SrTiO₃ surface, which controls the potential drop across the depletion layer and charge transfer at the solid-liquid junction. Based on DFT calculations the electric polarization results from the migration of oxygen vacancies between SrTiO₃ surface and sub-surface regions. The use of the surface ferroelectric effect to modify the junction and photoelectrochemical properties of a non-ferroelectric material is expected to be of interest for solar energy conversion and information technology applications.

11:45 AM EN05.04.05
Thermochemical Properties of ABO₃-Type Compounds for Solar Fuel Generation
Sussina M. Hailé; Northwestern University, United States

Solar-driven thermochemical production of chemical fuels using redox active oxides has emerged as an attractive means for storing solar energy for use on demand. In this process, a reactive oxide is cyclically exposed at high temperatures to inert gas, which induces partial reduction of the oxide, and subsequently to an oxidizing gas of either H₂O or CO₂, which reoxidizes the oxide, releasing H₂ or CO. While it is widely recognized that the capacity for fuel production is dictated by the thermodynamic properties of the oxide, here we show that the rate of fuel production is also often directly given by these properties. Recognizing this behavior, we report the thermodynamic properties, specifically the enthalpy and entropy of reduction, of a range of provenial scrap heap of history.

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**SESSION EN05.05: Carbonaceous Materials forPhotocatalysis**

**Session Chairs:** Demetra Achilleos and Katarzyna Sokol

**Tuesday Afternoon, April 23, 2024**

Room 335, Level 3, Summit

1:45 PM *EN05.05.01*

**Transient Absorption Spectroscopy/Microscopy of Carbon Nitride Photocatalysts for Biomass Photoreforming**

Robert Godin; The University of British Columbia, Canada

Polymeric photocatalysts made of Earth-abundant elements have been extensively developed over the past decade to take advantage of their synthetic tunability.¹ Within this family, carbon nitrides (CNx) are emerging as leading photocatalysts because of their high photocatalytic performance combined with good stability and facile synthesis.² However, significant gaps remain in our knowledge of the photophysical properties of these organic polymeric materials. Determining the pathways and mechanism of photoinduced processes will greatly aid our efforts to engineer better CNx photocatalysts for solar fuel production and other photocatalytic processes.

We are taking the next step to develop a full picture of the charge carrier dynamics by expanding our spectroscopic capabilities to transient absorption microscopy (TAM). Notably, our first-of-its-kind TAM system monitors the microsecond – timescales relevant to the complex multi electron redox reactions that occur to produce solar fuels. Spatial mapping of the charge carrier dynamics on the micron scale provides novel insights into the heterogeneity in individual CNx particles. This new tool allowed us to unearth a multiscale heterogeneity where the charge carrier dynamics differ from particle to particle and different behavior within individual particles on ~10 micrometer length scales can be observed. These new insights into the heterogeneity of charge carrier dynamics in CNx particles can push the field into uncovering the optimal structure and local environment in defect-rich organic semiconductors such as CNx. We are taking this knowledge and applying it to systems of biomass photoreforming for the simultaneous breakdown of organic matter and H₂ evolution.


2:15 PM *EN05.05.02*

**On The Scarcity or Not of Carbon-Based Overall Water Splitting Photocatalysts**

Martijn Zwijnenburg; University College London, United Kingdom

Since the discovery in 2010 that carbon nitride combined with suitable co-catalysts could in the presence of appropriate electron donors and acceptors drive both the reduction of protons to molecular hydrogen and the oxidation of water to molecular oxygen, carbon-based materials have received an enormous amount of interest as potential light absorbers for photocatalytic water splitting. Now probably more than 200 different carbon-based materials, mostly conjugated polymers, are known to be active for hydrogen evolution in the presence of a sacrificial donor such as triethanolamine orascorbic acid, and platinum or palladium nanoparticles that act as co-catalyst and site of the hydrogen evolution.¹ In contrast, a much smaller number of carbon-based materials have been reported to be active for the oxygen evolution half-reaction. The number of carbon-based materials experimentally active for overall water splitting can be counted on the fingers of one or two hands.

Based on the scarcity of materials that are active for overall water splitting one could naively assume that such activity is a rare property of carbon-based materials. That carbon-based materials generally just do not have the ionisation potential / valence band maximum position to drive water oxidation. In my contribution I’ll discuss the results of computational high-throughput screening of thousands of conjugated polymers which shows that this is not necessarily the case, or at least not for polymers.² Approximately, a similar fraction of the library of 3000+ conjugated polymers is predicted to be thermodynamically able to drive overall water splitting as is predicted to be active for sacrificial hydrogen evolution. Although the ability to drive overall water splitting combined with a small enough optical gap that a large part of the solar spectrum is absorbed is predicted to be relatively rare for this material class. Finally, I’ll discuss why we think the real reason behind the scarcity of carbon-based overall water splitting photocatalysts is not thermodynamics but the need for well-optimised co-catalysts and why thus future work on co-catalysts and/or combining polymers into heterojunctions, like recently explored experimentally by Kosco and co-workers,³ can rescue large numbers of carbon-based photocatalysts from the proverbial scrap heap of history.

2. B. Saunders et al. Sustainable Energy Fuels, 2022, 6, 2233.
Efficient Z-Scheme Configuration for Photocatalytic CO2 Reduction through g-C3N4 and Cs3Bi2Br9 Heterojunctions Enhanced by Reduced Graphene Oxide

Yasmine Baghdadi and Salvador Eslava; Imperial College London, United Kingdom

Photocatalytic CO2 reduction is pivotal for progressing solar fuel technologies, demanding catalysts with enhanced efficiency. Combining the optoelectronic characteristics of Cs3Bi2Br9 and the versatility of g-C3N4, this study aims to create a synergistic platform for photocatalysis, harnessing the unique strengths of each semiconductor to enhance overall performance in applications such as solar fuel generation and photocatalytic CO2 reduction.

Building on our previous studies where the ratio of g-C3N4 to Cs3Bi2Br9 was optimized for high CO2 conversion to CO, this study presents a dual-modification approach to amplify the performance of a Cs3Bi2Br9 as a photocatalyst. Surface modifications, including exfoliation for increased surface area and surface oxidation for improved charge separation, were employed on g-C3N4. The introduction of reduced graphene oxide (rGO) at various ratios, integrated into both bulk and exfoliated g-C3N4, effectively mitigated charge recombination. An optimal rGO/g-C3N4 ratio was identified, showing superior efficiency.

Importantly, the study also introduces a hybrid inorganic/organic heterojunction by combining the optimized rGO/g-C3N4 with Cs3Bi2Br9 into a Cs3Bi2Br9/rGO/g-C3N4 Z-scheme composite. This synergistic integration resulted in a remarkable increase in photocatalytic activity, reaching 54.3 (± 2.0) mmol g⁻¹ e⁻ h⁻¹ on an electron basis for CO2, H2, and CH4 production, surpassing pure Cs3Bi2Br9 (11.2 ± 0.4 mmol g⁻¹ e⁻ h⁻¹) and bulk g-C3N4 (5.5 ± 0.5 mmol g⁻¹ e⁻ h⁻¹).

A comprehensive characterization shows the charge transfer mechanism within the composite to take place via the rGO, acting as a solid redox mediator, in a Z-scheme heterojunction where Cs3Bi2Br9 drives the reduction and g-C3N4 the oxidation, explaining its enhanced photocatalytic activity. The successful formation of this high-performance heterojunction underscores the composite's potential as an efficient photocatalyst for CO2 reduction, promising substantial advancements in solar fuel technologies and aligning with sustainable energy goals.


3:00 PM BREAK

SESSION EN05.06: Value-Added Products

Tuesday Afternoon, April 23, 2024
Room 335, Level 3, Summit

3:30 PM *EN05.06.01
Turning Waste into High Value Chemicals with Electricity

Muahlena Titiri; Imperial College London, United Kingdom

In this talk, I will present our latest advances in converting bio-based products such as glycerol, 5-hydroxymethylfurfural or PET waste into valuable chemicals including lactic acid, FDCA and glycolic acid including some fundamental mechanistic studies, upscale opportunities and life cycle assessment of such processes.

4:00 PM *EN05.06.02
Coupling Hydrogen Production and Upgrading of Chemicals in Oxide-Based Photoelectrochemical Device

Fatwa F. Abdi; City University of Hong Kong, Hong Kong

Green H2 has been recognized as an important element in efforts to decarbonize our fossil fuel-dependent society. One method to produce green H2 is solar water splitting in a photoelectrochemical (PEC) device. Solar-to-hydrogen (STH) efficiencies of up to 30% have been demonstrated but these high efficiencies could only be achieved using expensive and non-scalable photoelectrodes—the approach therefore still results in a hydrogen cost that is not competitive. One obvious approach is to develop novel photoelectrode materials that are low-cost and highly efficient. For example, earth-abundant complex metal oxides have been explored, and several promising ones have been identified. Here, our efforts in developing tin tungstate (SnWO4) as a photoelectrode material will be discussed. [1-3] Alternatively, co-production of valuable chemicals can be introduced in the PEC cell to increase the competitiveness of the overall system. For example, we recently coupled a homogeneous hydrogenation reaction with PEC-generated hydrogen inside a single device.[4,5] Using the hydrogenation of itaconic acid (IA) to methyl succinic acid (MSA) as a model proof-of-concept reaction, solar-driven H2-to-MSA conversion as high as ~50% was demonstrated using our BiO4-based PEC device. Although still demonstrated in the laboratory scale, life-cycle net energy assessment and technoeconomic analysis reveal that the concept indeed offers a very promising return. Finally, further implications and optimization potentials of this coupled PEC hydrogenation approach, also beyond the demonstrated hydrogenation of IA to MSA, will be discussed.

References
2. P. Schnell et al., Chem. Mater. 34, 2022, 1590
3. P. Schnell et al., Solar RRL 7, 2023, 2201104
4. X. Zhang et al., Nat. Commun. 14, 2023, 991
5. K. Obata et al., Nat. Commun. 14, 2023, 6017

4:30 PM EN05.06.03
Aqueous Z-Scheme Photocatalytic CO2 Reduction by Dispersed Semiconductor Particles of Metal Sulfide and Oxide in Synergy with Dual-Functional Metal-Complex

Tomiko M.
Flow Photoelectrochemical Devices for Converting Carbon from the Ocean

The capture and utilization of the dissolved inorganic carbon in seawater, i.e., 2 mM bicarbonates, offers a promising approach to mitigate environmental concerns and advance the realization of a carbon-neutral society. Unbiased solar-driven photoelectrochemical (PEC) CO2 reduction leads to sustainable production of chemicals and fuels. However, the development of reactors for unbiased PEC CO2 capture and in-situ utilization has been scarce, due to the lack of reactors that can balance mass transfer and flow field design with PEC CO2 reduction. In this talk, we will discuss the design and realization of 3D printed reactors for unbiased PEC CO2 capture and in-situ utilization in seawater, in which the locally generated CO2 at BiVO4 photoanodes can be brought to the neighboring Si photocathodes for CO2 reduction by optimized flow field design, reducing the protons transfer distance and improving the local CO2 concentration on the surface of Si photocathodes. With this, we achieved excellent CO2 capture velocity and outstanding solar to fuels (STF) efficiency of 0.71%. CO selectivity was increased from 3 to 19% compared with the conventional "artificial leaf" configuration of back-to-back photoanodes and photocathodes. A flowing reactor module is demonstrated for realistic ocean operation.

References
Photocatalytic conversion of water using solar energy offers a clean solution to the world energy requirements of a sustainable future. Achieving its full potential depends on developing inexpensive photoanodes that can efficiently absorb solar light and drive the difficult oxygen evolution reaction (OER), which requires 4 electrons per molecule, and currently hampers reaching high solar to hydrogen efficiencies.

In this talk, I will first present recent developments we have achieved in my group in the preparation of inexpensive BiVO4 photoanodes functionalized with 2D bismuthene. Partially oxidized two-dimensional (2D) bismuthene is prepared by reduction of BiCl3, and demonstrated to be a stable, functional interlayer between BiVO4 and the archetypical NiFeOOH co-catalyst. Comprehensive (photovoltaic)electrochemical and surface photocatalytic characterizations show that NiFeOOH passivates hole trap states of BiVO4; however, it is limited in influencing electron trap states relative to oxygen vacancies (V02). Loading bismuthene on BiVO4 photoanodes fills the V02-related electron traps, leading to more efficient charge extraction. This is confirmed by kelvin probe measurements. Moreover, bismuthene increases adsorption sites for reaction intermediates and increases interfacial band bending boosting hole charge flux to the electrolyte. With the synergistic interaction of bismuthene and NiFeOOH on BiVO4, this composite photoanode achieves a 5.8-fold increase in photocurrent compared to bare BiVO4 reaching a stable 3.4 (±0.2) mA cm−2 at a low bias of +0.8 V RHE or 4.7 (±0.2) mA cm−2 at +1.23 V RHE. The use of 2D bismuthene also boosts other photoanodes such as hematite, demonstrating its wide potential to boost the performance of photocathodes for water conversion applications.

In a second part of my talk, I will present our work on the role of composition and interactions between BiVO4 and core-shell structured bimetallic nickel-cobalt phosphide co-catalysts with varying metal ratios to improve their photoanodic performance. The best performance obtained from BiVO4/Ni1.5Co0.5P and BiVO4/Ni0.5Co1.5P photoanodes achieved a photocurrent of 3.2 (±0.14) mA cm−2 at +1.23 V RHE, a 3.5-fold increase in photocurrent compared to bare BiVO4. Through an extensive characterization considering interfacial energetics, hole storage, and catalytic ability, we have discovered that the enhanced photocatalytic performance cannot be solely attributed to the catalytic activity of the co-catalysts. Instead, it arises from a synergistic interplay involving effective band bending, catalytic activity, and capacitive ability. The contact between the core-shell metal phosphides, BiVO4, and the electrolyte creates three pathways for hole injection into the electrolyte, all of which are notably enhanced by the presence of a second metal cation in the co-catalysts. Kinetic studies demonstrate that the BiVO4-metal phosphide photoanodes show significantly improved interfacial charge injection due to a lower charge-transfer resistance, enhanced OER kinetics, and larger surface hole concentrations. Moreover, by analysing the distribution of relaxation times, we can distinguish the kinetics of various processes, including bulk charge carrier transport, hole injection through different pathways, and surface recombination. This analysis provides deeper insights into the carrier dynamics within these photoanode/cocatalyst systems.

To conclude, these results provide key insights into the preparation of BiVO4 photoanodes boosted with interlayers and co-catalysts to achieve its full potential and pave the way to rationally design other complementary photocathodes.
Photo-Electrochemical Water Splitting to Generate Hydrogen Fuel: The Importance of Accurately Benchmarking Efficiency, Challenges with System Scale Up and Protective Barriers for Corrosion Mitigation

10:30 AM **EN05.08.01**

Photo-Electrochemical Water Splitting to Generate Hydrogen Fuel: The Importance of Accurately Benchmarking Efficiency, Challenges with System Scale Up and Protective Barriers for Corrosion Mitigation

Todd G. Deutsch, Myles Steiner and James L. Young; National Renewable Energy Laboratory, United States

Solar-to-hydrogen (STH) conversion efficiency is a common figure of merit for evaluating and comparing research results, and it largely establishes the prospect for successfully introducing commercial solar water-splitting systems. Present measurement practices do not follow well-defined standards, and common methods consistently overestimate performance. To remedy this need we confirmed underestimated influence factors and proposed experimental strategies for improved accuracy. Our focus was tandem (dual absorber) devices that have the potential for greater STH efficiency, but increased complexity that requires more careful consideration of characterization practices. We performed measurements on an advanced version of the classical GaInP2/GaAs design while considering (i) calibration and adjustment of the light source, (ii) validation of results by incident photon-to-current efficiency (IPCE), and (iii) definition and confinement of the active area of the device. We initially measured 21.8% STH efficiency using a tungsten broadband light source, a calibrated GaInP2 photovoltaic reference cell, and epoxy-encased photocathodes. In contrast, integrating experimental IPCE over the AM 1.5G reference solar spectrum showed that less than 10% of STH conversion is possible. We performed a set of on-sun measurements that gave 16.1% STH efficiency before eliminating indirect light coupled to the sample by using a collimating tube and 13.8% STH efficiency. However, the value still significantly exceeded the current density expected according to the quantum efficiency measured via IPCE. Finally, suspecting that the illuminated area is poorly defined by epoxy, we use a compression cell for an epoxy-free area definition, resulting in 9.3% STH efficiency – a number corroborated by our IPCE results.

The second part of this talk will identify the challenges encountered while scaling the inverted metamorphic junction (IMM) III-V absorber areas of from ~0.15 cm² up to 16 cm² and incorporating them in a photoreactor capable of generating 3 standard liters of hydrogen in 8 hours under natural sunlight. To successfully scale photo-electrochemical water-splitting technologies from bench to demonstration size requires addressing predictable and unpredictable complications. Despite using Consol multiphysics to model our photoreactor and identify suitable specifications for a prototype, several practical issues were uncovered during testing that led to multiple iterations of photoreactor design between the initial and final generation. Several bottlenecks that ranged from counter electrode composition and orientation to bubble removal needed redress in order to meet our performance targets. Ultimately, the demonstration-scale system was able to generate nearly twice the target volume of hydrogen in an 8-hour outdoor trial. While III-V semiconductors have achieved high photo-electrochemical STH conversion efficiencies, they are remarkably unstable during operation in a harsh electrolyte. The final part of this talk will focus on the degradation mechanism of IMM III-V cells and surface modification strategies aimed at protecting them from photocorrosion. We applied noble metal catalysts, oxide coatings by atomic layer deposition, and MoS2 in an effort to protect the GaInP2 surface that was in contact with acidic electrolyte. We also grew epitaxial capping layers from III-V alloys that should be more intrinsically stable than GaInP2. The ability of the various modifications to protect the IMM’s surface was evaluated by operating at each electrode at short circuit for extended periods of time. We will elaborate on the challenges of this mode of protection and new methods of protecting perovskite photo absorbers will be introduced.

11:00 AM **EN05.08.02**

An Artificial-Photosynthetic System Consisting of Solar-Driven Reaction and Product Isolation Processes to yield only Pure Formic Acid

Yasuhiro Takeda, Shintaro Mizuno, Masahito Shiozawa, Natsumi Nojiri, Takeshi Morikawa and Naohiko Kato; Toyota Central R&D Labs Inc, Japan

We proposed a concept of an artificial-photosynthetic system to produce pure formic acid using only CO2, water, and solar energy, generating no waste. The system consists of a solar-driven reaction process and a product isolation process. We proved the concept by small-scale experiments, and constructed a practically large-sized reactor as the first step toward widespread use of artificial photosynthesis.2,3
We adopted a single-compartment configuration of the solar-driven reactor without ion-exchange membranes and a near-neutral pH electrolyte of a potassium phosphate buffer aqueous solution to simplify the reactor structure. The large-sized reactor was composed of eight-stacked cathode/anode-electrode pairs of 1 m × 1 m in size and powered by crystalline-silicon solar cells on the reactor housing via a DC-DC converter. The raw material of 100% CO2 gas was dissolved in the electrolyte and supplied to the cathode-electrode surfaces uniformly with the help of well-designed flow channels. The electrochemically synthesized formic acid was dissolved in the electrolyte and ejected from the reactor. We developed a Ru-complex-based cathode catalyst and a IrO2-based anode catalyst, and achieved a Faradaic efficiency as high as 96% for the formic-acid synthesis at an extremely low operating voltage of 1.65 V (overpotential of only 0.22 V) and a large current of 65 A, resulting in a high solar-to-chemical energy conversion efficiency of 10.5%. In addition, we tackled to improve both activity and durability of the cathode and anode electrodes,4,5 and to realize direct reduction of CO2 in a flue gas to eliminate CO2 capture processes.6 Further, we designed tandem solar modules suitable for direct coupling with the reactors using organic-inorganic hybrid perovskite solar cells.7 The next challenge was isolation of the synthesized formic acid in the aqueous electrolyte. The formic acid cannot be isolated by distillation because of its boiling point (101 °C) almost the same as that of water. Thus, we developed an isolation process on the basis of reactive extraction, including three sequential steps.1 The first step was reactive extraction of the formic acid from the electrolyte using an extraction solution composed of an organic base (trioctylamine, TOA, boiling point 366 °C) as an extractant and an organic solvent (dichloromethane, DCM, boiling point 40 °C) as a diluent. Although formic acid is highly miscible in water, it was extracted into DCM because the formic acid formed a complex salt with TOA that is insoluble in water. The second step was removal of DCM from the mixture of the extracted formic acid, TOA, and DCM produced in the first step, by evaporation at 40 °C. Finally, the residue was heated at 160 °C for 4 h to decompose the formic acid into distillation in the third step. The large differences in the boiling points among these three chemicals secured few contaminations in the second and third steps. In addition, the composition of the electrolyte was tuned for promotion of the formation of the formic acid-TOA complex salt. Thus, we achieved an over 90% isolation efficiency before eliminating indirect light coupled to the sample by using a collimating tube and 13.8% STH efficiency. However, the value still significantly exceeded the current density expected according to the quantum efficiency measured via IPCE. Finally, suspecting that the illuminated area is poorly defined by epoxy, we use a compression cell for an epoxy-free area definition, resulting in 9.3% STH efficiency – a number corroborated by our IPCE results.

References

11:15 AM **EN05.08.03**

Utilizing Three-Terminal IBC-Based Si Solar Cells as a Platform to Study The Durability of Photoelectrodes for Solar Fuel Production

Darec Collins1,2, Zebulon Schicht1, Nathan Nesbitt1, Annie Greenaway1, Valentin Mihailetchi1, Daniel Tune3 and Emily Warren1; 1National Renewable Energy Lab, United States; 2Colorado School of Mines, United States; 3International Solar Energy Research Center, Germany

Utilized, photoelectrochemical (PEC) reactions, such as H2 generation and CO2 reduction, are limited by the durability of the immersed semiconductor and catalyst. While great strides have been made to improve stability under illumination, dark stability remains relatively unexamined and presents great challenges. Typically, semiconductors require the use of protection layers to drive the PEC reactions of interest. Cathodic protection is an established electrochemical method for preventing electrode degradation in harsh conditions. Similar protection strategies cannot be applied to traditional two-terminal (2T) photovoltaic electrodes because of their inability to pass reverse bias current in the dark. New, three-terminal (3T) photovoltaic (PV) architectures can remove the limitations of traditional 2T photovoltaics by the addition of an extra electrical contact which provides an alternative low resistance path to drive electrochemical reactions, even in the dark. 3T Si interdigitated back contacted (IBC) cells have n+ and p+ doped back contacts, similar to a traditional IBC cell, with an additional conductive front n+ contact to create the third terminal. Here, we investigate how 3T Si PV can be operated as photocathodes to understand new protection methods for photocathodes in aqueous environments without protection layers. We characterize performance of the 3T electrode in a regenerative redox electrolyte, methyl viologen, to decouple catalysis from photocathode device performance. The 3T Si electrode is used as a platform to understand the applications of cathodic protection to chemicals in photoelectrochemical systems. The 3T architecture provides additional capabilities to PEC
Simultaneous Photo Protecting and Tuning Selectivity of Cs$_3$Bi$_2$Cl$_9$ during Photoreduction of CO$_2$ to HCOOH Using Ir/IrOX

The presence of Ir/IrOX provided the reaction with much-needed hydroxyl groups for the photoreduction of CO$_2$. Further, Ir/IrOX delayed the catalyst deactivation thereby retaining its activity for longer cycles by altering the photo-generated charge recombination process and prolonging their lifetimes making them suitable photocatalysts for water splitting (HEPs) and oxygen evolution photocatalysts (OEPs) to split water into hydrogen and oxygen via two-step excitation. Such a process is widely known as the Z-scheme. Particulate photocatalyst sheets consisting of La- and Rh-codoped SrTiO$_3$ as HEP and Mo-doped BiVO$_4$ as OEP immobilized on Au and C layers split water into hydrogen and oxygen with STH efficiencies exceeding 1.0%.

The author’s group has studied various semiconductor oxides, (oxy)nitrrides, and (oxy)chalcogenides as photocatalysts for water splitting. SrTiO$_3$ is an oxide photocatalyst that has been known to be active in overall water splitting under UV irradiation since 1980. Recently, the apparent quantum yield of overall water splitting using SrTiO$_3$ has been improved to more than 90% at 365 nm, corresponding to an internal quantum efficiency of nearly unity, by refining the preparation conditions of the photocatalyst and the loading conditions of the cocatalysts.

Advancing Solar Harvesting Technology with Kesterite-Inspired Absorbers and High Throughput Materials Discovery

The quest for harnessing solar energy to produce both electricity and fuel represents an enduring pursuit in the realm of renewable energy. Although conventional solar panels have found application in solar fields and rooftops, the realization of this vision necessitates the development of advanced technologies involving innovative materials and novel manufacturing processes. These advancements aim to extend the application of solar energy to diverse contexts such as windows, vehicles, and complex substrates. Despite the identification of numerous photoabsorbers with potential as solar cell materials, only a limited few have transitioned into commercial use.

This presentation will delve into the recent endeavors of our research group, focusing on kesterite-inspired absorbers, with a specific emphasis on the effects of doping and cation substitutions in Cs$_6$CdSn$_2$S$_8$ photocatalysts. We will demonstrate how substitutions involving Ag and Ge impact the structure and optoelectronic characteristics of this material (unpublished results). Additionally, we will discuss our research in high-throughput synthesis and characterization techniques, which have led to the discovery of new dopants that enhance the transport properties of FeVO$_4$ photoanodes and ternary Fe-Co-Ni oxide catalysts for the Oxygen evolution reaction.

References
Designing New Metallic Catalysts by Transversing The ‘Hidden’ Compositional Terrain


Experimental characterization of three-terminal tandem photocathode voltages for photovoltaic applications to drive such a cascade CO₂R photoelectrochemically, using sunlight as the input.

A three-terminal tandem (3TT) is a type of multijunction photovoltaic device where a middle terminal is added between the two subcells that comprise the tandem, rather than having no extra terminal (as in a two-terminal tandem) or having the two subcells electrically connected (a four-terminal tandem). Connecting any two of the three contacts generates a different voltage, enabling a simple device to use all the potentials. The GaN/P/GaAs 3TT tandem used in this work has two terminals contacting the electrolyte, each of which drives one step of the CO₂R cascade: the photoelectrode is illuminated from opposite sides, through a third terminal. Previous modelling work has shown that a 3TT tandem could drive a PEC CO₂R cascade and possibly improve product selectivity over simpler photocathodes. However, the fundamental behaviors of 3TT photocathodes are not yet understood in relationship to the performance of 3TT photovoltaics. This work experimentally characterizes the PEC behavior of a 3TT photocathode. Potential and current relationships will be characterized both dry and under electrochemical conditions to provide insight into how standard reduction potentials are possible with a GaAs/GaNP 3TT device. Dry power contour plots will be used to find the max power point, as simple current-voltage curves cannot fully define 3TT operation due to the presence of mid-coupling. Non-aqueous PEC measurements, using regenerative redox couples, will be performed in combination with light filtering (to select the GaNP or GaAs subcell) to learn about the operational window of each photocathode electrolyte. In summary, this work aims to control a 3TT photocathode for PEC CO₂R as a step towards the goal of sustainable fuel production.

Experimental Results


5:00 PM EN05.10.02
Solar Driven CO₂ Reduction to CO Catalyzed by Mn-complex supported on Carbon Nanohorn in an All Earth Abundant System Teppei Nishit, Shunsuke Sato, Keita Sekizawa, Tomiko M. Suzuki, Keiichiro Oh-ishi, Naoko Takahashi, Yoriko Matsuoka and Takeshi Morikawa; Toyota Central R&D Labs., Inc., Japan

CO₂ conversion technology has been developed for a neutral society. A lot of catalysts to convert CO₂ to hydrocarbons have also been developed. Our group also reported CO₂ reduction catalysts. In particular, Mn-complex catalyst supported on multi-walled carbon nanotubes (MWCNTs) can catalyze CO₂ reduction reaction to CO at low overpotential (ca. 100 mV) [1]. In addition to the electrocatalytic activity, solar-driven CO₂ reduction to CO using Ni-doped β-FeOOH as a cathode and Si solar cell was also reported [2]. Here, we report a carbon support to enhance the electrocatalytic activity [3]. We used MWCNTs, carbon nanohorns (CNHs), graphene platelets (GNPs), carbon black (CB) and carbon nanofibers (CNFs). Electrocatalytic activities Mn-complex supported on various carbon supports were measured in CO₂ saturated aqueous 0.1M K₂B₄O₇ + 0.2M K₂SO₄ solution at an applied potential of -1.0 V vs Ag/AgCl. Among the various carbon materials, CNHs were the best supports to enhance the catalytic activity toward CO₂ reduction to CO. Faraday efficiency of CO was 87%. The superior activity was speculated to the high specific surface area and hydrophilic nature. The water-drop contact angle revealed hydrophobicity of CNHs and MWCNTs. It is expected that a superior local environment for highly selective CO₂ reduction can be provided by hydrophilic supports by keeping water away from the electrode surface. In contrast, hydrophilic carbon supports resulted in the increase of Faraday efficiency of H₂. Additionally, specific surface area of CNHs (410 m²/g) was larger than other carbon supports. It is concluded in the result that the enhancement of catalytic activity of Mn-complex. Because CNHs was revealed to enhance the catalytic activity of Mn-complex for CO₂ reduction to CO, we demonstrated solar-driven CO₂ reduction to CO using Mn-complex supported on CNH as a cathode electrode, Ni doped β-FeOOH supported on single walled carbon nanotube (SWCNT) as an anode electrode and polycrystalline Si solar cell. A solar-to-CO conversion efficiency was 3.3%.

5:00 PM EN05.10.03
Experimental Characterization of Three-Terminal Tandem Photocathode Voltages for Photoelectrochemical Applications Grace Romei1,2, Myles Steiner2, Emily Warren2 and Annie Greenaway2; 1Colorado School of Mines, United States; 2National Renewable Energy Laboratory, United States

Sustainably produced liquid fuels are necessary for a clean energy future, especially for energy intensive applications such as aviation where batteries are presently not sufficiently energy dense. Photoelectrochemical carbon dioxide reduction (PEC CO₂R) is a possible route to the production of sustainable fuels. However, there are an abundance of different products from CO₂R, making selection of a single product difficult and requiring expensive, energy intensive product separation. One method to improve selectivity is to design cascading reactions, such as reducing CO₂ to CO and then subsequently reducing the CO to higher order (C₂+ı) products [1]. Each reaction within the CO₂R cascade occurs at a specific thermodynamic potential, requiring a specific voltage, and has a specific stoichiometry, requiring a specific electron flux or current density. The reactions of interest for a PEC CO₂R cascade would take place on a single photocathode, requiring first step products to move only on the order of millimeters to the second reaction site. This work aims to develop and characterize a III-V-based photocathode that can drive such a cascade CO₂R photoelectrochemically, using sunlight as the input energy.

To discover materials with enhanced catalytic behavior, we convert the complex elemental feature space into a connected network, representing the similarities and underlying physics of catalytic alloys. A challenge in the design is due to limited number of property measurements, thereby making typical data driven modeling inaccurate and uncertain. To address this challenge, we apply a random walk approach to capture the reaction behaviors and link the kinetic and chemical behaviors of the alloys. The results lead to a more comprehensive understanding of metallic catalytic design with the most promising chemistries identified across a variety of gas reactions. Through this work, the design space is reduced and the necessary experiments are defined.

5:00 PM EN05.10.08
Supercharging Solar Fuel Production: Harnessing Sub Bandgap Energy in Mo-Doped BiVO₄ Photoanode to Enhance Photoelectrochemical Reaction via Triplet-Tritplet Annihilation Upconversion Prashanth Venkatesan and Rauzy-An Doong; National Tsing Hua University, Taiwan

Developing solar-based engineered technology is an important issue to realize a zero-carbon world. Among various forms of solar energy utilization, photoelectrocatalysis (PEC), which involves a direct solar to chemical energy conversion by light-matter interaction, exhibits a relatively high theoretical efficiency. PEC uses semiconductors to absorb photons to produce effective electron-hole pairs for a redox reaction. Several concepts have been proposed and demonstrated to improve the separation and utilization of the excitons. However, few attempts have been made to engineer the light to enhance the PEC efficiency by broadening the range of the solar spectrum that the semiconductor can utilize. The upconversion (UC) process induced by triplet-triplet annihilation (TTA) is an intermolecular energy transfer process by restoring the energy in triplet-state molecules to produce a high-energy singlet state to enhance the UC process. It is noted that the UC process, which uses the solar spectrum as the light source can convert the sub-bandgap photon into the absorbing range of the PEC semiconductors. Therefore, incorporating PEC with TTA-UC appears to be the most suitable process to enhance the efficiency of PEC by utilizing the abundant visible light from solar light. In this study, the benchmark TTA-UC chromophores, 1,2, Myles Steiner2, Emily Warren2 and Annie Greenaway2; 1Colorado School of Mines, United States; 2National Renewable Energy Laboratory, United States

Experimental results of TTA-UC phosphorescence are shown in Figure 1. The phosphorescence of POEPO is quenched by DPA based on the Stern-Volmer relation, indicating that the triplet energy transfer between the two chromophores is effective. The optimal concentrations of POEPO and DPA are 20 μM and 8 mM, respectively. For ease of implementation, POEPO/DPA containing oleic acid is emulsified and acts as soft templates during the sol-gel process of tetraethyl orthosilicate (TEOS), yielding to UC active SiO₂ nanocapsules. The TEM images suggested that a silica shell encapsulates oleic acid with a diameter of 200–300 nm with a thickness of 10 nm. The upconverting composite film is prepared using the SiO₂ nanocapsules. Semitransparent Mo:BiVO₄ photoanode is synthesized by spin coating technique. The incorporation of upconverting composite film with Mo:BiVO₄ photoanode shows an enhanced photocurrent density from 1.09 mA cm⁻² to 1.24 mA cm⁻², equivalent to an increase of 14%. With a 490 nm long pass filter a 45% increase at 1.23 V vs RHE is observed corresponding to a current density increase from 0.24 mA cm⁻² to 0.35 mA cm⁻².
A Novel Approach to Anti-Soiling Coatings for Solar Modules by use of Lanthanide Oxide Films Jayven K. Patel, Ivan Parkin and Claire Carmalt; University College London, United Kingdom

Advances in solar module utilities underpin an important approach for novel sources of renewable energy. However, soiling remains a major obstacle when considering the use of solar modules as a sustainable replacement for electricity generation. Thus, there is an evident need for self-cleaning solar utilities. We present the design, synthesis and application of inorganic rare oxide layers (CeO2, Er2O3) which have been deposited by aerosol assisted chemical vapour deposition (AACVD) with intrinsic hydrophobicity. Water contact angles of up to 103 ° were established across the deposited thin films, inferring their self-cleaning potential.

The reduced number of examples of lanthanide oxide complexes for hydrophobic coatings using AACVD within the literature, prompted our investigation into the synthesis of volatile lanthanide β-diketone precursors, a novel approach to self-cleaning solar modules. Notably, inorganic rare Earth oxide layers (Ce, Y, Lu, Er) have proven through various applications to be durable, UV stable, oxidant resistant and have intrinsic hydrophobicity with a water contact angle range of 110-125 °. Likewise, β-diketone ligands complexes have proven to serve as effective and stable precursors. Compounds of the type [M(βdik)_3] have been synthesised via adaption of a known synthetic route to [Ce(thd)_4] and [Er(thd)_3]. Where; M = lanthanide metal (Ce, Er) and βdik = dipivaloylmethane, dbn (dibenzyloinethane).

AACVD of the synthesised complexes yielded lanthanide oxide films on fluorine tin doped (FTO) glass under a constant flow of nitrogen. Thermogravimetric analysis of these compounds indicated suitable deposition temperatures ranging from 400-600 °C. The most hydrophobic coatings were attained by deposition of cerium oxide onto FTO at temperatures between 400-500 °C. These rare oxide thin films were intrinsically analysed using surface analysis and characterisation techniques. Whereby X-ray photoelectron spectroscopy confirmed the presence of a mixed phase system of Ce(III) and Ce(IV) across the surface. Further analysis of the deposited thin films was conducted using SEM and XRD to determine the surface morphologies of these hydrophobic coatings.

References

Highly Efficient and Stable Dye-Sensitized Photoelectrochemical Cells via Cascade Charge Transfer Jun-Hyook Park, Ji-Wook Jang and Tae-Hyuk Kwon; Ulsan National Institute of Science and Technology, Korea (the Republic of)

Dye-sensitized photoelectrochemical devices (DSCs) have shown promise in artificial photosynthesis for water splitting, but they face obstacles such as low photocurrents (0.01-2.2 mA/cm²) and limited stabilities (0.01-2 months, maintaining over 90% of initial photocurrent) due to degradation/decomposition of dye-sensitized photoelectrodes, along with inefficient charge transfer processes in aqueous electrolytes forming adaptive junction. To overcome these fundamental issues, we developed a “cascade-type” dye-sensitized photoelectrode utilizing platinum-sputtered nickel foil to encapsulate both the dye-sensitized TiO2 layer and redox mediator electrolyte. This buried junction design enables spatially controlled cascade charge transfer, highly effective photoconversion, and active water oxidation facilitated by Ni-based catalysts, all without undesirable current leakage. By conducting a comprehensive study involving three redox electrolytes and optimizing water oxidation catalysts, our best-performing photoelectrode achieves a photocurrent of 14.5 mA/cm², Faradaic efficiency of approximately 98%, and photostability of 30 h under AM 1.5G illumination.

Two Dimensional Janus Ga2SX2 (X = O, S, Se, and Te) Monolayers as Efficient Piezo- and/or Photocatalyst for Green Hydrogen Generation Devender Takhar1; Balaji Birajdar1 and Ram Krishna Ghosh1; Jawaharlal Nehru University, India; IIIIT, India

Developing innovative and environmentally friendly hydrogen generation technologies are pivotal for transition to a carbon-neutral future. In this regard, the integration of photocatalytic and piezoelectric properties of semiconductor catalyst have proved beneficial. As polar nature of piezoelectric materials provides a drive force to photo-generated charge carriers thus enhancing their separation and reducing recombination. Additionally, piezoelectric materials generate a potential under oscillatory strain, commonly known as piezo-potential, can alone initiate the water redox reaction. Therefore, in this study we explore the potential of piezoelectric Janus Ga2SX2 (X=O, S, Se, Te) monolayers as efficient piezo- and/or photocatalyst, leveraging density functional theory (DFT) simulations. Our investigation encompasses a comprehensive examination of the structural, electronic, optical, mechanical and piezoelectric properties. Except Ga2O3 all monolayers exhibit semiconducting behaviour, featuring indirect band gaps within the range of 1 eV to 2.7 eV. The band edges are favourable to straddle the photocatalytic water redox reaction under the solar illumination. Moreover, the generated piezo-potential exceeds 3 V which originate from superior piezoelectric and mechanical properties demonstrating the piezocatalytic water splitting ability. In summary, these findings open new avenues for the development of piezo- and photocatalytic technologies for clean and sustainable hydrogen production.

Modulation of Structural, Electronic and Electrochemical Properties of Pulsed Laser Ablated Ruthenium Oxide Thin Films for Oxygen and Hydrogen Evolution Reactions Ikenna C. Chris-Okoro1; Sheilah Cherono1, Swapnil Nalawade1, Mengxin Liu1, Valentin Craciun1,2, Shayam Aravamudhan1, Maria D. Mihai2,3, Soyoung Kim4, Junko Yano4 and Dhananjay Kumar1,5

This study was supported by a DOE EFRC on the Center for Electrochemical Dynamics and Reactions on Surfaces (CEDARS) via grant # DE-SC0023415. The authors (IK, VC, and DK) also acknowledge the support of the NSF PREM via grant # DMR-2122067 PREM.

Enhanced Stability, Photoelectrochemical and Charge Transport Properties of TiO2-Coated CsPbBr3 Quantum Dots for Photoelectrochemical Solar Fuel Production Parvaneh Vas- Umnavy and Parina Nuket; Chulalongkorn University, Thailand

All-inorganic cesium lead bromide perovskite quantum dots (CsPbBr3 QDs) exhibit excellent optical and electrical properties such as strong light absorption, tunable band gap, long diffusion lengths, ambipolar charge transport, and high charge carrier mobility. Therefore, they have been widely used for light-energy conversion including photovoltaic (PV) and photoelectrochemical (PEC) applications. However, CsPbBr3 QDs have suffered from instability against the environmental factors in broad applications due to the inherent perovskite properties. This work thus
aimed for two purposes. The first is to enhance the stability of CsPbBr$_3$ QDs, and the second is to use CsPbBr$_3$ QDs as a light-harvesting material incorporated with TiO$_2$ electrode for PEC oxidation of methanol. For the first aspect, TiO$_2$ coating on CsPbBr$_3$ QDs by ex-situ and in-situ methods was performed to prevent the agglomeration of the nanocrystals and to improve the stability of CsPbBr$_3$ QDs without heat treatment at high temperatures. The stability test revealed that TiO$_2$-coated CsPbBr$_3$ QDs prepared from the in-situ method exhibited a significant stability improvement against toluene, ultrasonication treatment in water, and light illumination. Furthermore, the results demonstrated the remarkable enhancement of photocurrent generation due to a suitable alignment of energy levels of TiO$_2$ and CsPbBr$_3$ and a stable structure of QDs, which plays an important factor in improving the PEC performance. Therefore, it was proved to be used as a good light-harvesting and electrode material in various photoelectrochemical applications. For the second aspect, the photocurrent generation via PEC oxidation of methanol was studied using surface-modified TiO$_2$-coated fluorine-doped tin oxide (FTO) as a photoanode in combination with CsPbBr$_3$ QDs dispersed in an electrolyte solution. Detailed studies revealed that surface modification of the TiO$_2$ layer was crucial for good interfacial adhesion of CsPbBr$_3$ QDs, which were surrounded by hydrophobic ligands, with the TiO$_2$ surface. Self-assembled monolayers of octadecylphosphonic acid (ODPA) were applied on the TiO$_2$ surface, resulting in the change of hydrophilic nature to a superhydrophobic surface. The photoluminescence measurement of the ODPA-modified TiO$_2$/FTO photoanode demonstrated a significantly higher photoluminescence intensity than that of the unmodified one, indicating that CsPbBr$_3$ QDs were well adsorbed on the TiO$_2$ surface. The photocurrent was generated via methanol oxidation by holes in CsPbBr$_3$ QDs. The current-voltage measurements revealed that in the presence of methanol, the current density was increased from 1.2 mA/cm$^2$ (without methanol) to the maximum of 1.6 mA/cm$^2$ under visible light irradiation, indicating that methanol was a sacrificial hole scavenger. As a consequence, the multicomponent ODPA-modified TiO$_2$/FTO photoanode in combination with CsPbBr$_3$ QDs together with the efficient hole scavenger of methanol in the system has been shown to promote the PEC oxidation performance, which can be applied in any PEC solar fuel production.

5:00 PM EN05.10.17
Preparation of MOFs Coupled-LaFeO$_3$ Nanosheet for Electrochemical CO$_2$ Conversion
Ilhaaf Khan, Munzir H. Suliman and Muhammad Usman; King Fahd University of Petroleum and Minerals, Saudi Arabia

The rapid growth of modern industries has led to increased energy demand and worsened fossil fuel depletion resulting in global warming while organic pollutants pose significant threats to aquatic environments due to their stability, insolvency, and non-biodegradability. So, scientists are investigating high-performance materials to resolve these issues. In this study, we prepared LaFeO$_3$ nanosheets (LFONS) employing a solvothermal method via a soft template such as polyvinylpyrrolidone (PVP). The LFONS have good performance regarding surface area and charge separation as compared to LaFeO$_3$ nanoparticles (LFONP). To improve the efficiency of LFONS, it was further modified with Ag and ZIF-67 and utilized for CO$_2$ conversion. Herein, the results confirm that Ag-doped and ZIF-67 coupled LFONS (ZIF-67/LaFeO$_3$/Ag-LFONS) exhibit superior performance compared to pristine LFONP. In addition, the stability tests confirm that our optimal sample is the most active and stable among various nanocomposites. Ultimately, our studies will pave the new gateway for cost-effective, eco-friendly, and electroactive nanomaterials for CO$_2$ conversion.

5:00 PM EN05.10.18
Unveiling the Optimal Interfacial Synergy of Plasma Modulated Trimetallic Mn-Ni-Co Phosphides: Tailoring Deposition Ratio for Complementary Water Splitting
Nageh K. Allam; American University in Cairo, Egypt

Designing highly active, durable, and nonprecious metal-based bifunctional electrocatalysts for overall water electrolysis is of urgent scientific importance to realize sustainable hydrogen production, which remains a grand challenge. Herein, an innovative approach is demonstrated to synthesize flower-like 3D homogenous trimetallic Mn, Ni, Co phosphide catalysts directly on nickel foam via electrodeposition followed by plasma phosphidation. The electrochemical activity of the catalysts with varying Mn: Ni: Co ratios is assessed to identify the optimal composition, demonstrating that the equimolar trimetallic phosphide yields an outstanding HER catalytic performance with a current density of 10 mA/cm$^2$ at an ultra-low overpotential of $-14$ mV, outperforming the best-reported electrocatalysts. This is asserted by the DFT calculations, revealing a strong interaction of the metals and the P atom, resulting in enhanced water activation and optimized $G_{1e}$ values for the HER process. Moreover, this optimal composition appreciably catalyzes the OER by exposing more intrinsic active species in-situ formed on the catalyst surface during the OER. Therefore, the Mn$_{1}$-Ni$_{1}$-Co$_{1}$-P$_{1}$/NF catalyst exhibits a decreased overpotential of $-289$ mV at 10 mA/cm$^2$. More importantly, the electrocatalyst sustains perfect durability up to 48 h at a current density of 10 mA/cm$^2$ and continued 5000 cycling stability for both HER and OER. Meanwhile, the assembled MNC-P/NF[MNC-P/NF full water electrolyzer system attains an extremely low cell voltage of 1.48 V at 10 mA/cm$^2$. Significantly, the robust stability of the overall system results in remarkable current retention of ~96% after a continuous 50 h run. Therefore, this study provides a facile design and a scalable construction of superb bifunctional ternary MNC-phosphide electrocatalysts for efficient electrochemical energy production systems.

5:00 PM EN05.10.21
Empirical and Theoretical Investigations into the Mechanism of Wireless CO$_2$ Reduction over Modified g-C$_3$N$_4$ Photocatalyst
Mahmoud K. Hussien$^1$, Amr Sabbah$^1$, Putikam Raghunath$^2$, Shu-Chih Haw$^3$, Kuei-Hsien Chen$^4$ and Li-chyong Chen$^5$; $^1$National Taiwan University, Taiwan; $^2$National Yang Ming Chiao Tung University, Taiwan; $^3$National Synchrotron Radiation Research Center, Taiwan; $^4$Academia Sinica, Taiwan

The light-driven reduction of carbon dioxide holds promise for CO$_2$ mitigation and the conversion of CO$_2$ into valuable fuels and chemicals. While extensive efforts have been dedicated to elucidating the mechanistic aspects of photocatalytic CO$_2$RR, the majority of reported studies have primarily focused on liquid-phase reactions using metal-based photocatalysts. In this investigation, we systematically explore the water-vapor assisted CO$_2$RR employing a modified, metal-free g-C$_3$N$_4$-based photocatalyst without the incorporation of any cocatalyst, photosensitizer, or sacrificial reagent. Our approach utilizes In-Situ FTIR, DFT calculations, and operando XAS to deepen our understanding of the reaction mechanism. Furthermore, this study yields significant insights into the dynamics of charge carriers and the identification of active sites, thereby advancing our comprehension of the entire photocatalytic process.

SYMPOSIUM EN03

Sustainability of Emerging Photovoltaics
April 24 - April 25, 2024

Symposium Organizers
Juan-Pablo Correa-Baena, Georgia Institute of Technology
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Improvement of Optical Properties of CZTSSe-Based Solar Cells and Photocathode Devices via Cd Doping

Suyoung Jang and Jin Hyeok Kim; Chonnam National University, Korea (the Republic of)

C-s-ZnSn(S,Se)4 material is a material that replaces CusnGaSe2, which is currently being researched, and is attracting attention as an eco-friendly and economical material because it does not use indium or gallium. However, various studies are being conducted to improve CZTSSe devices due to their low solar cell efficiency and low hydrogen conversion efficiency in PEC water splitting. Among them, cation doping is known to significantly contribute to improving device performance by improving the optoelectrical properties of CZTSSe thin films. Cations doped into CZTSSe include various elements such as Ge, Cd, and Ag, and among these, Cd can be easily doped using the Chemical Bath Deposition method. Cd is doped into CZTSSe to control secondary phase and void formation, and when applied to a device, it improves photocurrent and improves light-hydrogen conversion efficiency. In this study, CZTSSe was doped with Cd by deposition time (9.5, 10.5, 11.5 minutes) using the CBD method to analyze its single thin film properties, and solar cells and PEC photocathodes were manufactured under the same conditions to measure device characteristics. As a result, the thin film sample doped with Cd for 11.5 minutes showed excellent photoelectric properties, solar cell efficiency was measured up to ~8%, and photocurrent was measured up to ~15 mA/cm2 as a PEC photocathode.

Perylene Diimide Derivatives with Various Ionic Functionalities as Cathode Interlayers for ZnO-Free Inverted Non-Fullerene Organic Solar Cells

Done Hwan Son; Rahmatia Fitri Binti Nasrun, Qurrotun Ayuni Khoirun Nisa, Indah Salma Sausan, Young-Seok Lee, Ka In Kang and Joo Hyun Kim; Pukyong National University Daeyeon Campus, Korea (the Republic of)

Perylene diimide (PDIN) derivatives, possessing various ionic functionalities, have been synthesized and utilized as cathode interlayers (CIL) in inverted-type non-fullerene organic solar cells (NFOSCs). CILs including polyfluorene derivatives and PDIN are commonly employed as prospective non-fullerene CILs due to their advantageous low-energy levels. However, the main drawback of PDIN derivatives is exhibiting strong aggregation, primarily due to their pronounced p-p stacking tendency, and this aggregation adversely impacts their morphology and transport characteristics. Therefore, it is necessary to modify the geometry with appropriate functional groups of PDIN derivatives to adjust the planarity of PDINs and control their energy level. In this study, we modified CILs based on PDIN derivatives for inverted NFOSCs. To our knowledge, perylene diimide featuring ammonium oxide as its terminal group (PDIN-O) was inserted between the active layer and the metal cathode, typically placed on top of the photovoltaic layer, in conventional OSCs. This positioning helped eliminate the need for heat treatment. To overcome the thermal issue, we modified PDIN by changing the side-chain functionality. We synthesized a series of materials based on PDIN with different terminals which are amino N-ethyl-iodo (PDIN-I), amino N-ethyl-bromo (PDIN-Br), amino N-butane sulfone (PDIN-BS), and amino N-oxide (PDIN-O). In our study, we introduced various counterions into the PDIN to examine their impact on photovoltaic performance to replace the ZnO layer. Inverted-type NFOSCs were constructed with the following configuration: ITO/PDIN derivatives/P666:Y6BO/MoO3/Ag. The reference device (ITO/ZnO/P666:Y6BO/MoO3/Ag) was also prepared for comparison to investigate the photovoltaic characteristics of PDIN derivatives in NFOSCs. The power conversion efficiency (PCE) of the inverted-type device utilizing PDIN-O is 12.5%, which is lower due to its poor thermal stability, with degradation starting at around 100°C. In contrast, devices employing PDIN-I, PDIN-Br, and PDIN-BS achieved PCE values of 15.5%, 15.0%, and 15.0%, respectively. These values are nearly identical to the PCE of the device employing ZnO (15.0%). The combined improvements of short circuit current (Jsc) and fill factor (FF) contribute significantly to the performance of the device. The highest PCE obtained is 15.5% achieved by PDIN-I as CIL which is slightly higher than the device based on Zno. This improvement is a result of the increase in the Jsc of 28.2 mA/cm2 from the device based on ZnO (25.9 mA/cm2). However, in terms of the FF of the device based on PDIN-Br showed a slightly lower value of 68.6% than that of the device based on ZnO (70.8%). Introducing the quaternary ammonium ion and zwitterion into the PDIN backbone enhanced the performance of the devices compared to a device based on PDIN-O. Expanding the size of the counter anion led to a reduction in the effective work function of ITO. The size of the counterion affects the magnitude of the interfacial dipole and results in increasing the device performance. In addition, these CILs retained their original PCE after 30 hours of thermal and photo-aging, proving their effectiveness as an oxygen-blocking layer at the device interface. This study demonstrates the capacity to regulate CIL and thus provides insight into the fabrication of low-temperature processible ZnO-free NFOSCs.

Physical Structure Effect of TiO2 Compact Layer for Enhanced Photoelectric Efficiencies

Chia-Yi Huang1 and Tz-Feng Lin2; 1,2; 1Tunghai University, Taiwan; 2Feng Chia University, Taiwan

One of the urgent challenges for sustainable energy is to hold the global warming back before 2050 in response to the global net-zero mission. An awareness of that is the green energy in demand and the use of solar energy would continue to cover the deficient of clean energy. Dye-sensitized solar cells (DSCs) would one of the promising photovoltaic technologies for renewable applications since 1990 in balancing an infrastructure cost and electricity production. This study fabricates a planar and stereo TiO2 compact layer on a fluoride-doped tin oxide glass substrate with a Pt layer. Photolithography and physical structural design were used to build planar and stereo structures. The Pt layer gives rise to the protrusive structure of the counter electrode by spattering and lift-off process. Then, porous semiconductor materials made of fine or coarse TiO2-nanoparticles was coated on the planar and stereo structure. Experimental results reveal that the photoelectric efficiency of the DSCs is higher than that of a DSCs without a specific physical structure one. As a result, the protrusive Pt layer not only can increase the photoelectric efficiencies of DSCs but also serves as a facilitated electron transport channels. In addition, this result was verified by the electrochemical impedance spectra of the two DSCs. The proposed method has advantages in easy fabrication of electrode structures with respect to acceptable production cost.

Assessment of Potential Environmental and Health Risks for Key Components of Solar Module

Hi Gyu Moon, Jong-Su Seo and Chang-Beom Park; Korea Institute of Toxicology, Korea (the Republic of)

To address the serious challenges of climate change and global energy security, investment in renewable energy sources has increased significantly in Asia, Europe and globally. Among them, wind and solar power plants are expected to make the largest contribution to global decarbonization, ranking first and second in projected capacity by 2050. To date, the development and improvement of photovoltaic technology based on energy storage technology has received considerable attention, but the potential environmental risks are still unknown. Additionally, there is currently insufficient toxicological and environmental risk information to assess potential risks. However, several studies have reported that lead, tin, cadmium, silicon, and copper, which are the main components of damaged products, are harmful to the ecosystem and human health when discharged to landfills. Therefore, we evaluated the toxicity and human risk of the main components of solar panels, including related research trends, and then propose optimal government policies for solar cell to protect the environment and the human body.
The solar photovoltaic (PV) energy has become a fast-growing competitive sector. Innovation is a prerequisite for the survival of many PV companies. In the last years, the perovskite solar cells has gained much attention in the solar community because of the high efficiencies obtained in single and multi-junction devices and low fabrication projected cost. Due to the massive scale of the energy sector, it is essential that this new emerging PV technology progresses in a way that is consistent with the requirements of sustainable development before large scale deployment.

Sustainability is defined as an interaction between economic, social, technical and environmental criteria. Nevertheless, R&D activities are often focused on technical and economic improvements as a priority to enter the market. In addition, the limitations of current eco-design tools, as identified in the literature, hinder their adoption by R&D organizations. In fact, environmental impact assessment is relatively complex for a non-mature technology under development because its characteristics and manufacturing processes are not yet fully defined. Life Cycle Assessment (LCA) is a reliable environmental assessment tool, but it is limited to the evaluation of the investigated technology without proposing eco-design alternatives.

This study proposes a methodology to provide eco-design strategies from the earliest stages of design to develop sustainable all-perovskite tandem technology. In the research stage, the device architecture is often not defined yet. Therefore, we start with a review of the existing LCA studies on perovskite solar cells to identify the hotspots from an environmental point of view. Then, the list of the reported materials that could be used for the solar cell, including packaging materials, is defined. We analyze this list from an environmental point of view based on results obtained from the literature and legislative constraints. Finally, we propose eco-design guidelines that could reduce the cost, increase the performance, and decrease the environmental impact for the development of a sustainable perovskite tandem solar cell technology.

Based on this approach, key recommendations toward a sustainable perovskite tandem technology are:

1. For the metal electrodes, copper should replace silver for economic and environmental criteria. However, there are few studies in the literature on its technical reliability.

2. The challenges addressed by this recycling process are i) green solvent recycling development, ii) complex perovskite composition separation and recovery (with a focus on lead recovery and reuse), and iii) functional layer recovery.

These recommendations will help to guide technological choices from the early design process to ensure the development of sustainable perovskite tandem technology.

5:00 PM EN03.13.02

Breaking News on Highly Efficient Inorganic Tin-Lead Perovskite Solar Cells

Timo Zhang¹, Feng Qian¹, Shihao Yuan¹, Zhi D. Chen² and Shihbin Li¹;
¹University of Electronic Science and Technology of China, China; ²University of Kentucky, United States

To date, hybrid lead halide perovskite (LHP) solar cells have achieved great advances on a PCE from 3.8%1 to an impressive certified value of 26.1%2 within fourteen years. Despite the high efficiency of state-of-the-art lead-based perovskite solar cells is approaching the market-dominant silicon photovoltaic technology, they still face two concerns, e.g. poisonous Pb and non-ideal situ characterizations as well as molecular dynamics calculations6. Then, a novel synchronous alloying process is developed using a novel Sn-perovskite-targeted crystallization regulator. The provide guidance of the solidification process of cesium tin-lead perovskites and therefore high optoelectronic films and devices.

Inorganic tin-lead perovskites have been investigated with low excitation energy, high charge mobility, high absorption coefficients and thermal stability. Encouraged by these outstanding properties, lead-rich CsPb0.9Sn0.1IBr2 PSCs with a wide bandgap of 1.79 eV were first reported in 20174, which obtained an efficiency of 11.33%; up to 2023, Zhang et al. reported a record PCE of 17.19% based on low-bandgap (1.34 eV) CsPb0.7Sn0.3I3 PSCs via a post treatment method5. As seen from the simple development of inorganic Pb-Sn PSCs progress, the PCE still lags far behind their Pb-based analogs and SnPb hybrid counterparts and the origin remains unclear. In addition to the common challenges of easy oxidation of Sn5, crystalization regulation has been crucial yet less explored in low-bandgap CsPbSn0.9I3.1 PSCs. This could be ascribed to the lower enthalpy of the CsI in comparison with MA+ or FA+, which endows the crystalization kinetics quite different from their hybrid counterparts. It is thus imperative to acquire in-depth understanding of the unique crystalization dynamics of cesium tin-lead perovskites, which would provide guidance of the solidification process of cesium tin-lead perovskites and therefore high optoelectronic films and devices.

In this breaking news, for the first time, Shihbin Li and colleagues propose the B-site initiated asynchronous crystalization of inorganic tin-lead halide perovskites by comprehensive in-situ and ex-situ characterizations as well as molecular dynamics calculations. Then, a novel synchronous alloying process is developed using a novel Sn-perovskite-targeted crystalization regulator. The regulator suppresses the asynchronous crystalization by enhancing the formation barrier energy of CsSnI3, endowing a synchronous Sn and Pb alloying reaction in precursor film, achieving a homogeneous film after the annealing process. Finally, a record-high PCE of 17.55% is obtained for modified CsPb0.9Sn0.1I3 solar cells, in a sharp contrast to the control device which shows a PCE of 3.6%. More importantly, B-site synchronous targeted alloying devices show improved stability with negligible degradation even at 65 °C over 3500 h for the net films or under continuous LED illumination for 700 h.

Research on Pb-Sn alloyed perovskites mostly focuses on the anti-oxidation of tin and is still at a relatively early stage, but the work of Shihbin Li and colleagues provides a valuable B-site initiated synchronous crystalization approach to create highly efficient PSCs. Their proposed approach would be applicable to other high-performance and stable optoelectronic devices based on Pb-Sn alloyed perovskite.

Reference


5:00 PM EN03.13.03

Theoretical Guided Material and Interface Optimization for High Performance Perovskite/Organic Tandem Solar Cells

Zongzong Zhu; City University of Hong Kong, Hong Kong

Addressing the pressing challenges of rising global energy needs and achieving carbon neutrality to protect the environment necessitates the development of a practical solution. The emergence of solution-processed organic and metal halide perovskite semiconductors, and their resultant solar cells, could potentially instigate a revolution in photovoltaic technology, enabling the delivery of scalable, high-performance green solar energy production. Despite the power conversion efficiencies of both single-junction organic solar cells and perovskite solar cells rapidly reaching over 19% and 26% respectively, their maximum efficiency is confined to around 30% as per the Shockley-Queisser model for single-junction devices. However, by fabricating a multi-junction device with multiple light absorbers possessing significantly varied bandgaps, the efficiency of solar cells could potentially be augmented to over 40%.

In this talk, we will introduce high-performance monolithic perovskite/organic tandem solar cells with PCE=26%. These encompass a wide bandgap perovskite front cell and a narrow bandgap organic rear cell connected via a recombination junction. We have selected wide bandgap perovskite solar cells for the front cell due to their robust absorption for visible light, minimal voltage loss, and superior photostability. Meanwhile, narrow bandgap organic solar cells could potentially offer superior near-infrared absorption tunability and stability, making them ideal candidates for the rear cell of the tandem cells. To demonstrate the potential of perovskite/organic tandem solar cells, we employ an integrated strategy that combines materials, interface, optical, and process engineering.

5:00 PM EN03.13.05

Stable and Efficient Halide Perovskite Solar Cells by Using Guanidinium-Incorporated Quasi-2D Perovskite Layer

Matthew T. Bamidele and Do Young Kim; Oklahoma State University, United States

Halide perovskite solar cells are a rising star in the photovoltaic community due to their remarkable performance and rapid progress. Solution processability of hybrid perovskite...
semiconductors makes these materials especially attractive for low cost and scalable manufacturing. While halide perovskite solar cells already show remarkable improvement with a power conversion efficiency above 25%, poor stability under ambient environmental conditions of heat, humidity, and light is the major issue hindering the commercialization of this technology. Layered two-dimensional (2D) perovskites have been extensively investigated for improving the stability of perovskite solar cells while sacrificing efficiency. In this study, we have explored pathways to improve the stability of perovskite solar cells while maintaining their efficiency by using a 2D perovskite layer. First, halide perovskite solar cells using quasi-2D guanidinium-based halide perovskites synthesized with lead acetate (PbAc) have higher efficiency and stability compared to perovskite solar cells with quasi-2D perovskite synthesized from traditional lead iodide (Pbl). This is due to a characteristic perpendicular orientation of the quasi-2D perovskite crystal structure, which can facilitate charge extraction. The power conversion efficiency of quasi-2D perovskite solar cells using PbAc is approximately two times higher than solar cells using PbI₂. Another intriguing aspect of guanidinium-based quasi-2D perovskite solar cells is a continuous improvement in efficiency that spans several weeks. This observed enhancement is attributed to age-induced recrystallization, showcasing the material's potential for prolonged stability and delay in the onset of device degradation. As a result, the quasi-2D perovskite solar cells maintained almost the same performance even after 3,000 hours. Also, we present an alternative approach that improves the performance of halide perovskite solar cells by introducing an orderly stacking of MAPbI₃ film as a 3D halide perovskite light-harvesting layer on top of a quasi-2D Ga₄MA₅Pb₁₆I₃₆ halide perovskite layer. The power conversion efficiency of quasi-2D/3D perovskite solar cells is approximately 20% higher than that observed for 3D perovskite-based solar cells fabricated under the same conditions. The observed improvement is attributed to the superior crystallinity and excellent film quality achieved by the coherent stacking of 3D MAPbI₃ on top of quasi-2D Ga₄MA₅Pb₁₆I₃₆ perovskites. Additionally, the improved photovoltaic performance of these quasi-2D/3D perovskite solar cells does not compromise their durability. Even after 1,900 hours of storage, the devices maintained about 98% of their initial performance.

SESSION EN06.04/EN03.04: Joint Session: Advances in Solution Processed Photovoltaics
Session Chair: Ian Marius Peters
Wednesday Morning, April 24, 2024
Room 333, Level 3, Summit

8:15 AM EN06.04/EN03.04.01
Biocarbon from Algae, Cellulose and Sewage Sludge as Sustainable Composites for Energy Storage Theotime Béguerie,1 Amel Cédric Ghojia,1 Lina Maria Romero Milliana,1 Shamala Gowri Krishnan,1 Majd El Saddik,2 Elsa Weiss,1 Claire White2,2 Kuo Zeng,3 and Anež Nizhov3,2
1Université de Toulouse, France; 2Princeton University, United States; 3Huzhou University of Science & Technology, China

This presentation will discuss the synthesis, characterization, and utilization of a novel family of biocarbon-based composites for electrochemical and heat storage. The composites are produced by the pyrolysis and carbonization of various biomass (algae, cellulose biomass, and municipal sewage sludge) inherently containing or doped with catalytic metal such as Iron and Calcium at lower temperature (<1400°C) than the standard carbonization temperature (>1800°C) or processed with molten salt (Na2CO3-K2CO3). In this process, the biocarbon is transformed from a randomly organized carbon to a graphite-like material (organized and structured carbon) showing a high graphene rate structure. The Carbon structure and composition changes in the composites have been investigated from nano to bulk scales in combining XRD, HRTEM and Raman. This has enabled to probe changes in biocarbon nanostructure and crystalline graphite domains catalyzed by the inclusion of metal such as iron and Calcium. The encapsulation of iron particles by graphitic phase (graphene sheets) and the carbon-metal bonding during the pyrolysis and carbonization were uncovered using XPS. Key properties for energy storage applications such as the remanent magnetization, the coercive field, the specific heat, the thermal and electrical conductivities, the thermal stability including the mechanical properties will be discussed. Biocarbon from algae for example, rich in nitrogen showed a high specific surface area of 209.26 m²/g with high specific capacitance of 230.2 F/g at 0.25 A/g and a capacitance retention of 75.54% at 2 A/g. This work provides a green and promising approach to produce heteroatom-doped capacitive biocarbon with superior properties for energy storage.

8:45 AM EN06.04/EN03.04.02
Heterospinital Crystal Growth of Halide Perovskite for n-i-p Structure Yun-Kyeang Hong, Sanghee Yang and Hui-Seon Kim; Inha University, Korea (the Republic of)

Perovskite solar cells (PSCs) have rapidly achieved high power conversion efficiency since its first solid-state application in 2012, leading to an outstanding PCE of 26.1% in 2023. Nevertheless, the stability issue still hinders the commercialization. While the chemical composition of perovskite material has been carefully engineered to extract the best optoelectronic properties and the phase stability as well, the lattice strain has recently emerged as one of the key parameters determining the phase stability of perovskite film. Here we employ an interlayer, formamidinium tin halides (FASnCl₃Br₂), between SnO₂ (electron transport layer) and perovskite, where the heterospinital crystal growth of perovskite film on the interlayer is enabled by tuning its lattice distance (d), ranging from 0.342 nm (FASnCl₃Br₂) to 0.365 nm (FASnBr₃), as evidenced by transmission electron microscopy. While the large difference in d between the interlayer and the perovskite film (~10%) negligibly affect the crystal growth, the smaller mismatch in d (<10%) affects the perovskite crystal growth and thus leads to a strain relaxation at the interface of perovskite film. Therefore, the resulted relaxation of tensile strain at the bottom interface of perovskite film is comparably beneficial for the phase stability of n-FAPbI₃, though 2% in-plane residual tensile strain is still remaining, which is in accordance with the monitored film stability in ambient air. Kelvin probe force microscopy is also measured to elucidate the effect of FASnCl₃Br₂ interlayer on energy level alignment, where the changed band bending, coupled with defect reduction, at the interface is likely responsible for the enhanced recombination resistance and open-circuit voltage of PSCs.

9:00 AM EN06.04/EN03.04.03
New Dopant for FAPbI₃ Film in Perovskite Solar Cells Ju-Hye Choi1, Yu-Na Kim,2 and Hui-Seon Kim1,1; Inha University, Korea (the Republic of); 2Korea Institute of Energy Research, Korea (the Republic of)

A great effort has been made on the chemical composition of perovskite film in perovskite solar cells (PSCs), where formamidinium lead iodide (FAPbI₃) recently achieved the highest power conversion efficiency (PCE) of 26.1% in 2023. One of the most important challenges is securing the phase stability of FAPbI₃, which is prone to convert from α-phase to δ-phase without additive engineering. Therefore, additive plays an important role in FAPbI₃ not only by affecting the phase stability via interaction in the grown lattice but also by controlling the crystal growth through interaction with precursors. In this study we incorporate hydroxylammonium formate (HAHCOO) in the perovskite precursors for FAPbI₃, coupled with methylammonium chloride. Fourier transform-infrared spectroscopy reveals that lone pairs in HA⁺ and HCOO⁻ act as Lewis base and interact with Pb⁺ as Lewis acid in perovskite precursors and leads to increased grain size (~1500 nm) and uniformity (1500 nm of FWHM), as evidenced in scanning electron microscope images. In the meantime, HA⁺ is assumed to substitute for FA⁺ because the ionic radius of HA⁺ (0.216 nm) ranges between methylammonium cation (MA⁺, 0.18 nm) and FA⁺ (0.22 nm), which is indirectly evidenced with a variation in binding energy from x-ray photoelectron spectroscopy measurement. On the other hand, HCOO⁻ acts as an anion vacancy passivator at grain boundaries and top surface and closely correlates with the increased surface recombination resistance of PSCs. The inclusion of new additive, HAHCOO, therefore successfully leads to PCE increase from 18.9% to 20.1% with an increased long-term stability.

9:15 AM EN06.04/EN03.04.04
Organic Photovoltaic Materials: Decreasing Synthetic Complexity through Scalable “Cascade” Approaches Dario Pasini, Andrea Nitti, Riccardo Pož̋ and Gabriele Bianchi
1University of Pavia, Italy; 2Eni S.p.A., Italy

Organic electronic materials offer advantages such as flexibility, low cost, and easy processability using simple solution processing methods. They are π-extended organic compounds and polymers with simultaneously processable properties, typically obtained through linear and multi-step synthetic approaches. Such approaches have yielded highly performing compounds and polymers through complex, multi-step synthesis, limiting their scalability for industrial applications. Sustainability and scalability of the synthetic process plays a fundamental role for definitive conservation of the organic electronic materials, and generally they depend on: (a) the number of synthetic steps; (b) the cost of the materials; (c) yields; (d) the number of steps of purification that require column chromatography. A unique parameter (synthetic complexity, SC) have been recently proposed to rationalize the field of materials used in the Organic Photovoltaic arena (OPV)1. In this contribution, we will report recent developments on the use of “cascade” reaction protocols to address annihilations and formation of π-extended polymers for OPV. Such protocol can be a one-pot cascade reaction in a single and double annulation fashion. ADT and BDT derivatives were incorporated into polymers and the properties of bulk-heterojunction solar cells will be presented.

Final Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Follow-up: Recycling and Recycling in Perovskite Solar Cells

Kai Zhu; National Renewable Energy Laboratory, United States

Organic-inorganic hybrid halide perovskites have rapidly become a focal point of the photovoltaic (PV) community as a promising next-generation PV technology. The certified efficiencies of single-junction perovskite solar cells (PSCs) and perovskite-based tandem cells have reached 26.1% and 33.7%, respectively. However, all of the current state-of-the-art perovskite-based PV devices contain lead (Pb) ions. The toxic Pb could pose a potential threat to the environment and public health. To address this potential challenge for future market adoption of perovskite PV technologies, we need to develop proper Pb management strategies for both perovskite devices in operation and those at the end-of-life. In this talk, I will first provide an overview of the potential Pb toxicity issue and some common strategies to address it. Then I will present our recent studies in this research area. Specifically, I will discuss our efforts on developing on-device Pb sequestration to prevent the leakage of Pb ions from broken perovskite PV devices under severe weather conditions. I will also discuss how to make our Pb sequestration approach scalable for industrial applications. In addition, I will discuss our efforts on recycling Pb from end-of-life perovskite PV devices. Finally, I will present our perspective on making perovskite PV a sustainable technology.
Our analyses emphasize the importance of examining a suite of metrics to identify priorities and tradeoffs, and inform design or lifecycle management decisions holistically. Previous analyses have demonstrated the central importance of PV module lifetime to support energy transition while minimizing impacts. High levels of material circularity (>90%) enable minimizing lifecycle wastes, can reduce virgin material demands if paired with improving efficiency, but demonstrate tradeoffs in energy return on investment. In the fervor of new material and technology development, it is important to remember that CE is not the end goal; decarbonization and energy transition are the end goal. CE should be used in service to improve the sustainability of PV, and R-actions evaluated for their usefulness and efficacy to this end.

2:00 PM EN06.06/EN03.06.02
Novel Mechano-Chemical Approach to Achieve Rapid Delamination of Glass from Solar Panels Ankita Ankit, Jeremy K. Ang, Ying Sim and Nripan Mathews; Nanyang Technological University, Singapore

With growing global cumulative photovoltaics (PV) installation, end-of-life (EoL) PV panels are expected to grow as well, with reports predicting this number to reach 78 million tonnes by 2050. This huge amount of PV waste does not only present a looming environmental challenge but also an opportunity to recover valuable materials embedded in the panels.

Different generations of PV technologies (1st Gen - Crystalline silicon (c-Si), 2nd Gen - Thin film (CIGS, CdTe) and 3rd Gen - Emerging PV (Perovskite, Bifacial)) have presence in the market currently. Out of all of these technologies, c-Si modules have the largest market share. Irrespective of their differences, the device stack for these PV technologies follows a sandwich structure, with the active layer (comprising metals and semiconductors) layered between polymeric encapsulants and glass. These insulating layers ensure a longer lifetime for panels in the field.

However, the same device structure creates challenges to recover valuable materials efficiently. Different approaches have been developed to separate the layers of solar panels. Thermal approaches burn the polymeric layers. However, they can produce toxic gases and affect the purity of active layer materials. Mechanical approaches crush the panel and sieve into different fractions. However, that often leads to undesired cross-contamination and affects the output yield and quality. Chemical approaches can give high output yield and purity and rely on dissolution of the polymeric encapsulant to separate the layers. However, they can take a long time (up to 7 days) making it less attractive.

Herein, we report a novel mechano-chemical approach that relies on weakening of bonds between glass layer and encapsulant layer through use of a green solvent. Cleaving of glass from the solar panels is achieved through mechanical processing. This process achieves rapid delamination of glass from solar panels (<4 hours) and high purity (>98%) glass cullet, while providing access to the active layer of the panel. The process has been demonstrated for c-Si panels and can be translated to different generations of solar panels.

2:15 PM EN06.06/EN03.06.03
From Lead Bullets to Solar Cells: A Two-Step Approach to Repurpose Contaminated Lead Misha Sytnyk, Zhenni Wu, Jiyan Zhang, Benfang Niu, Jens Hauch, Christoph J. Brabec, Ian Marius Peters and Albert These; 1Forschungszentrum Jülich GmbH, Germany; 2Friedrich-Alexander-University Erlangen-Nuremberg (FAU), Germany

Lead perovskite solar cells have emerged as a groundbreaking technology. The unique properties of lead perovskite materials, such as their high absorption coefficient and tunable bandgap, allow them to be ideal candidates for next-generation photovoltaic applications. Despite their promise, perovskite solar cells pose environmental concerns, particularly in the recycling and sourcing of lead halides. Conventional methods of lead extraction and processing contribute to ecological degradation. To address these challenges, this research proposes a sustainable solution grounded in the principles of a circular economy, aiming to repurpose lead waste into valuable materials for solar cell fabrication.

The environmental challenge posed by lead waste is twofold. On the one hand, there is the potential for lead waste from the burgeoning perovskite industry. On the other, there are existing sources of lead waste, such as metal plating industry, mining industry, homes built before 1986, lead-acid batteries, that are highly contaminated and pose a long-standing environmental hazard.

It’s important to note that even so-called “lead-free” plumbing may contain up to 8 percent lead. Our approach is a two-step process designed to tackle this issue head-on. The first step involves a novel electrochemical method that will be presented in detail at the conference to convert contaminated lead into lead iodide (PbI2). As the lead waste source, we utilized XVII century lead bullet balls. The electrochemical recovery process is robust, accommodating a wide range of contaminants including the 15% Carbon, 10% Oxygen, 0.5% Silicon, 1% Bismuth, 1% Copper, and 1% Zinc we found in the bullets. Remarkably, the process achieves a Faradaic efficiency close to 1, indicating near-complete conversion of lead to PbI2.

The second step involves further purification of the synthesized PbI2 through single-crystal growth. This results in a 35% yield of pure PbI2, with the remaining material being recyclable for subsequent purification loops. The synthesized PbI2 is not only suitable for immediate use in solar cells but has also been successfully utilized to fabricate a working solar cell. Additionally, it offers a high yield rate of approximately 1g per hour. This yield rate is scalable by simply increasing the electrode area, making the process suitable for industrial applications. This research has far-reaching implications. It not only addresses the immediate problem of recycling perovskite solar cells for a circular economy but also offers a viable solution to the broader issue of lead waste management. By converting contaminated lead into a valuable material for efficient perovskite solar cell fabrication, we can potentially eliminate both current and future concerns related to lead waste.
Scalable Routes to Functional Materials: Photocatalytic, TCO and Anti-Soiling Coatings Claire Carmalt and Mingyue Wang; University College London, United Kingdom

The search for efficient materials for sustainable infrastructure is a key challenge to address the global environmental crisis. Sunlight-activated coatings, particularly those produced from scalable technologies, are sought in the glass industry for applications in self-cleaning windows. Current research involves developing processes towards sustainable and inexpensive functional materials including photocatalysts, anti-soiling coatings, transparent conducting oxides (TCOs) and photoelectrochemical films on float glass. For example, we have been developing sustainable up-scaled routes to TCO materials from precursors containing earth abundant elements (titanium, aluminium, zinc) with equivalent or better figures of merit to existing TCOs. Our method uses aerosol assisted chemical vapour deposition (AACCVD) to develop large scale coatings. Compared to conventional CVD, the AACVD method uses aerosol droplets to transport precursors, with the aid of an inert carrier gases. Therefore, in AACVD volatility is no longer crucial and this allows for a wider choice of precursors being available for use and can lead to high quality films at low cost.

Recent work has also investigated a range of bismuth-based materials for a number of applications. For example, adherent coatings of phenethylammonium bismuth iodide have been deposited via AACVD. The film morphology was found to depend on the deposition conditions and substrates, resulting in different optical properties to those reported from their spin-coated counterparts. Bulk photovoltaics, SNX ($X = \text{Cl}, \text{Br}, \text{I}$), are of interest in a range of applications including photocatalytic (PEC) sensing, pollutant degradation and water splitting, with particular focus as emerging materials in photocatalytic applications. We recently reported visible-light-active iodide-doped BOBr thin films fabricated via AACVD. The impact of dopant concentration on the structural, morphological, and optical properties was studied and the photocatalytic properties of films were evaluated. An optimized material was identified as containing 2.7 atom% iodide dopant. We have also synthesised B0I and ZnO heterojunction materials. It was found that the BOI/ZnO structure was far less active towards PEC water oxidation, while the ZnO/BoI heterojunction showed a significant enhancement in activity compared with their parent materials. The ZnO/BoI heterojunction, with a 120 nm thick ZnO film, exhibited the best PEC performance through studying the influence of the ZnO film thickness and deposition temperature.

AACVD has also been used to develop thin films of other functional materials, including processes towards sustainable and inexpensive anti-soiling coating on float glass and photocatalytic films.

References:

Efficiency Improvement Method by Light and Dark Soaking for CdSe$_x$Te$_{1-x}$ Thin-Film Solar Cells through Novel In-Situ Dopant Profiling Sanghyun Lee$^1$ and Kent Price$^2$.

$^1$University of Kentucky, United States; $^2$Morehead State University, United States

Cd2mium Telluride (CdTe) thin-film solar cells have shown remarkable efficiency and durability in the past decade, with over 22.1% in laboratory-scale tests, close to the theoretical Shockley-Queisser limit of 30%. Furthermore, they have also been widely deployed in commercial applications, with more than 30GW of modules installed worldwide. CdTe is the leading thin-film technology for cost-effective solar energy production due to its low fabrication costs, high-power conversion efficiency, reasonable long-term performance stability, and low-energy payback time. Recently, researchers have explored the use of Se to create band grading in addition to or as a replacement for CdS. CdSe$_x$Te$_{1-x}$ is a promising material with bandgap lowering below 1.4 eV, which allows the short-circuit-current (Jsc) to approach its theoretical limit. For a long period, CdS was regarded as a crucial component for achieving high performance. Cells made without CdS (i.e. a direct CdTe junction to the transparent conducting oxide electrode) exhibit very low open circuit voltages (Voc and fill factors (FF), implying that the CdTe/oxide interface is inferior. Although CdS has a benefit in that intermixing the lattice mismatch at the interface, this approach has a drawback: it also reduces the photocurrent by absorbing light in the 300 - 525 nm range. This means less light reaches the active layer of the solar cell, resulting in efficiency loss. Hence, recent efficiency improvement has focused on introducing Se to create band grading either in addition to or as a replacement for CdS. CdSe$_x$Te$_{1-x}$ is promising, with bandgap lowering below 1.4 eV, enabling Jsc to be close to its theoretical limit.

In this study, we have fabricated CdSe$_x$Te$_{1-x}$ devices by vapor transport technology (VTD) and investigated the detailed improvement mechanism of efficiency improvement through in-situ Cu dopant profiling under various light and dark soak conditions. Moreover, devices were stressed at elevated temperatures simultaneously under various bias conditions, both with illumination and in the dark. During light soaking, different intensities of light and wavelengths were tested to characterize devices. In addition, we modeled the result with our in-house MATLAB modeling suites, which we developed in our group to understand the efficiency improvement mechanism. Connected to external TCAD simulators (Synopsys Sentaurus), we modeled and explained the results with different input parameters based on the in-situ profiling results. The results indicate that CdSe$_x$Te$_{1-x}$ devices have shallow donor and acceptor energy states near the main front junction interface, and acceptor activation energy (EA) is approximately 0.3 – 0.4 eV based on light and voltage-biased quantum efficiency at different temperatures. The Cu dopant concentration is approximately 5 x 10$^{-4}$ cm$^{-2}$ under no bias conditions. However, a peak doping concentration evolves toward the front CdSe$_x$Te$_{1-x}$junction during in-situ measurements. The weak blue light (0.01 sun at 450 nm) can dramatically improve the carrier collection as compared to the same intensity of red light (660 nm). Interestingly, the stability of CdSe$_x$Te$_{1-x}$ solar cells was found to be bias-dependent and device-specific during light and dark soaking. CdSe$_x$Te$_{1-x}$ devices without Cu dopant demonstrated a reduction of depletion width under voltage and light-biased conditions. The depletion width of CdSe$_x$Te$_{1-x}$ devices without Cu is reduced to approximately 24% under applied voltage biases and dark soaking conditions as compared to no bias condition, while efficiency, Jsc, and Voc decreased. Under light soaking conditions at 85°C, the increase in Voc and efficiency depends on the thickness of CdSe deposition thickness.

Efficiency Improvement Method by Light and Dark Soaking for CdSe$_x$Te$_{1-x}$ Thin-Film Solar Cells through Novel In-Situ Dopant Profiling Sanghyun Lee$^1$ and Kent Price$^2$.

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One of the biggest difficulties in the commercialization of perovskite solar cells (PSCs) lies in their charge transport layers. Charge transport materials are needed to achieve high performance with PSCs, but hole transporting materials (HTM) and electron transporting materials (ETM) used in high-performance lab-scale PSCs are relatively high-cost. Meanwhile, high-performance HTMs typically require the use of dopants that are detrimental to cell stability, while the commonly used metal oxide ETLs suffer from low electron mobility and photo-generated oxygen vacancies, which result in photocurrent hysteresis and serious interface recombination that affects the performance of the device.

Carbon-based materials, in particular carbon nanoflakes (CNF) and carbon quantum dots (CQD), have been increasingly used in charge transport layers and electrodes for PSCs. There are practically limitless possibilities of designing such materials with different sizes, shapes and functional groups, which allows modulating their properties such as band alignment and charge transport. Solid-state packing further modifies these properties. However, there is still limited insight into electronic properties of this type of materials as a function of their chemical composition, structure, and packing.

Here, we study the dependence of band alignment and charge transport characteristics on chemical composition and structure of commonly accessible types of nanoflakes and functional groups and further consider the effect of their solid-state packing. We use a combination of density functional theory (DFT) and density-functional-based tight binding (DFTB) to get electronic structure level of insight at scales relevant to experiments. We find that CNFs must have sizes as small as 1.3 nm to provide band alignments suitable for their use as hole transport materials with the commonly used MAPb[I]$_3$, certain functional groups are able to change the band alignment so strongly that the same carbon nanoflake might act as either hole transport material or electron transport material. We show that both the shape of the CNF and inter-flake interactions can significantly modify band alignment by more than half an eV; solid-state packing has a moderate effect on HOMO of less than half an eV, whereas the effect on LUMO can be on the order of one eV.

Control of the electrochemical conditions tuning C2CNT® to selectively produce 17 unusual nanocarbons is described in: "Controlled Growth of Unusual Nanocarbon Allotropes by Molten Electrolysis of CO$_2$", Liu, Licht, Wang, Licht, Catalysis, 12, 125, 2022.

The Genesis Device®: A Revolution in Large Scale Decarbonization Stuart Licht$^{1,3}$; 1George Washington University, United States; 2Carbon Corp, Canada; 3C2CNT LLC, United States.

C2CNT® is a highly stable molecule. This stability has been considered an insurmountable barrier to Its transformative removal from its role as a greenhouse case. The C2CNT® (CO$_2$ To Carbon Nanomaterial Technology) process breaks through this barrier by using an energetic (high temperature), carbon rich (molten carbonate), transition metal nucleated environment, electrolytically splitting of CO$_2$ to graphite carbon nanomaterials (and O$_2$). Built from the same fundamental graphene structure as graphite, which has a geologic lifetime, these nanocarbon products can permanently bind the transformed CO$_2$ to mitigate global warming. Their value arises from the properties of graphene such as high strength and conductivity, solid lubrication, electronic and catalytic activity tuned by distinctive 0D, 1D and 2D morphologies.

The value of these nano graphitic carbons arises from the unique properties of graphene such as exceptional strength, high conductivity, solid lubrication, electronic and catalytic activity as modified by their distinctive 0D, 1D and 2D shapes. These nanocarbons are useful in a range of applications in the carbon fiber, polymer, electronic, medical, transportation, steel, cement and power sectors.


A C2CNT® process® Genesis Device® CCUS demonstration using the has been built in Calgary, and a large-scale Genesis Device® CCUS plant, the GC3 project, is scheduled in Edmonton, producing 7,500 tonnes of carbon nanotubes transforming the CO$_2$ emission at the Genesee power plant. Some of the 30 C2CNT® related publications are presented at: https://carboncorp.org/climate-change-solution/

These publications include:


"Dee Materials Sustainability": From Sourcing, to The Use Phase, to End-Of-Life Vanni Lucchi, University of Trieste, Italy

For a material to be truly sustainable, all phases of the material’s life cycle should be sustainable: sourcing, manufacturing, transport, use, End-of-Life (EoL). In this contribution, I will introduce the concept of “Deep Materials Sustainability”, where all phases of the life cycle are addressed simultaneously, and will discuss some examples. The ideal case is one where a material is synthesized through a sustainable process utilizing renewable and/or recycled material sources, it minimizes the transport phase impact (e.g. by being
A self-cleaning effect can be achieved using superhydrophobic surfaces (i.e., water contact angle > 150°) through the Lotus effect, where water droplets can remove contaminants back by the necessary inclusion of a high-temperature, long-duration curing process to produce high-performance thermoelectric (TE) films. This work investigates the synergistic effect of four Additive manufacturing has been investigated as a more time, energy, and cost-efficient method for fabricating thermoelectric generators (TEGs). Early results have been promising but are held back by the necessary inclusion of a high-temperature, long-duration curing process to produce high-performance thermoelectric (TE) films. This work investigates the synergetic effect of four factors – a small amount of chitosan binder (0.05%wt.), a heterogeneous particle size distribution, the application of mechanical pressure, and thickness variation – on the performance of Pb0.53Sn0.47Te (p-BST) and Nb2Te5–Sn0.5Te (n-BTS) TE composite films. The combination of these four factors controls the micro and nanostructure of the films to decouple their electrical and thermal conductivity effectively. This resulted in figures of merit (ZT) of 0.89 and 0.5 for p-BST and n-BTS, respectively comparable to other additive manufacturing methods despite eliminating the high-temperature, long-duration curing process. The process was also used to fabricate a 6-couple TEG device which could generate 357.6 μW with a power density of 5.0 mW/cm² at a temperature difference of 40 K. The device demonstrated air stability and flexiblity for 1000 cycles of bending. Finally, the device was integrated with a voltage step-up converter to power a LED and discharge capacitor at a temperature difference of 17 K, demonstrating its applicability as a self-sufficient power source. Deepa Madan; University of Maryland, United States

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High Performance Flexible and Scalable Thermoelectric Device and its Application as a Self-Sufficient Power Supply for Wearable Electronic Devices Deepa Madan; University of Maryland, United States

Functional thermoelectric devices offer a direct and highly efficient approach for converting heat into electricity, relying on two key factors: Carnot efficiency and the materials-dependent property, ZT. In the last two decades, tremendous efforts have been made to develop high ZT thermoelectric materials, and the bulk ZT has reached above 3. Energy converters for renewable or sustainable energy technologies have to be based on materials that are not a burden to the environment, do not contain critical elements and guarantee a short energy payback time. Besides improving the conversion efficiency and other performance factors, sustainability has to be considered when designing novel thermoelectric materials and devices. In this talk, we will introduce novel synthesis strategies for oxide and silicon-based thermoelectric materials. We will delve into the concept of Entropy Engineering, a method that can extend the lifetime of (oxide) thermoelectric materials. Moreover, we will showcase one example where waste Si from the solar cell industry is transformed into valuable products, specifically in the synthesis of MnSi1.5 alloy. This underscores the potential to convert waste into valuable resources, contributing to both sustainable energy and responsible material usage.

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Emerging Chalcogenides: A New Family of Perovskite-Inspired Sustainable Energy Materials
Ivan Caño Prades1, Cibrán López Álvarez1, David Rovira Ferrer1, Marcel Placidi1,2, Claudio Cazorla1, Joaquim Puigdollers1 and Edgardo Saucedo1,1 Universidad Politécnica de Catalunya, Spain; 2Institut de Recerca en Energia de Catalunya, Spain

In the last ten years, lead-halide perovskites have achieved outstanding performance in photovoltaics, X-ray detectors and other optoelectronic applications. Significantly, they can be synthesized via cost-effective low-temperature methodologies, which represent an improvement in terms of sustainability compared to physical vapor processes, normally requiring high temperatures and vacuum. However, the presence of Pb and stability issues have raised the question of whether the exceptional properties present in lead-halide perovskites could be replicated in other materials. Among the different approaches known to develop perovskite-inspired materials, here we have fabricated emerging chalcogenide semiconductors with structure analogous to perovskite, and others which have different structure but similar electronic features.

Belonging to the first group, silver and copper chalcogenides - (Ag,Cu)Sx (X=I,Br) - stand out for their crystalline structure analogous to perovskites, albeit switching cation sites by anions and vice-versa. They are constituted by earth-abundant and non-toxic components, and their bandgap in the 0.9 - 1.1 eV range indicates that they could be suitable for single-junction solar cells or tandem configurations. So far, powders and pellets have been mostly fabricated using costly and time-consuming approaches which involve high temperature and vacuum, and lack adaptability in terms of composition and doping. Alternatively, in this work we present a novel procedure to prepare (Ag,Cu)Sx (X=I,Br) polycrystalline thin films by molecular precursor ink deposition, using thiol-amine solvent mixtures. This methodology offers advantages in terms of cost-effectiveness, versatility, scalability and sustainability, opening the door to explore new compositions, properties and applications of the electronically benign chalcogenide anti-perovskite samples. System have been extensively studied by X-ray diffraction, microscopy and optoelectronic characterizations.

Another approach to develop perovskite-inspired materials consists in developing materials which are electronically analogous, i.e., they have similar electronic characteristics at the band structure. In this regard, it is particularly interesting to seek materials which exhibit the same features which make lead-halide perovskites tolerant to defects. Indeed, despite having high defect densities, hybrid perovskites exhibit low non-radiative recombination rates. This phenomenon has been suggested to emerge from having bonding orbitals at the conduction band, and antibonding contributions at the valence band. Therefore, it is expected that materials with similar electronic structure, such as ternary chalcogenides SbSx and BiSx (X=I,Br), can replicate the beneficial defect tolerance of perovskites. In addition, these materials are constituted by relatively earth-abundant and low-toxic components, they are stable, have bandgaps in the 1.5 - 2.0 eV range, and can be synthesized at low temperatures, which makes them ideal as a viable alternative to perovskites. In this work, experimental and theoretical analyses will be presented, including the characteristics of the band structure (obtained by first-principle calculations), structural and optical properties (X-ray diffraction, spectroscopy analyses), and prototype PV devices, demonstrating their potential as a sustainable alternative for energy harvesting applications.

To sum up, this work presents two different families of emerging chalcogenide materials, constituted by relatively earth-abundant elements and manufactured by low-temperature environmentally-friendly techniques, which are inspired in different ways by the successful lead-halide perovskites (structure analogous and electronic analogous respectively) and demonstrated new, more sustainable ways to develop semiconductor materials for energy applications.

1 Chem. Mater. 29, 11, 4667-4674 (2017)

Solution Processed Nanomaterials for Solar Technologies
Federico Rossi1,2, 1University of Trieste, Italy; 2INRS, Canada

We describe wet chemistry solutions, solution based synthesis and hydrothermal processing of various nanomaterials, primarily Quantum Dots (QDs). By varying the size, shape and composition of the QDs we are able to optimize their bandgap and optoelectronic properties. The QDs are then used as building blocks to fabricate three types of solar technologies: (i) Quantum Dot Solar Cells [1,2]; (ii) Quantum Dot Photoelectrochemical cells for Hydrogen Production [3–11]; (iii) Luminescent Solar Concentrators [12–15] and in optical nanothermometers [16–18].

References

Fabricating Air-Stable Copper Films with Exceptional Electrical Conductivity without Sintering
Jessica Pereira1,2, Oleg Makarovsky1, David Amabilino3 and Graham Newton1
1University of Nottingham, United Kingdom; 2University of Southampton, United Kingdom; 3Consejo Superior de Investigaciones Científicas, Campus Universitari de Bellaterra, Spain

Copper is an excellent electrical conductor, nearly matching the conductivity of silver (Cu: 5.96 × 107 S/m vs Ag: 6.30 × 107 S/m), but at a fraction of the cost (Cu: $0.28/oz vs Ag: $21.6/oz), making it an ideal choice for cost sensitive large area applications which are in high demand. However, unlike silver, copper has a much higher susceptibility towards oxidation, a risk that is particularly acute in particulate atmospheres with high surface to volume ratio, which generates additional processing complications including the need for surface passivation and inert environments for processing as well as sintering. The use of fossil fuel based long-chain hydrocarbon ligands to passivate copper is the common approach in the field but decomposition of such ligands to fabricate functional conductive films require high sintering temperatures and controlled conditions. Moreover, with the rapid growth of the ﬂexible and wearable electronics industry, sintering becomes increasingly less practical as most substrates used in this sector are temperature sensitive. Herein, a new approach to fabricating conductive air-stable copper films with resistivities close to that of bulk copper is demonstrated which only requires compression at room temperature, completely removing the need for any form of sintering. This approach facilitates the generation of highly conductive single unsupported copper films as well as intricate patterns on paper and printed circuit board substrates with an aqueous, biopolymer stabilised copper ink formulation. The remarkable conductivity and oxidative stability of the copper films, coupled with the sustainability of the approach have the potential to precipitate a paradigm-shift in the use of copper inks for printable electronics.

Designing Sustainable Permanent Magnets: Alloying Additions and Magnetocrystalline Anisotropy in L10 FeNi
Christopher D. Woodgate1, Laura H. Lewis2,3 and Julie Staunton1
1University of Warwick, United Kingdom; 2Northeastern University, United States

We report results from an holistic approach for modelling both atomic ordering and subsequent magnetocrystalline anisotropy energy (MAE) of magnetic materials with application to the design of novel, rare-earth-free permanent magnets. This computationally efﬁcient technique allows for fast exploration of the materials design space and could open up a new route for materials discovery and manufacturing. Here we report recent results concerning the class of magnetic materials which chemically order into the L10 structure. These materials typically have large MAE values appropriate for advanced permanent magnets, with prime examples being FePt and CoPt that contain elements of high criticality. Ab initio theory has previously conﬁrmed that it is the tetragonal, L10 phase that produces the high MAE values measured in these materials [1]. There is therefore a desire to discover new L10 materials which are made using more abundant elements, but which still retain desirable magnetic properties. One such candidate material is L1 FeNi, found in meteoritic, tetrataenite samples. This material is known to have a high
uniaxial anisotropy, but a low chemical ordering temperature and sluggish kinetics make it challenging to manufacture in a laboratory setting.

Here, we consider introducing a third element into the binary Fe-Ni composition to promote ordering tendencies and enhance its predicted MAE. Systems with the general formula Fe_{50-x}Ni_{50-x}X_{3y} (X=Pd, Co, Pt, Al) were investigated. Crucially, our modelling predicts the nature of any chemical order [2] and goes on to predict the MAE for a given system [1], using the same ab initio formalism for both aspects of the modelling approach. The ordering behaviour predicted on adding these dopants is rich and a variety of chemical orderings are obtained. Interestingly, we find that it is often the addition of light elements such as Al which enhance the MAE the most. We are also able to study the impact of magnetic order on predicted atomic order and show that annealing samples in an applied magnetic field may enhance chemical ordering [3].

Acknowledgements

We gratefully acknowledge the support of the UK EPSRC, Grant No. EP/W021331/1. C.D.W. is supported by a studentship within the UK EPSRC-supported Centre for Doctoral Training in Modelling of Heterogeneous Systems, Grant No. EP/S022848/1. This work was also supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences under Award Number DE SC002168 (for atomistic insight) and by the U.S. National Science Foundation under Award ID 2118164 (for advanced manufacturing aspects).

References


SESSION EN06.07/EN03.07: Joint Session: Photovoltaics and Superconductors

Wednesday Afternoon, April 24, 2024
Room 333, Level 3, Summit

3:30 PM EN06.07/EN03.07.01

Lead-Free Perovskite Derivatives Toward Eco-Friendly Indoor Photovoltaics

Vincenzo Pecunia; Simon Fraser University, Canada

Indoor photovoltaics present a compelling solution for powering the ever-expanding array of Internet-of-Things (IoT) smart sensors in a sustainable manner. The emergence of halide perovskites as promising absorbers for indoor photovoltaics has ignited significant interest due to their favorable optoelectronic characteristics. Nevertheless, the deployment of indoor photovoltaic devices in close proximity to end-users raises concerns about the toxicity associated with the lead content found in mainstream halide perovskites. This has spurred the search for alternative, lead-free perovskite derivatives for efficient indoor photovoltaics without lead toxicity concerns. We first demonstrated this concept with Cs$_3$SnI$_{3y}$Cl$_y$, enabling indoor photovoltaic efficiencies already in the range of mainstream, commercial indoor photovoltaics. Furthermore, our investigations revealed that the spectroscopic limited maximum efficiency for this and other lead-free perovskite derivatives under indoor lighting conditions can reach approximately 60%, showcasing their immense potential through further materials and device optimization. In fact, the demonstrated photovoltaic efficiency of Cs$_3$SnI$_{3y}$Cl$_y$ was sufficient to power printed digital gates via millimeter-scale indoor photovoltaic devices, confirming the opportunity already provided by this technology toward self-powered electronics with potentially low environmental impact. We extended our exploration to Cs$_x$Ag$_{1-x}$Bi$_x$ absorbers, tailoring the microstructure and device architecture to achieve enhanced indoor photovoltaic efficiencies and ensuring reliable operation under realistic illuminance levels as low as 200 lx, all while exhibiting favourable air stability. Recognizing the importance of sustainability in emerging technologies, we additionally conducted a thorough assessment of the environmental impacts of various lead-free perovskite derivatives in the context of indoor photovoltaics. Our findings identified the most promising compositions from a sustainability perspective, offering crucial guidance to the research community developing lead-free perovskite derivatives to enable eco-friendly self-powered smart sensors for a green IoT revolution.

4:00 PM EN06.07/EN03.07.02

Oxide-Halide Perovskite Composites for Simultaneous Recycling of Piezoceramics and Solar Cells

Mohadesheh Tabeshfar1, Sivagnana Sundaram Anandakrishnan1, Mikko Nelo1, Malihia Siddiqui2, Jani Perintie1, Pavel Tofel1, Heli Jantunen1, Jari Juuti1 and Yang Bai1; 1University of Oulu, Finland; 2CEITEC-Central European Institute of Technology, Czechia; 3Brno University of Technology, Czechia

Global concerns regarding energy and the environment have created an urgent demand for sustainable manufacturing, usage, and disposal of electronic components. Piezoelectric and photovoltaic components are being extensively used due to the rapid development of the Internet of Things (IoT) and green energy production, which require large quantities of piezoelectric sensors/energy harvesters and solar cells as functional components and power sources. Thus, recycling these two essential types of components needs to be carefully considered. This work develops upside-down composites to recycle waste oxide perovskite-based piezoceramics and organometal halide perovskite-based solar cells. Production of the recycled and reusable materials requires only a marginal energy budget, while achieving a high level of material densification and excellent sensing capabilities. This work offers an energy- and environmentally friendly approach for recycling hazardous and high energy-consuming elements, as well as giving a second life to the functionality of waste piezoelectric and photovoltaic components.

4:15 PM EN06.07/EN03.07.03

Enhancing Fluorophore-Induced Plasmonic Current for Converting Solar Energy

Lahari Saha1 and Chris D. Geddes1,2; 1University of Maryland, Baltimore County, United States; 2Institute of Fluorescence, United States

Biological chromophores and certain model organisms present a unique opportunity in solar energy harvesting. Currently, solar energy conversion efficiency rates are in the low 20s, necessitating multiple panels to generate electricity. This is a problem since many agricultural farms are transitioning into solar farms, supporting the growing demand for electricity and further deepening existing food crisis. Therefore, the system’s efficiency, stability, and longevity are crucial. Advances in plasmonic materials offer promising results due to their compatibility with fluorescent biosensors and various fluorophores, suggesting potential applications in solar energy conversion. In this presentation, we discuss a technology called fluorophore-induced plasmonic current (FIPC), where plasmonic thin films and a fluorophore solution are used to generate current. We consider a few methods to increase current produced by FIPC for example, annealing thin films and incorporating metallic colloids in the fluorophore solutions. Key takeaway on annealing thin films suggests an increase in current response within the working range and lowering signal to noise ratio, leading to a stable baseline current. Preliminary data on metallic colloids mixed with fluorophore solutions indicate an exceptional increase in current generation. Future work in this project will translate our findings to biological chromophores.

4:30 PM EN06.07/EN03.07.04

Carbon-Based Photoabsorbers for Sustainable Energy Applications

Demetra S. Achilleou1, Cacimba Maher1, Hatice Kasap2 and Erwin Reisner2; 1University College Dublin, Ireland; 2University of Cambridge, United Kingdom

The continuous air and water pollution arising from the accelerated consumption of fossil fuels and organic pollutants, respectively, emphasize the need for society to move towards renewable “green” resources, and environmentally sustainable processes. Photocatalysis is a promising approach for mitigating simultaneously both the energy and environmental concerns.1 However, the development of economically and environmentally sustainable photocatalytic processes creates the pressing need for new materials of low cost and toxicity, such as photoabsorbers and catalysts, which maintain substantial performances. Carbon dots (CDs) and carbon nitride (CN$_x$) can efficiently serve as photoabsorbers for this purpose since they fulfill these requirements.2-6 In particular, they are hydrophilic materials of low toxicity which are chemically and photochemically robust, can be synthesized at low cost, and show optimum photocatalytic properties upon pre-designed synthesis. In this work, we describe the synthesis of CN$_x$ and CDs from low-cost organics and/or Earth abundant waste (circular economy), the structure of which bestows the derived photoabsorbers with distinctive photocatalytic performances. These light harvesters, when combined with noble-metal free catalysts in aqueous photocatalytic systems, not only facilitate “green”, solar-driven fuel synthesis but also waste/water pollutant utilization. The use of waste and aqueous pollutants, eliminates the need for additional sacrificial reagents traditionally used in great excess, which add to the overall cost of the process, and result in toxic by-products.7 We anticipate that this approach could be a breakthrough in the development of scalable, economically, and environmentally sustainable systems, which can efficiently serve energy and environmental applications.
Aniruddh Vashisth and Surabhit Gupta
Closed-Loop, Rapid Polymer Welding Using Radio-Frequency Heating

References

SESSION EN06.08: Poster Session
Session Chairs: David Cahen, Clara Santato and Anke Weidenkaff
Wednesday Afternoon, April 24, 2024
Flex Hall C, Level 2, Summit

5:00 PM EN06.08.01
Closed-Loop, Rapid Polymer Welding Using Radio-Frequency Heating
Aniruddh Vashisth and Surabhit Gupta
University of Washington, United States

Polymer components are becoming more prevalent in load-bearing applications due to their superior strength-to-weight ratio. Thermoplastics, particularly, have gained traction in recent years due to their ability to be molded, recycled, and reused. Effective welding and joining methods are essential to facilitate the assembly of intricate thermoplastic parts; but these manufacturing processes are energy expensive and depend on the processed materials. We have developed and energy efficient closed-loop method that utilizes a recent discovery that radiofrequency (RF) fields rapidly heat up carbonaceous materials. We developed a machine capable of monitoring the material's pressure, deformation, and thermal response during the assembly process; this closed-loop system does not require human intervention to process the materials. In this work, we will show that the closed-loop machine can rapidly weld thermoplastics using RF heating at the bondline; to process these materials, we can control the pressure or displacement of the weds to ensure desired mechanical properties. Our initial experiments showed that we can successfully weld polyacrylic acid (PLA) coupons with graphitic RF capacitors at the bond line in less than 2 minutes, utilizing less than 50 W of RF power. The weld properties show no significant variation within a ±0.3 MPa pressure range. However, an increase in out-of-plane welding displacement enhances the modulus and strength of the weld. This work introduces an energy-efficient, automated system for welding polymer composites using RF fields, showing promise for diverse manufacturing applications. The machine can be used in three control settings: hold, displacement, and pressure control. We saw excellent RF heating response of conductive carbonaceous coatings on polymers; this rapid heating was used for RF processing and bonding thermoplastics using less than 50 W of RF input power in an automated manner.

5:00 PM EN06.08.02
Electrochemical Methods of Carbon-Negative Ironmaking for Green Steel
Paul A. Kempler, Berkley Noble and Anastasia Konovalova
University of Oregon, United States

Iron and steel are important feedstocks for energy materials and infrastructure but are produced with concomitant greenhouse gas emissions. Iron reduction, typically accomplished using coal or natural gas, can be driven electrochemically which provides a potential path to a fully electrified and carbon-neutral steelmaking process. We have developed the chlor-ion iron process, a low-temperature (<100 °C), electrochemical cell that directly reduces solid iron oxide particles to high-purity iron metal at the cathode while co-producing sodium hydroxide and chlorine. The production of co-products consumed at the ~100 million tons per year scale provides a cost-competitive pathway for electrochemical ironmaking. Moreover, the co-produced hydroxide can be used for direct CO2 capture and mineralization, leading to a net-negative process for ironmaking. Here, we report results on the mechanism of electrochemical direct oxide reduction, the effects of iron ore feedstocks on selectivity towards iron metal, and prototypes for a cell producing iron and chlorine at current densities > 100 mA cm-2.

5:00 PM EN06.08.03
Soumyabrata Basak1,2, 1Korea Institute of Industrial Technology, Korea (the Republic of); 2University of Ulsan, Korea (the Republic of)

The influence of carbonaceous components (graphene oxide, GO) on the microstructure and mechanical properties of aluminum (Al) matrix composite fabricated by single-pass friction stir solid-state processing (FSP) is studied. GO powder is introduced onto the commercially pure Al plate using adhesive, eliminating typical secondary manufacturing stages. As a result, this technique becomes more cost-effective and energy-efficient than other conventional approaches. The presence of GO within the Al matrix is initially characterized using Raman spectroscopy and secondary ion mass spectrometry, followed by detailed electron microscopy studies. TEM studies show a reasonable amount of dislocation accumulation at the matrix particle interface without other chemical reactions. Due to continuous dynamic recrystallization, EBSD analysis reveals a significant grain refinement in FSPed Al (FSP-only condition without GO reinforcement) and FSP with GO conditions. The microhardness map of FSP with GO characterizes an overall improved hardness value than the FSPed Al and reveals the maximum hardness around the advancing side of the stir zone. The advancement of mechanical properties is primarily due to GO particles and their interaction with the Al matrix. The tensile strength and ductility are improved in the FSP with GO condition compared to the base material and FSPed Al condition.

5:00 PM EN06.08.04
Boron Nitride Nanomaterials for Gas Storage and Separation Using Mechanochemistry
Srikanth Mateti and Ying Chen
Deakin University, Australia

2D h-BN, also known as white graphene, has a similar honeycomb structure to graphene, with alternating boron and nitrogen atoms consisting of strong sp² covalent in-plane bonding and weak van der Waals forces between layers. h-BN has unique properties; it is a lubricant due to its layered structure. BN is an electrical insulator (with a bandgap of approximately 5.9 eV) that the same thermally conductive and also has high mechanical strength, large thermal conductivity and low dielectric constant. Hydrogen is increasingly being touted as one sustainable solution to globe clean energy problem. But one of the main challenges is the lack of a safe and cost-effective storage and transport technique. Solid-state storage technology is considered to overcome this problem. Currently, hydrogen storage and transport happen majorly in three ways, compressed gas, liquid hydrogen and carrier gas then compressor. Due to reasons of material properties and operating costs, large amounts of gaseous hydrogen are usually not stored at pressures exceeding 100 bar in underground vessels and 200 bar in underground storages [1]. Currently commercially available have utilized an onboard storage pressure of 700 bar, but storage tanks capable of storing hydrogen at such pressures are expensive. To decompose ammonia to form hydrogen, transport losses are 34-36% [2]. And Liquid hydrogen storage needs an extremely low boiling point of hydrogen (~253°C at 1 bar) which is energy intensive and expensive. Thus, urgent need to find alternative and sustainable ways to store hydrogen gases. In this, we discuss possible and sustainable and safe ways of storing and transporting hydrogen in powder form. This talk will provide insights on the mechanochemical approach to store and separate various gases.


5:00 PM EN06.08.06
Recycle Waste Gloves for Oxygen Evolution Reduction in Alkaline Water Electrolysis
Tzu Hsuan Chiang, Ji-Min Chang and Rui En Li
National United University, Taiwan

Nitrile gloves have gained widespread use as disposable gloves in various sectors, including hospitals, scientific laboratories, manufacturing facilities, halls, and museums, thanks to their superior mechanical strength compared to vinyl gloves and other alternatives. Due to the ongoing COVID-19 pandemic, the global production of discarded gloves has soared, estimated at more than 76 million monthly. Unfortunately, dealing with and reintroducing this waste into the reuse cycle is costly and time-consuming. Regrettably, many disposable gloves eventually find their way into oceans and other water bodies, slowly deteriorating and fragmenting into microplastic particles. Marine animals swiftly ingest these microplastics, leading to blockages and permanent damage to their internal organs. Consequently, finding a practical solution to this substantial waste issue is paramount.

A study was conducted to create FeWOx-NH electrocatalysts by recycling waste nitrile gloves through the oxygen evolution reaction (OER) in alkaline water electrolysis (AWE). While AWE is a preferred technology for green hydrogen production, its adoption has been impeded by the high cost associated with the necessary capital investment in electrolysis and renewable energy systems. Furthermore, the commonly used precious electrocatalysts contribute to AWE’s elevated costs and superior gas evolution performance. The oxygen evolution reaction (OER) is the rate-limiting step in alkaline water electrolysis. It makes electrocatalyst performance in OER a crucial factor in enhancing its hydrogen evolution reduction (HER) capabilities. Leveraging

recycled waste nitride gloves, this study developed an OER electrocatalyst with Fe and W precursors (FeWOx-NG) to reduce the electrocatalyst’s cost. The results demonstrate that FeWOx-NG exhibits a smaller overpotential and Tafel slope at a 10 mA/cm² current density in alkaline electrolytes compared to RuO₂. This improved performance could enhance alkaline water electrolysis efficiency and promote more efficient hydrogen evolution.

5:00 PM EN06.08.07
Exploring The Potential and Performance Constraints of Ni-Rich LiNi₀.₉Co₀.₁O₂ through DFT Research
Temitayo O. Ikuorolu 1, Omotayo Salawu 2 and Olusegun Tomonowo 1;
1University of North Dakota, United States; 2Texas A&M University, Qatar
The high-capacity but unstable LiNiO₂ (LNO) cathode material for lithium-ion batteries can be improved through partial substitution with cobalt. First-principles calculations were performed to study the impact of 10% cobalt doping on the structural, electronic, defect, and lithium diffusion properties of LiNi₀.₉Co₀.₁O₂ (NC91). The layered structure is retained but the band gap decreases significantly with 10% Co. Formation energies reveal oxygen vacancies and antisite defects still occur; however, Ni sites near Co are least favorable for antisite formation. The energy barrier for Li migration is substantially lower in NC91 than LNO, indicating enhanced lithium mobility with 10% Co. While the Co doping improves Li transport, additional doping is likely required to sufficiently suppress cation mixing and oxygen loss. This work provides fundamental insights into the structure-property relationships resulting from low levels of cobalt doping in Ni-rich cathodes.

5:00 PM EN06.08.09
Synergistic Interaction between Ruthenium Catalysts and Grafted Niobium on SBA-15 for 2.5-Furan dicarboxylic Acid Production using 5-Hydroxymethylfurural
Hyun Sung Kim1 and Hangi Lee2; 1Pukyong National University, Korea (the Republic of); 2Sookmyung Women’s University, Korea (the Republic of)
This study entailed the synthesis of a novel Ru-bound catalyst decorated on Nb-grafted SBA-15. An Nb-grafted SBA-15 support with varying Si/Nb ratios was utilized as a support for Ru nanoparticles. The effect of Nb grafting on the immobilized Ru nanoparticle catalyst was systematically investigated, and its catalytic performance in the synthesis of furan dicarboxylic acid using 5-hydroxymethylfurfural (HMF) under base-free reaction conditions was evaluated. The results indicate an increased productivity of the Ru/Nb-grafted SBA-15 catalyst, with a yield exceeding 99%, representing a significant advancement in catalysis. This study also affords insights into the complex relationship between the catalytic activity and selectivity and its surface attributes. Moreover, acidic sites were created, and the electron density within the active sites was modulated by generating monomeric Nb oxide species on the SBA-15. Additionally, the role of high-electron-density Ru atoms in facilitating the efficient adsorption and activation of HMF, resulting in enhanced catalytic efficacy, was highlighted.

5:00 PM EN06.08.12
Lead Halide Perovskite Pixel Arrays Fabricated by Ultrathin Reusable Metal Mask
Zhao Sun1, Zhuaofei Gan1, Jianwen Zhong1, Liyang Chen2, Zijie Jiang1 and Wendi Li1; 1The University of Hong Kong, China; 2ETH Zurich, Switzerland
In recent decades, metal halide perovskites have emerged as a highly promising class of materials for optoelectronic devices, owing to their exceptional properties, which include a tunable bandgap, a significant optical absorption coefficient within the visible light, and long carrier diffusion length(1-4). Nonetheless, achieving high-resolution patterning of perovskite arrays presents challenges due to their inherent instability when exposed to conventional photolithography solvents. In this work, we proposed a universal approach to pattern high-resolution perovskite arrays using an ultrathin reusable metal mask. A two-step sequential approach utilizing a designed metal mask is employed to achieve the controlled fabrication of micro and nanometer-resolution perovskite arrays. Through this generic and straightforward patterning process, we successfully fabricated perovskite arrays in red, green, and blue (RGB) colors, varying in shapes and sizes, with a minimum diameter of 500 nm perovskite pixel arrays. Moreover, the patterned perovskite arrays exhibit excellent photoelectric properties, including comparable light absorption and considerable lifetime. Furthermore, we investigated a transfer method to assemble multi-color perovskite arrays, enabling the creation of full-color images that significantly contribute to the progress of screen display technologies. Additionally, we presented photodiode stack arrays with a sandwich structure for each stack, demonstrating the capability of our approach in both solution and evaporation processes, which is unprecedentedly achieved. The patterned perovskite photodiode stack arrays exhibit outstanding electronic performance, showcasing lower open circuit voltage and comparable stability under diverse levels of illumination intensity. The fabricated ultrathin and high-resolution metal mask holds significant potential in the development of micro and nanoscale optoelectronic devices such as LEDs and solar cells. This method enables the patterning of perovskite micro-arrays on versatile substrates with reusable metal mesh templates and can be further applied to other materials to facilitate the development of micro-structured optoelectronic devices.

References

5:00 PM EN06.08.14
Shadi Houshyar1, Lijing Wang1, Manoj Kumar Gupta 1,4,3 and Manoj Kumar Patel 2,3; 1RMIT University, Australia; 2CSIIR-Central Scientific Instruments Organisation, India; 3Academy of Scientific and Innovative Research, India; 4CSIR-Advanced Materials and Processes Research Institute, India
In this work, we have synthesized the zinc-aluminum layered double hydroxide (ZnAl LDH) nanosheets using cost-effective hydrothermal technique. The ZnAl LDH and graphene-based poly(vinyl alcohol) (PVA) nanocomposites are fabricated. The crystal structure, morphology, thermal, and dielectric properties of pristine PVA and ZnAl LDH and graphene-based PVA nanocomposites films were investigated using X-ray diffraction, HR-transmission electron microscopy, thermo gravimetric analysis, and impedance analyzer. HRTEM analysis reveals the hexagonal nanoplates shape-like morphology of Zn-Al layered double hydroxides with an average thickness of 40-50nm and size of 400-600nm. High thermal stability was observed from ZnAl LDH and graphene-reinforced nanocomposites. Enhanced thermal stability of 250°C and low weight loss was observed from ZnAl LDH reinforced PVA-based nanocomposites compared to pristine PVA. Zn-Al LDH nanolaminate-graphene-PVA based nanocomposites showed ultra-high dielectric constant of 794 as compared to the ZnAl LDH-PVA nanocomposites (334) and pristine PVA sample (35). Low dielectric loss of 0.27, 0.18, 0.38 was observed for pristine PVA, ZnAl-LDH-PVA and ZnAl-LDH-graphene-PVA nanocomposites. The large enhancement of the dielectric constant and thermal stability were discussed in terms of improved crystallinity, interfacial polarization and formation of nanodipoles in the matrix. This study reveals a significant role of LDH-graphene-based hybrid nanocomposites in optoelectronics, energy storage, sensors, energy conversion and thermally stable devices.

5:00 PM EN06.08.15
Exploring Hydrogen Storage Efficiency in MgH₂ Using Charred Nanomaterials: A Computational Analysis Integrating DFT and Machine Learning Approaches
Fernando Soto and Joshua Lilly; Penn State University Greater Allegheny, United States
Hydrogen, as a clean energy carrier, holds significant potential for reducing CO₂ emissions and diversifying the energy mix (1-3). However, the practical implementation of solid-state hydrogen storage, particularly in hybrid energy systems (HES), faces challenges related to kinetics, stability, and safety (4). This study performs a computational exploration of magnesium hydride (MgH₂) integrated with char nanomaterials, aiming to enhance the efficiency of hydrogen storage systems. We investigate the use of charred novel nanomaterials as a novel approach to address the fire risk and safety concerns associated with MgH₂, as well as to improve its hydrogen desorption kinetics. We hypothesize that charred nanomaterials can act as dual-function agents, catalyzing hydrogen release while also offering protection against combustion.
To test our hypothesis, we employ Density Functional Theory (DFT)-based simulations complemented with machine learning techniques. Our study models include various configurations of MgH₂ clusters in contact with charred carbon fragments doped with heteroatoms like Oxygen, Nitrogen, and Iron, alongside O₂ molecule environments to simulate combustion processes. These models are analyzed to understand the stability and interaction dynamics under varying conditions. Our findings reveal that charred nanomaterials significantly influence the hydrogen desorption properties of MgH₂, indicating a promising pathway towards safer and more efficient hydrogen storage. The charred structures, particularly when doped with heteroatoms, not only catalyze hydrogen release but also mitigate risks associated with MgH₂’s reactivity, offering a holistic solution to the current limitations in hydrogen storage technology.
This computational study provides crucial insights into the design of advanced materials for hydrogen storage, offering a sustainable solution to energy storage challenges in HES. It opens up
vantages for further experimental validation and development of MgH$_2$-based hydrogen storage systems, contributing to the advancement of clean energy technologies.

References

5:00 PM EN06.08.16
Building a Rechargeable Voltaic Battery via Reversible Oxide Anion Insertion in Copper Electrodes Jose F. Florez Gomez1, Nischal Oh1, Songyang Chang2, Shen Qiu2, Swati Katkar2, Ram Katyar1, Gerardo Morell1 and Xianyong Wu2; 1University of Puerto Rico at Rio Rico, Puerto Rico; 2University of Puerto Rico at Rio Piedras, Puerto Rico

The voltaic battery (zinc-copper battery) is the very first battery built by humanity, which plays a critical role in battery development history. However, the inevitable copper ion dissolution-reversibility crossover issue leads to its primary battery nature. The ion-exchange membranes and alkaline electrolytes represent two leading approaches to mitigate this issue; however, they incur the disadvantages of complicated battery design, high cost, and zinc anode corrosion. Herein, we build a rechargeable zinc-copper Voltaic battery from simple and cost-effective electrode/electrolyte materials, where the cathode is a nano-sized copper, and the electrolyte is a near-neutral zinc sulfate solution. Interestingly, the copper electrode experiences a synergistic cation-anion insertion reaction, where copper transforms to zinc-copper alloy (Zn$_x$Cu$_{1-x}$) during discharge and converts to copper (I) oxide (Cu$_2$O) during charge. Therefore, multivalent Zn$^{2+}$ cations and multivalent O$_2^-$ anions participate in the redox reaction, giving a high capacity of ~370 mAh g$^{-1}$. Moreover, the structural similarity between Zn$_x$Cu$_{1-x}$ and Cu$_2$O endows high reaction reversibility, leading to impressive cycling of ~500 cycles. Such a concerted cation-anion insertion reaction is rarely reported in the battery field, which offers a mechanism-based approach for developing high-capacity and long-cycling multivalent-ion batteries.

SESSION EN06.09/EN03.09: Joint Session: Decarbonization
Session Chairs: David Cahen, Jiho Kim, Clara Santatito and Anke Weidenkaff
Thursday Morning, April 25, 2024
Room 333, Level 3, Summit

8:15 AM EN06.09/EN03.09.01
Fit-To-Purpose Batteries. An Ecodesign-Based Approach to Power Portable Applications Marina Navarro-Segarra1, Carles Tortosa2, Neus Sabate3, and Joan Pablo Esquivel1,2,4,5
1BMCMaterials, Spain; 2Fuellum, Spain; 3Instituto de Microelectrónica de Barcelona, IMB-CNM (CSIC), Spain; 4Ikerbasque, Spain

Batteries have become an essential power source, due to their capability to deliver high energy densities in a portable manner. However, a close look into conventional portable battery life cycles reveals, that they still follow an obsolete linear model. They are manufactured at specific locations causing scarce material exhaustion, transported thousands of kilometres for its use and then disposed of, sometimes before even its complete depletion. Then, during portable batteries' end-of-life, only a small percentage are recycled, typically using energy intensive processes, whereas the rest ends up incinerated or in landfills, generating greenhouse gas emissions and poisoning terrestrial and marine ecosystems. Furthermore, it is forecasted that the upcoming wave of power-hungry Internet-of-Things (IoT) sensing nodes will increase exponentially the portable battery demand in the near future. Thus, aggravating the environmental impact associated with electronic devices production and the generation of waste electrical and electronic equipment (WEEE). For portable batteries to stop contributing to environmental damage, and become an example for sustainable technological development, it is crucial to change the way the batteries value chain is approached.

This work presents a rationale for ecodeSIGN portable batteries by re-thinking their life-cycle under an environmentally conscious framework. Through careful device design and advocating for a 'fit-to-purpose' approach, the development of these batteries is paired with the application value chain, in such a manner that even the power source end-of-life is redefined according to the use-case scenario. In order to ground these ideas, several examples of these ecodesign portable power sources will be presented.

First, a paper-based battery in a lateral flow assay format intended to power portable diagnostic devices. These liquid activated batteries can be fabricated under the same procedures used in the rapid test industry and have shown the ability to power the most relevant features needed in portable medical devices, such as sensors, displays, wireless communications or heating. Secondly, a bio-based battery using laser induced graphene current collectors in a cardboard tape format for smart packaging. These batteries have the capability to power typical applications envisioned by the sector, such as digital displays and wireless trackers. As validated by normalized evaluation methods, these batteries are compliant with current paper and cardboard recycling processes.

Finally, different approaches of biodegradable batteries for precision agriculture will be presented. These batteries made with organic materials can power sensing devices that measure parameters in soil and the environment and then send the data by Bluetooth communication. The capability to undergo biodegradation has been assessed experimentally using normalized tests as a way to minimize energy consumption at the end-of-life.

Developed under this rationale, environmental sustainability has been placed as a core priority to guide the batteries' conception and materialization, from materials to end-of-life. Hence all materials used as electrodes, electrolytes, or structural components are abundant, non-toxic and renewable; selected to meet the specific end-of-life requirements and endow a safe and ethical manufacturability.

8:30 AM EN06.09/EN03.09.02
A Coplanar Edible Rechargeable Battery with Increased Redox Capacity and Durability Valerio Galli1,2, Valerio F Annese1, Giulia Coco1,2 and Mario Cairoini1,1; 1Istituto di Tecnologia, Italy; 2Politecnico di Milano, Italy

Edible electronics is an emerging research field focused on developing safe-to-ingest devices entirely made of food and food additives. Being intrinsically non-toxic and biodegradable, this technology can find applications in many scenarios, from healthcare to agriculture. Starting from common food additives like activated carbon, edible gold, electrolyte, and beeswax, we developed the first edible rechargeable battery entirely made of food materials. The chemistry is based on two small redox-active molecules found in food, riboflavin, and quercetin, used as the anode and the cathode, respectively. [1]

Here we present a coplanar edible battery, characterized by an electrode configuration that eases compatibility and integration with electronic components. The battery provides an open-circuit voltage of ~0.65 V with a specific capacity of 20 µAh cm$^{-2}$, a two-fold increment with respect to our first prototype, thanks to increased electrode mass loading. The beeswax encapsulation yields excellent operational stability, characterized over a two-week period and in different environmental conditions. As proof of the compatibility with traditional electronic devices, the battery was successfully used to power up resistive sensors, including thermistors and photoresistors. Multiple batteries were also employed to supply power to an Internet of Things module which can acquire humidity and temperature information and transmit data in real-time via Bluetooth.

The high degree of versatility of our technology goes beyond the proposed proof-of-concept: we envision edible batteries as a promising alternative to traditional ones in low-power applications, such as agrifood sensor networks and food monitoring.


8:45 AM EN06.09/EN03.09.03
Advanced Characterization and Modeling to Understand Hydrogen Production by Solid Oxide Electrochemical Cells David S. Ginley2, Michael J. Dzara3, Brandon Wood2, Harry W. Abernethy3, Olga A. Marina1, Brian Gorman1, Heather Slomski2, Mike Tucker4, Miah Casteel7, Nicholas Strange8 and Sarah Shulda1; 1National Renewable Energy Laboratory, United States; 2LLNL, United States; 3NETL, United States; 4Pacific Northwest National Laboratory, United States; 5Colorado School of Mines, United States; 6Lawrence Berkeley National Laboratory, United States; 7Idaho National Laboratory, United States; 8SLAC National Accelerator Laboratory, United States

Functional oxides are becoming more important in a wide variety of renewable applications, ranging from high temperature electronics, electric vehicles, and solid oxide electrolysis/fuel cells (SOEC/SOFC). They must meet a diversity of characteristics to achieve desired functionality in these harsh environments. Hydrogen is considered an enabler for the transition to sustainable and renewable society. Production of green hydrogen is a strong focus of modern research given the current global market of 170 billion dollars. Among the approaches for hydrogen generation are the use of SOECs. These utilize a stack of high temperature operating in H$_2$ stream. While direct electrochemical measurements are key for quantifying progress towards the DOE
Hydrogen Earthshot Goal of 15 kg in the next decade is not sufficient to provide detailed materials science investigation of degradation pathways. We report on the development of a suite of synchrotron and conventionally based analysis tools to provide a set of detailed morphology, phase, and composition data which both provide detailed information about degradation mechanisms and provide foundational information for predictive models leading to ultimate materials improvement.

The solid oxide layers that comprise SOECs typically feature a layered structure composed of a Ni–YSZ fuel electrode/YSZ electrolyte/Gadolinium doped Ceria barrier layer and a Lanthanum Strontium Cobalt Iron Oxide oxygen electrode. The phase behavior especially at interfaces is complex starting from the deposition of materials to behavior during extensive aging. Recent analysis has confirmed a number of potential degradation mechanisms are operable including Sr, Ni, and Ag migration, interfacial phase formation and grain coarsening. We will discuss how a combination of synchrotron X-ray diffractions (XRD), nanoscale X-ray computed tomography (nano-XCT), and other X-ray spectroscopy techniques combined with electron microscopy can provide coupled insights on the nature of these mechanisms which can be incorporated into computational models which can provide predictive insights on cell/stack longevity. We also discuss how button cells can inform large area and stack behavior.

We will discuss our recent development of an in-operando system intended for the synchrotron techniques, especially XRD, to probe cell performance in real time.

Advanced characterization can couple to cell development and electrochemical testing towards achieving DOE Hydrogen Earthshot Goals.

This work is authored by the National Renewable Energy Laboratory (NREL), operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. David Ginley, Sarah Shulda, Robert Bell, Nick Strange, Heather Slomski and Michael Dzara are funded primarily by the EERE Hydrogen and Fuel Cell Technology Office; the views expressed in the article do not necessarily represent those of the DOE or the U.S. Government.

9:15 AM EN06.09/EN03.09.04
Artificial Chlorophyll II-Inspired: Photonic Crystals-Based Photocatalyst for Carbon Dioxide Conversion as Gaseous Fuel

Fang-Yu Liang
1National Sun Yat-Sen University, Taiwan; 2National Central University, Taiwan

The PCN-222(M)/IOT heterostructure is constructed (created) by combining the narrow bandgap metalloporphyrin metal-organic framework (PCN-222) with the wide bandgap inverse opal TiO2(IOT). PCN-222 grows in situ on the surface of the inverse opal under hydrothermal conditions, forming a tightly connected interface that enables the rapid separation and transfer of electrons and holes.

Inspired by natural photosynthesis, this research contributes to the development of artificial CO2 photocatalysis catalysts. The construction of Z-scheme heterojunctions is an effective strategy for enhancing the photocatalytic activity of semiconductor materials by isolating photogenerated electron-hole pairs. In this study, the morphologies, structures, and photoelectric characteristics of materials acquired through the synthesis of P(M:metal)/IOT heterostructures were characterized. These heterostructures were evaluated for their photocatalytic CO2 reduction capabilities, revealing their superior performance compared to IOT and PCN-222. Under visible light illumination, the P(Fe)/IOT heterojunctions achieve impressive yields of CH4 and C2H4. The enhanced photocatalytic activity is attributed to the efficient spatial separation of photogenerated electrons and holes via a Z-scheme charge transfer mechanism. This research provides valuable insights into the design and fabrication of novel Z-scheme photocatalytic systems for environmental remediation and energy conversion. The P(M)/IOT heterojunctions combine a narrow bandgap metalloporphyrin metal-organic framework (PCN-222) with a wide gap inverse TiO2(IOT) via in-situ growth under hydrothermal conditions. This results in a tightly connected interface that facilitates rapid electron-hole separation and transfer. The high photocatalytic activity of P(M)/IOT is attributed to its strong visible light absorption and efficient charge separation within the heterointerface, also providing bionic chloroplast microenvironmental strategies for effective photocatalytic carbon dioxide reduction.

9:30 AM EN06.09/EN03.09.06
Highly Efficient Carbon Mineralization Using Amine-Functionalized Magnetic Nanoparticle Clusters

Hyunsu Han and Songmin Jeon; POSTECH, Korea (the Republic of)

Carbon mineralization, which transforms carbon dioxide (CO2) into a stable form such as calcium carbonate or magnesium carbonate, has emerged as a promising technology for long-term CO2 storage. In this study, we developed amine-functionalized magnetic nanoparticle clusters (A-MNPs), that enhance both CO2 capture and its subsequent mineralization, by hydrothermal method and immobilization of (3-Aminopropyl)triethoxysilane (APTES). The surface of A-MNPs was covered by the APTES monolayer with approximately 100% coverage. A-MNPs expanded the surface area of CO2 bubbles and led to amine-CO2 coupling, improving CO2 uptake. Subsequently, the injection of calcium chloride into the CO2-saturated A-MNP solution resulted in carbon mineralization (i.e., CaCO3 formation) with improved efficiency. Additionally, the shapes of CaCO3 could be adjusted by adding anionic surfactants to the solution. Since A-MNPs can be controlled by magnetic force, they can be recovered using a magnet and reused more than 10 times without a loss in their catalytic activity, offering an efficient and sustainable method for CO2 storage.

9:45 AM EN06.09/EN03.09.07
N-Doped Carbon Dots Embedded in Electrospun Cellulose-Derived Nanofibers: A Novel Approach to Pseudocapacitors with Enhanced Faradic Activity

Jesus Vazquez-Chavez, Michael W. Thielke, Carlos Mingues and Ana Jorge Sobrido; Queen Mary University of London, United Kingdom

The sustainable energy storage landscape is rapidly evolving, with innovations driven by the necessity to meet increasing global energy demands. In this context, pseudocapacitors emerge as a new solution, closing the gap between batteries and supercapacitors, by achieving both high-energy density of batteries with the rapid charge-discharge cycles of supercapacitors. The key to harnessing the potential of pseudocapacitors lies in the development of electrodes that demonstrate superior faradic activities and high-capacity retention.

Our research presents a pioneering effort in this direction, focusing on the synthesis of pseudocapacitor electrodes from electrospun cellulose acetate nanofibres embedded with N-doped carbon dots. Electrospinning is a widely used technique known for its adaptability in fabricating carbon fibres. With its intrinsic capability to produce fibres boasting a high surface-to-volume ratio, electrospinning not only permitted the integration of the N-doped carbon dots in the fibres, but also allowed fine control over the fibre diameter and nitrogen concentration. By manipulating electrospinning parameters, we achieved fibres ranging from 220 nm to 850 nm, presenting a trade-off between surface area and mass transport efficiencies. Cellulose acetate was chosen as carbon source and as an alternative to usually employed polycrylonitrile (PAN), to increase the sustainability of our approach.

The carbon dots, synthesized through a microwave-assisted method using citric acid and urea, showcased a high faradic activity (here include values for faradic capacity and capacity retention after xx cycles) even after the deacetylation and carbonization as they were incorporated into the cellulose acetate matrix. Their N-doped nature contributes to enhanced electronic properties. Pyridinic N and pyrrolic N have been shown to be responsible for active redox sites for faradic activity whereas graphitic N is thought to contribute to the enhancement of conductivity of the resultant electrodes.

In conclusion, we present a multidimensional approach to a novel pseudocapacitor electrode fabrication. By integrating microwave-assisted synthesized n-doped carbon dots within electrospun cellulose acetate nanofibres, we not only address the technical challenges of achieving high specific capacitance, but also present an environmentally conscious blueprint. With promising preliminary results in electrochemical and analytical characterization, our research aims to expand the current design of pseudocapacitor and their implications for sustainable energy storage.

10:00 AM BREAK

SESSION EN06.10/EN03.10: Joint Session: Resource Recovery
Session Chairs: David Cahen, Jihye Kim, Clara Santato and Anke Weidenkaff
Thursday Morning, April 25, 2024
Room 333, Level 3, Summit

10:30 AM *EN06.10/EN03.10.01
Recovery of Lithium and Heavy Non-Ferrous Metals from Spent Lithium-Ion Batteries

Valery Kaplan, Ellen Wachtel and Igor Lubomirsky; Weizmann Institute of Science, Israel

When compared with nickel-cadmium or nickel-hydrde batteries, lithium-ion batteries (LIBs) provide significant advantages as a power source for electric vehicles and for small mobile devices. However, LIBs contain a variety of toxic and ecologically harmful substances, such as heavy metals, organic and inorganic compounds, thereby creating a challenge for clean end-of-life (EoL) disposal. But why throw away EoL LIBs when the grade of cobalt and lithium in the complex lithium/cobalt oxide cathodes is higher than that in pristine lithium and cobalt ores?
Recycling these valuable metals efficiently and with minimal environmental impact has therefore become an effort of significant economic, health and ecological importance, as well as of reducing tense international relations. To this end, we have worked to develop a (laboratory-scale) procedure for recycling eOL laptop LIBs containing LiCoO₂, LiNiCoO₂, and/or lithium-nickel-cobalt-aluminum oxide without the necessity of using acid/bases or costly reagents and without generating hazardous liquid waste. Following removal of the non-metallic container, the battery elements undergo crushing/milling; no other component separation procedure is performed or required. One hour dilute natural gas (4 vol.% in N₂) sintering under reducing conditions (673–1123 K), followed by ice-water leaching, is used to efficiently separate Li from the heavy metals in the form of lithium carbonate at high yield and purity; 0.5 h smelting (1773 K) of the remaining metal clinker in air with sodium tetaborate as flux, allows recovery of the heavy, non-ferrous metals (Ni, Co, Cu and their alloys) as mm-size ingots (39% Co, 32.2% Ni, 26.3% Cu). Iron compounds, remnant Li, Al and unburnt graphite are removed as slag. Neither corrosive acids nor costly reagents are required, and hazardous liquid waste is not generated.

11:00 AM EN06.10/EN03.10.02

Separating Materials for Recycling Processes Mmantsae M. Diale; University of Pretoria, South Africa

Recycling is a circular economy system that allows participants to add value to cleaning the environment. Materials have been the major role player in improving old engineering systems and producing newest technologies to reduce the carbon footprint. There is a great effort in plastic recycling where profits are made, and poverty reduced to address the UN sustainable goals for 2030. Phosphors and other identifiers have been used to identify different plastics during separation. Similarly, paper and bottles can have additives and nanostructures that will make it easy to separate such materials during recycling. We report on the work done to identify glass, paper and plastic in recycling and make it a smooth process to produce new products. In addition, we have also embarked on educating the garbage pickers to enhance profits by proper separation.

11:15 AM EN06.10/EN03.10.03

Electrochemical Separation Technologies for Resource Recovery and Recycling Seonki Kim1 and Jin Soo Kang2; 1Ewha Womans University, Korea (the Republic of); 2Seoul National University, Korea (the Republic of)

Global efforts toward carbon neutrality have impacted the industry and market in various directions, and this is causing rapid changes in the production, use, and supply chain of various resources. For instance, explosive growth of the electric vehicle (EV) market induced significant increments of demands for lithium and other relevant elements. Meanwhile, it should be noted that the production of such resources from ores often result in a large amount of CO₂ emission and environmental pollutions, which endangers the sustainability of our world. Therefore, there is a wide agreement on the importance of developing clean technologies for recovering and recycling resources from various sources, which even include wastes. Herein, our recent research works on electrochemical separation technologies for efficient resource recovery and recycling will be presented. Electrode materials that have favorable crystallographic structures for highly selective extraction of specific elements are introduced, together with discussions on their behaviors during the operation. Based on these understandings, rationally designed resource-recovery electrodes are developed, and their performance and reliability are evaluated and demonstrated.

11:30 AM EN06.10/EN03.10.04

Selective and Sequential Precipitation for Critical Mineral Extraction from Electronic Waste Qimpu Wang1, Elias Nakouzi1 and Chimmyee Subban1,2; 1Pacific Northwest National Laboratory, United States; 2University of Washington, United States

The recycling of critical materials from electronic waste (e-waste) shows a great potential for urban mining. However, conventional separation methods are often chemical- and energy-intensive as they mainly rely on organic ligands, ionic liquids, and ion-selective membranes and/or electrodes. The sustainable production of valuable critical elements from e-waste requires a paradigm shift away from currently used resource-intensive processes. We present a novel approach based on the coupling of ion diffusion and precipitation kinetics. Simply by placing a mixed salt solution on top of a hydrogel loaded with a precipitating agent, we obtained spatially separated precipitates along the reactor. Our proof-of-concept has been demonstrated for sequentially precipitating transition metals with modeled feedstocks representative of lithium-ion battery cathodes and rare earth elements from NdFeB permanent magnets. We expect this approach to be broadly relevant to chemical separations from complex feed streams and diverse chemistries—enabling more sustainable materials extraction and processing.

11:45 AM EN06.10/EN03.10.05

Economically Sustainable Recycling of MAPbI₃ Perovskite Solar Cells Zhenni Wu1,2, Misha Shtynk1, Jiyun Zhang1,2, Gülüsüm Babayeva2, Simon Arnold2, Jens Hauch1,2, Christoph J. Brabec1,2 and Ian Marius Peters1,2; Forschungszentrum Jülich, Helmholtz Institute Erlangen-Nürnberg for Renewable Energies (HI ERN), Germany; 2Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Recycling becomes ever relevant with exponentially expanding photovoltaic deployment. Yet, the recycling of commercial silicon photovoltaic modules often falls behind in preserving the quality of materials due to inadequate separation of mixed components. Conversely, the solution processing feature of nascent but propitious perovskite solar cell facilitates simplified component separation. Herein, we report a recycling approach for a planar MAP₃bI₉ perovskite solar cell, resulting in recycled materials that can be integrated into new cells without compromising their quality. Prior to integration into cell construction, all the collected materials underwent corresponding purification or modification treatments. The hole transport material, Spiro-OmTeTAD, was purified with column chromatography. The absorber material, MAPbI₃, was crystalized using anti-solvents. And the recovered old ITO/SnO₂ was coated with fresh SnO₂ for quality rejuvenation. The resulting recycled materials, whether used individually or combined, all lead to cell efficiencies comparable to those of cells constructed with entirely virgin materials. Based on a techno-economic analysis, the developed recycling approach has demonstrated economic viability at both laboratory and industrial scales.

1:45 PM EN06.11/EN03.11.01

Sustainable Off-Grid Hybrid Energy Systems: The Case of The Astronomical Telescope AtLAST Sahrina Sarker; University of Oslo, Norway

Production and use of hydrogen as a green and renewable fuel are increasingly considered as a central component in the transition to a green economy. Green hydrogen, i.e. hydrogen produced by water electrolysis with electricity from renewable energy sources, could abate CO₂ emissions and replace fossil fuel usage within transport, heating, stationary applications and various industrial processes. In this talk we will present our latest work on off-grid low carbon renewable energy-based systems (RES) setups for the newly planned Atacama Large Aperture Submillimeter Telescope (AtLAST) and compare them to business-as-usual diesel power generated systems. We consider systems built near the telescope on the Chajnantor plateau at 5000 m above sea level, near the town of San Pedro de Atacama (also off-grid). Technologies included in the designed systems are photovoltaics, batteries, and hydrogen technology, sizing them according to the telescope’s projected energy demand and reliability requirements, cost assumptions for the 2030 year and site-specific characteristics (including a particular interest on the effect of high altitudes on hydrogen-based components). We assess whether 100% RES scenarios are favorable from an environmental point of view in the categories climate change, mineral resource depletion and water use. The system boundary includes the production of components, their transport to the energy system site, and the operation and maintenance of the system. We find that 100% RES scenarios have a lower CO₂e impact than high-renewable scenarios, however, the latter lower the mineral resource depletion and water use by about 27% compared to 100% RES scenarios. Applying hybrid energy storage systems increases the water use impact, while reducing the mineral resource depletion. An additional aspect of interest in our study is the proposition of a socially accepted renewable energy system where we combine an energy system model with a participatory multi-criteria analysis.

Results reveal that a renewable energy system supplying the telescope could also cover 66% of the nearby community’s energy needs of San Pedro de Atacama, without additional capacity. Stakeholders inputs show this as the most attractive solution by developing an energy system where all of them benefit. Replicating similar energy systems at nearby telescopes could reduce fossil fuel-based energy generation by 30GWh annually, cutting emissions by 18-24ktCO₂eq while contributing to acceptability of new infrastructures and energy justice.

Acknowledgments

This work received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No. 951815 (AtLAST project). Acknowledgments to the...
team of WP5 (Environmental Sustainability) at UiO, Isabelle Viole, Guillermo Valenzuela-Venegas, Marianne Zeyringer. Special thanks to our astronomy colleagues for the cooperation in the interdisciplinary project AtLAST.

2:15 PM EN06.11/EN03.11.02
Analysis of Inception Sites of Vented Water Trees in a Laboratory Aged High Voltage XLPE Subsea Cable

Sofia B. Harberg1, Cedric Lesaint2, Sigurd Wenner3, Inger-Emma Nylund1, Per Erik Vollum1, Sverre Hvidsten1 and Mari-Ann Einarasrud1, 1NTNU, Norway; 2SINTEF Energy, Norway; 3SINTEF Industry, Norway

The use of lead sheaths in future subsea high voltage power cable designs will not be possible, or subject to a strict authorization processes because lead is a candidate for future inclusion by the European Chemicals Agency in the REACH Annex. “Wet design” subsea cables with no metallic barrier have been developed and are available for voltages up to 66 kV. Using the wet design also for higher voltages is very attractive to avoid the use of lead or metallic sheaths. However, in such cables, water molecules can permeate into the polymeric cable insulation system during service. As subsea high voltage cable cores have up to now been in dry service conditions, the knowledge on their performance when subjected to water is not known.

In this work, XLPE cable cores have been subjected to wet ageing following the recommendations in CIGRE TB 722. The electrical ageing was performed at 500 Hz with an equivalent electrical stress at the conductor screen of 10 kV/mm. The cable was helically spiraled into 2 mm thick samples. Thevented water trees which appeared from the semi-conductive screens were made visible using a water pre-treatment supersaturating the tree channels. The water trees were located, and the inception sites were cryo-microtomated. The sites were assessed using Energy Dispersive X-ray analysis (EDX) and Electron Energy Loss Spectroscopy (EELS) to determine the chemical composition of the section analyzed by Scanning Transmission Electron Microscopy (STEM). More than 5 vented water tree inception sites from the same cable were analyzed. The overall composition of inorganic elements was analyzed using Inductively Coupled Plasma Mass Spectrometry (ICPMS).

The cable insulation and semi-conductor sections that were analyzed by ICPMS revealed the presence of ionic species such as Na+ or K+. More localized investigation at the inception sites of the water trees was conducted by EDX and EELS analysis with respect to inorganic elements, and the results were compared to those obtained by ICPMS.

2:30 PM EN06.11/EN03.11.03
Innovative Energy Harvesting from Salinity Gradients: Asymmetric Flow-Electrode Capacitive Mixing with MnO Coated Activated Carbon

Insung Hwang1, Seungcheol Myeong1, Seunggun Choi1, Hyoungun Lee1, Minsoo Kim1, Han Seung Min1,2, Hongjun Park1, Bobae Lee1, Ungyu Paik1 and Taesung Song1,2, 1Hanyang University, Korea (the Republic of); 2Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of)

Since salinity gradients are available in coastal environments like estuaries and saline lagoons, this innovative approach allows for the conversion of thermal and chemical energy into electric energy. The key to this approach is the use of activated carbon coated with MnO as a flow electrode in an asymmetric flow-electrode capacitive mixing (F-CapMix) system. The MnO-coated carbon facilitates the conversion of the chemical energy contained in the salinity gradient into electrical energy. The overall efficiency of the system is determined by the concentration of the salinity gradient and the temperature difference between the two sides of the F-CapMix system. This approach is particularly promising for remote islands and coastal areas where a consistent supply of renewable energy is needed.

2:45 PM EN06.11/EN03.11.05
Stretchable Plant-Based Redox-Diffusion Batteries

Aiman Rahmanuddin1,2 and Klas Tybrandt1,2, 1Kungliga Tekniska högskolan, Sweden; 2Wallenberg Wood Science Centre, Sweden

Conventional batteries are not stretchable and can’t be used in wearable electronics, such as health monitoring devices. Plant-based redox diffusion batteries are a promising solution to this challenge. These batteries use plant-based redox molecules that can diffuse through plant-based electrolytes. The redox molecules are redox-diffusion batteries. In this study, we introduce a new type of redox-diffusion battery that is made from plant-based redox-diffusion molecules and a cellulose-based 3D scaffold. The redox reaction is mediated by diffusion of dissolved redox molecules within the pores of the scaffold. This approach is particularly promising for applications in stretchable electronics, such as stretchable wearable devices.

Efficient conversion and storage of solar energy are crucial steps in the establishment of a renewable and carbon neutral energy supply. Photocatalysis and photoelectrochemistry are considered promising to make use of the large amounts of sunlight that reach the surface of earth. They render the direct conversion of light into chemical energy possible, e.g. solar fuels like hydrogen or biofuels. However, conventional F-CapMix systems encounter limitations in power density due to the restricted charge storage capacity inherent in porous carbon materials, which operate via the electrical double-layer mechanism. In this study, we introduce manganese dioxide-coated activated carbon (MnO@AC) as a novel flow-electrode material for F-CapMix systems, placing specific emphasis on the introduction of an asymmetric flow-electrode system. We conduct a comprehensive assessment of the electrochemical properties of both activated carbon (AC) and MnO@AC-based flow-electrodes, with particular attention to their suitability as positive and negative electrodes for symmetric and asymmetric F-CapMix configurations. Notably, it becomes evident that remarkable performance enhancements are exclusively observed in the context of the asymmetric F-CapMix system, thus underscoring the heightened efficiency of the MnO@AC material within this asymmetric framework. Employing MnO@AC as the flow-electrode in the asymmetric F-CapMix configuration yields an impressive power density of 2.22 W/m² through reversible redox reactions involving Na+ ions. These findings not only expand the horizons of potential applications but also underscore the transferability of our strategies to various materials engaged in redox reactions with Na+ and Cl− ions within the realm of F-CapMix systems.

3:30 PM EN06.12/EN03.12.02
Nanostructured Sustainable Materials for Solar Energy Conversion: Fe-Based Absorbers and Catalysts

Roland Marschall- University of Bayreuth, Germany

Efficient conversion and storage of solar energy are crucial steps in the establishment of a renewable and carbon neutral energy supply. Photocatalysis and photoelectrochemistry are considered promising to make use of the large amounts of sunlight that reach the surface of the earth. They render the direct conversion of light into chemical energy possible, e.g. solar fuels like hydrogen or ammonia. In recent years, earth-abundant Fe-based materials have emerged as promising materials for these applications. They have the inherent ability to absorb a large part of the visible light spectrum with band gaps around 2 eV, while some of them being also very good photocatalysts. My group utilizes modern synthesis techniques to prepare nanostructured Fe-based materials for the generation of solar fuels.

In recent years, we have developed fast microwave-assisted sol-gel syntheses yielding phase-pure spinel ferrite nanoparticles of e.g. MgFe2O4, CuFe2O4, NiFe2O4, MnFe2O4 and ZnFe2O4 at temperatures as low as 170-200 °C.[1,2] The crystallite size can be tailored in-situ or post-synthetic heat treatment, however the materials are already (partly) crystalline as-prepared, with specific surface areas around 200 m²/g. Some syntheses even take only several minutes. Photocatalytic and electrochemical studies have been presented, as well as the conversion of some spinel oxides into (oxy)sulfides and pendlandites for electrocatalytic water splitting.[3,4] Moreover, a direct microwave-assisted synthesis for nickel-iron sulphide nanospheres for electrocatalytic CO2 reduction and photocatalytic HER will also be presented.[5,6] Finally, the potential of using a heterojunction of iron sulphide and carbon nitride for light-induced reduction of N2 to ammonia will be introduced.[7]

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Literature:

3:45 PM EN06.12/EN03.12.03
Mesoporous Zn-Doped MnCo2O4 Nanoparticles for Asymmetric Supercapacitor Application

Prem Sagar Shukla1, Anant Agrawal2, Anurag Gaur3 and Ghanshyam D. Varma1, 1Indian
Energy sources that are reliable as well as sustainable have become essential in the present technological world. Our dependency on fossil fuels has its limitations, is not sustainable, and has a number of consequences, including greenhouse gas emissions, water pollution, and hazardous waste. Researchers have focused on supercapacitors as next-generation energy storage devices due to their quick charge/discharge rate and outstanding cycle stability. Because of their excellent power delivery and quick charging characteristics, supercapacitors have significant advantages for high-power applications. This study aims to determine how Zn doping at the coreshell site of MnCo2O4 affects its electrochemical properties. In this approach, we have synthesized Zn-doped MnCo2O4 nanomaterial abbreviated as ZMCO for supercapacitor electrodes. The XRD and HRTEM results confirm the presence of cubic phase of ZMCO. Surface area and morphology were studied through BET and FESEM measurements, respectively. Among all the samples, MnZn0.4Co1.6O4 shows better electrochemical performance due to its larger specific surface area and mesoporous distribution of pore size. Moreover, the single electrode showed excellent cycling stability along with good coulombic efficiency. To evaluate the practical utility of the synthesized nanomaterial, an asymmetric supercapacitor (ASC) device was fabricated. The device was fabricated with the ZMCO nanomaterial as a cathode and activated carbon as an anode electrode. The device exhibited a higher power density and specific energy density. The device also showed excellent cycling stability in PVA/KOH gel electrolyte. Additionally, a single device illuminates a red LED, while connecting two devices in series illuminate red and green LED. We believe Zn doped MnCo2O4 provides a lot of potential for making higher-performance supercapacitor devices because of its simple synthesis process and superior electrochemical characteristics.

4:00 PM EN06.12/EN03.12.04
Forming Nanoscale Sculptured Surfaces for Advanced Electrical Bonds by Environmentally Friendly Electrochemical Etching
Jannik Rank, Jörg Bahr, Jürgen Carstensen and Rainer Adelung; Kiel University, Germany

With the modern advances in high performance adhesives, bonded joints are more and more competitive or are even outperforming mechanical joints and welds. Bonded joints exhibit many benefits compared to mechanical joints in respect of thickness, weight, force distribution, application and especially for dissimilar material bonding. The connection of different materials with fundamentally different properties is cruciﬁc for applications such as multi-material automotive bodies and composite materials for the aerospace sector. Therefore, the wide range of different favorable materials and the resulting different surface properties create high demands on the adhesives and often require complex surface preparation involving hazardous chemicals. This work uses an electrochemical nanoscale sculpturing process with a seawater-like electrolyte for an eco-friendly surface preparation and nearly perfect bonding on various metals such as aluminum, stainless steel and brass. The strong adhesion is achieved by creating sub-micron underruts that facilitate mechanical interlocking of adhesive and material. Chemical surface-to-surface interaction becomes less relevant, resulting in bonds that are limited by intrinsic fracture strength of the used adhesive. The underruts are produced by a highly selective pulsed electrochemical etching, resulting in three-dimensional formation of chemically stable surfaces. Additionally, brass can selectively beached by the same process. Upon leaching, the structured surfaces are copper-rich and show extraordinarily good wettability for solder. For common tin-based solders, this work shows a contact angle near zero with several times larger spreading compared to a mechanical cleaned and roughened surface. Since the chemical surface interaction is no longer decisive for the bonding strength, it also becomes possible to use completely new types of adhesives with superior bulk properties, that would otherwise lack the chemical properties for sufficient surface adhesion. This can not only be used to increase mechanical strength of a joint but is also promising for joining with electrically conductive adhesives as an alternative to soldering. Typical conductive adhesives consist of a conductive filler (e.g., metal particles) and an adhesive as binder, resulting in a tradeoff between bonding and conductivity properties. This work will evaluate nano structured surfaces and their use for mechanically strong, conductive-bonded joints.

4:15 PM EN06.12/EN03.12.05
A Biodegradable and Stretchable Battery
Filipina Wentz1,2, Animan Rahamanadin1,2 and Klas Tybrandt1,2; 1Linköping University, Sweden; 2Wallenberg Wood Science Center, Sweden

Next generation wearables will interface intimately with the human body. They will be used for health monitoring, soft robotics, and futuristic consumer electronics such as e-skis and e-textiles. For seamless integration with the human body, mechanical properties such as stretchability, softness and bendability need to be optimized. Extensive research has already been done on improving the mechanical properties of various components, such as transistors, conductors, diodes, sensors etc., to complement next-generation wearables. Batteries give autonomy to these wearables, by providing a portable electrolyte for an eco-friendly surface preparation and nearly perfect bonding on various metals such as aluminum, stainless steel and brass.

Zn-ion batteries show great potential as a sustainable alternative to current Li-ion battery technology. Zn has a high theoretical capacity, is biodegradable and abundant, and can operate in safe energy sources that are reliable as well as sustainable have become essential in the present technological world. Our dependency on fossil fuels has its limitations, is not sustainable, and has a number of consequences, including greenhouse gas emissions, water pollution, and hazardous waste. Researchers have focused on supercapacitors as next-generation energy storage devices due to their quick charge/discharge rate and outstanding cycle stability. Because of their excellent power delivery and quick charging characteristics, supercapacitors have significant advantages for high-power applications. This study aims to determine how Zn doping at the coreshell site of MnCo2O4 affects its electrochemical properties. In this approach, we have synthesized Zn-doped MnCo2O4 nanomaterial abbreviated as ZMCO for supercapacitor electrodes. The XRD and HRTEM results confirm the presence of cubic phase of ZMCO. Surface area and morphology were studied through BET and FESEM measurements, respectively. Among all the samples, MnZn0.4Co1.6O4 shows better electrochemical performance due to its larger specific surface area and mesoporous distribution of pore size. Moreover, the single electrode showed excellent cycling stability along with good coulombic efficiency. To evaluate the practical utility of the synthesized nanomaterial, an asymmetric supercapacitor (ASC) device was fabricated. The device was fabricated with the ZMCO nanomaterial as a cathode and activated carbon as an anode electrode. The device exhibited a higher power density and specific energy density. The device also showed excellent cycling stability in PVA/KOH gel electrolyte. Additionally, a single device illuminates a red LED, while connecting two devices in series illuminate red and green LED. We believe Zn doped MnCo2O4 provides a lot of potential for making higher-performance supercapacitor devices because of its simple synthesis process and superior electrochemical characteristics.

8:30 AM EN06.13/EN03.14.02
Unleashing Moisture Content as a Capacitance Deciding Factor for Supercapacitors derived from Wild Orchid
Abhay Deshmukh, Rashtrasant Tukadoji Mharaj Nagpur University, India

All carbonaceous materials manifest Electrical double layered capacitor (EDLC) type behaviour. Still, drawbacks like cost-effectiveness and availability of precursor materials provide a spotlight on “Biomass derived carbons” as electrode material for supercapacitors. Nevertheless, different types of biomasses show uniqueness in their properties and thus reveal differences in carbon materials derived from them. During carbonizing or pyrolysis of biomass, a factor called moisture is generally ignored or removed by simply drying the sample in an air oven. Here in this work, we choose leaves of a wild orchid (Vanda Tasselleta) which is an abundantly available species of plant from the Indian subcontinent to Indochina, to establish a relation between “Biomass derived carbons” as electrode material for supercapacitors. Nevertheless, different types of biomasses show uniqueness in their properties and thus reveal differences in carbon materials derived from them. During carbonizing or pyrolysis of biomass, a factor called moisture is generally ignored or removed by simply drying the sample in an air oven. Here in this work, we choose leaves of a wild orchid (Vanda Tasselleta) which is an abundantly available species of plant from the Indian subcontinent to Indochina, to establish a relation between moisture content in biomass, rate capability and capacitance of electrode material. Interestingly out of five variations viz normal leaves without treatment, dried leaves, soaked leaves, a mixture of dried and normal leaves, and -20°C samples, carbon derived from normal leaves shows the highest capacitance of 213.43 F/g at 0.5 A/g without any activation. But fascinatingly normal leaves without treatment show the lowest rate capability of only 35.53 % which is approximately half of the rate capability obtained for dry leaves of wild orchids exhibiting 124.78 F/g capacitance at 0.5 A/g. Moreover, our work demonstrates the dependence of pore size distribution on the amount of moisture intact in wild orchid leaves with the help of characterization techniques. Finally, a two-electrode symmetric device was fabricated showing high capacitance and capacitance retention which shows practical application of wild orchid leaves as supercapacitor electrode material.

8:45 AM EN06.13/EN03.14.03
Cost-Effective Fabrication Process in 24 Hours for Supercapacitors
Satnam S. Mattu; Rastrasant Tukadoji Maharaj Nagpur University, India

In the ever-expanding realm of modern science and electronics, the demand for miniaturized and flexible energy storage devices is growing to enhance people’s lives with compact and adaptable electronics. Currently, the prevalent use of micro-batteries in potable devices presents a significant drawback, marked by their short life spans of only a few hundred to several thousand cycles, thus frequent replacement is required but becomes problematic in the context of implantable bioshops. Not only this, connecting micro-batteries by some combination to
provide high power makes it even bulkier. In stark contrast, micro-supercapacitors with an increase in a number of advantages like flexibility, remain lightweight with high power discharge. Apart from this manufacturing cost-effective micro-supercapacitors in less time is a task. Thus, this work addresses the making of micro-supercapacitors from highly porous pseudocapacitive material MOFs (metal organic framework) using LASER ablation technique. The substrate used here is a normal paper where deposition of material is exhibiting using a very simple method and finally scribing it using CO2 LASER scribing. Different designs of MSCs are also explored and finalized in-plane concentric shape which provides a wide voltage window from 0 to -0.8 V as well as from 0 to 0.8 V at high scan rates showing the highest areal capacitance of 57 μF cm⁻². Moreover, making use of gel electrolyte and showing capacitance in microns increases its feasibility for flexible devices. Finally, to show the practical application of the electrode several LEDs were blinked by stacking prepared MSC. Thus, the cost-effective method is implemented with a claim of manufacturing micro-supercapacitors in a single day.

9:00 AM EN06.13/EN03.14.04
Fabrication of Fully Sustainable Electrop spun Fiber-Reinforced 3D Carbon from Waste as Scalable Electrodes in Energy Storage Materials
Michael W. Thielke, Luis M. Murillo Herrera, Carlos Mungo and Ana Jorge Sobrido; Queen Mary University of London, United Kingdom
Carbon fibers for the new batteries have been of interest for a long time based on their advantageous shape that provides stability, flexibility and a high surface area, lightweight, and high electrical conductivity. Most of the current reported and commercial carbon fibers are derived from using polyacrylonitride, a synthetic polymer obtained from crude oil. Due to the finite nature and environmental impact of sourcing and refining crude oil, it is necessary to find sustainable alternatives to ensure the filling of the demand in the future.

Fully sustainable carbon fiber alternatives have been reported based on the use of biopolymers. A promising candidate as precursor for carbon fibers is lignin, the main byproduct of the paper and pulp industry and the second most abundant biopolymer that is rich in aromatic carbon groups. Carbonizing lignin therefore, results in a high yield of carbon fibers. To ensure enough entanglement of the molecular chains, that allows the formation of stable fibers, the high molecular weight fraction of lignin is extracted, allowing the fabrication of pure lignin fibers without the use of additional synthetic polymers as carrier.

One technique to fabricate fibers that have been of particular interest is electrospinning. Through the use of a high voltage field, the electrostatic forces draw a polymer solution to fibers in submicron diameter ranges, lower than any of the other commercially used techniques to fabricate fibers. Due to the enormous surface area to volume ratio, these fibers have been at the center of interest in various applications, including energy storage systems and (electro)catalysis. In addition to the relatively simple setup, electrospinning is the ideal technique to explore the properties of new materials in a laboratory scale. In larger scaled energy storage systems, such as flow batteries, electrop spun fibers show a disadvantage due to the limited thickness of the fiber mat can reach to compared other spinning processes due to the relatively small fabrication scale and process that uses the electric field.

To overcome this issue, we created a 3D structure based on lignin fibers through the lyophilization of the electrosprun lignin fibers. The structure was obtained through a sonification process of the fibers in an aqueous solution of potato-based protein, another byproduct of the potato starch industry.

As the subsequent processes for the production of mixed mesoporous carbon. In this work, we have developed a novel approach to the production of this class of carbon fiber by using lignin as a precursor material. The production of lignin fibers is achieved through a simple, one-step process that involves the lyophilization of an aqueous suspension of lignin and a polysaccharide. The resulting structure is a highly porous material with a large surface area and is capable of retaining its structure over a wide range of temperatures. This material has potential applications in various fields, such as energy storage and environmental remediation.

9:15 AM EN06.13/EN03.14.05
Long-Term Stability of Hygroscopic Hydrogels by Preventing Metal Ion-Mediated Degradation
Chad Wilson, Carlos D. Diaz, Lorenzo Masetti, Xiao-Yun Yan, Will Chang Liu, Shucong Li, Gang Chen and Xuanhe Zhao; Massachusetts Institute of Technology, United States
Recent developments in material chemistry highlight hygroscopic hydrogels as promising candidates for use in sorption systems, with applications ranging from atmospheric water harvesting to energy storage and thermal management. However, material lifetime remains a significant limitation to realizing cost-effective high-performance devices. In this work, we consider deployment of lithium chloride-loaded polycrylamide (PAM + LiCl) hydrogels at elevated temperatures on a variety of potential system substrates, correlating lifetime and cyclability of the gels to device design and material choice. We show that the presence of metallic ions in the system leads directly to material degradation via radical formation in the gels. Moreover, metallic ion absence results in consistent sorption performance and a gel lifetime of over 8 months. This work demonstrates the long-term stability of PAM + LiCl hydrogels, and provides initial design guidelines for its repeatable, cost-effective implementation in future sorption systems.

9:30 AM EN06.13/EN03.14.06
Recycling Polyolefine Waste into Electromechanically Responsive Materials by Producing Multilayered Films from Bilayers with Asymmetric Triboelectric Properties
Andris Rutka1, Anna Rutka1, Artis Linarts5 and Peter C. Sherrell1; Riga Technical University, Latvia; RMIT University, Australia
Millions of tons of foamed polyolefine (FPS) are produced annually. FPS is a major environmental problem. Polyolefine is slow to biodegrade, with an estimated decomposition time of up to 500 years. FPS contains 95% of air, and thus, it has a very low extent of recycling. According to a study by the California Integrated Waste Management Board, less than 1% of FPS was recycled in 2019. At the same time, FPS fills up 25% to 30% of landfill space by volume around the world.

Here, we report the recycling of FPS waste into electromechanically responsive triboelectric laminates (TLs). These TLs possess internal triboelectric dipoles offering an alternative to ferroelectric fluoropolymers. The piezoelectric contact-mode testing showing a FPS laminate is comparable to state-of-the-art piezoelectric fluoropolymers for overall electromechanical conversion. Piezoelectric fluoropolymers are critical electromechanically responsive materials for flexible energy harvesting and sensors. However, their production results in the release of significant amounts of toxic substances into the environment, and as such, these fluoropolymers are at risk of being banned by the European Union. Our alternative flexible electromechanically responsive materials can replace piezoelectric fluoropolymers, thus enabling rapid integration into current technology standards.

10:15 AM EN06.13/EN03.14.07
Waste to Product: Green Production Processes for a Circular Economy
Andris Weidenkaff, Wenjie Xie and Jinxue Ding; Technical University of Darmstadt, Germany
The energy transition to defossilisation will be built on renewable energy converters which require tailored materials and a new infrastructure partially based on critical materials. This transformation to a future fossil free green circular economy will be based on sustainable materials production processes and ecologic innovations. The development of renewable materials for renewable energy converters requires sustainable large-scale production from secondary raw materials. The decision making for future resilient energy systems has to be based on environmental aspects as well as on performance criteria defined by a holistic life cycle assessment.

In this lecture an efficient recycle precursors production for materials with a programmable lifetime and regeneration will be introduced as a suitable approach. The design of circular high performance materials uses theoretical predictions and the criticality analysis of applied elements to improve the cycle life of future energy converters such as thermoelectric generators and refrigerators, batteries, electrolyzers, fuel cells, plasmaphysers, hydrides and solar watersplitting cells.

10:00 AM BREAK

10:30 AM EN06.13/EN03.14.08
Supercritical CO2 Assisted Aerosol Synthesis of HKUST-1 Nanoparticles in a Continuous Flow Reactor
Xi Feng, Almond Lau and Igor Novoselov; University of Washington, United States
Metal-organic Frameworks (MOFs) are very promising materials for gas sensing, catalysis, energy storage, water purification and drug delivery due to their high porosity, tunable pore sizes, adequate chemical and thermal stability, and various structures and compositions. Downsizing MOFs to the nanoscale brings superior properties over their bulk analogs, such as high surface-to-volume ratio, rich exposed metals and ligands, short diffusion path for reactants, which all contribute to improved performances. While great efforts have been made to reduce the particle sizes by controlling the reaction kinetics or terminating the particle growth with additives, large-scale synthesis of MOF nanoparticles with simple methods remains a challenge. Here, we report supercritical CO2 assisted aerosol synthesis of HKUST-1 in a continuous flow reactor. This method yields pure and thermal stable HKUST-1 nanoparticles with median sizes of 98-212 nm and BET surface area of 1613-1887 m²/g in the residence time of just 3 seconds without any additives. Supercritical CO2 and ethanol with a mole ratio of 9:1 are used as co-solvents for the fast precipitation of HKUST-1 nucleus and crystal growth. A typical dry yield of 53.7 wt% is achieved with 0.1 M copper precursor at 75 °C and 13 MPa. Size analysis of the products obtained at different copper concentrations shows the influence of supersaturation and fluid phase behavior to the nanoparticle formation. Fractal dimension analysis indicates that the growth is caused by aggregation of primary nanocrystals, indicating a non-classical crystal growth mechanism. The use of supercritical CO2 saves the use of organic solvents. In addition, super critical CO2 has physical properties such as natural abundance, non-flammability, and low toxicity, making this synthesis a green and sustainable method for the scalable production of MOF nanoparticles.

10:45 AM EN06.13/EN03.14.09
Laster-Induced Graphitization of Lignocellulosic Cellulose Nanofiber Films Intended for Electronic and Energy Storage Applications

Material Stability and Durability Testing Using the Extreme Space Environment in Low Earth Orbit

Material stability and durability of materials for use in multiple applications in space and on Earth. Materials exposed to the harsh space environment in low Earth orbit (LEO) are subject to atomic oxygen (AO) erosion, ultraviolet (UV) radiation, ionizing radiation, vacuum, thermal cycling, and temperature extremes. Depending on the material, each of these factors can lead to significant material degradation. For materials used in space applications, space exposure testing is critical for evaluating the performance of the material. For materials designed for Earth applications, long-term space exposure provides a mechanism for accelerated material degradation testing, where the impact of space-exposure can be correlated to degradation via Earth-based testing to identify failure modes and evaluate the lifespan of the material.

The International Space Station (ISS) National Laboratory offers an ideal platform for long-term exposure to the extreme space environment in LEO, particularly because power, data, and imaging can be provided "in-situ" and samples can be returned to Earth for postflight analysis and comparison to ground samples. Some materials that have been investigated using ISS external platforms include silicon-, organic-, copper-zinc-tin-sulfide (CZTS), and perovskite-based 3D photovoltaic cells; methylammonium lead tribromide (MAPbBr3) and methylammonium lead triiodide (MAPbI3) perovskites; Beta Barium Metaborate (BBO) lenses; biomaterials; polymers; ceramics; and metals. In addition, several electronic, photonic, and other devices have been tested in the harsh space environment outside the ISS.

** Keynote Speaker

+ JMR Distinguished Invited Speaker

* Invited Paper

** Keynote Speaker

^ MRS Communications Early Career Distinguished Presenter

SYMPOSIUM EN07

Thermal Transport and Energy Conversion

Symposium Organizers

Woochul Kim, Yonsei University
Sheng Shen, Carnegie Mellon University
Sunmi Shin, National University of Singapore
Sebastian Volz, The University of Tokyo

April 22 - May 7, 2024

10:45 AM EN07.01.01

Solid-State Electrochemical Thermal Transistors with Large Thermal Conductivity Switching Width

Ahrong Jeong, Zhiping Bian, Mitsuki Yoshimura, Bin Feng, Yuichi Ikuhara, Yusaku Magari, and Hiromichi Ohhta

Hokkaido University, Japan
The University of Tokyo, Japan

Thermal transistors that electrically switch heat flow on and off have attracted growing attention as thermotronic devices such as thermal shutters and thermal displays. In 2023, we
demonstrated the world’s first solid-state electrochemical thermal transistors with SrCoO$_2$ ($2 \leq x \leq 3$) as the active layer.\textsuperscript{1-3} The thermal conductivity ($\kappa$) on/off ratio was approximately 4 and $\kappa$ switching width was 2.85 W m$^{-1}$ K$^{-1}$. Here, we demonstrate solid-state thermal transistors with a large $\kappa$ switching width of 9.5 W m$^{-1}$ K$^{-1}$. We used CeO$_2$ thin films as the active layer directly deposited on the solid electrolyte YSZ substrate using the PLD method. A Pt thin film was deposited on the surface of the CeO$_2$ thin film and the back surface of the YSZ substrate using the sputtering method to create an all-solid-state thermal transistor. When the CeO$_2$ thin film was once reduced and then oxidized, the $\kappa$ was approximately 2.5 W m$^{-1}$ K$^{-1}$ in the most reduced state, and $\kappa$ increased with oxidation to 11.8 W m$^{-1}$ K$^{-1}$. This reduction/oxidation was repeated 5 times and the average value of $\kappa$ was 2.5 W m$^{-1}$ K$^{-1}$ after reduction and 12 W m$^{-1}$ K$^{-1}$ after oxidation. The CeO$_2$-based solid-state electrochemical thermal transistors might have the potential for thermotronic devices such as thermal shutters and thermal displays.


11:00 AM EN07.01.03

Active Heat Transfer Fluids: Liquid Coolants Containing Self-Propelled Microparticles for Heat Transfer Enhancement
Jacob Velazquez\textsuperscript{1}, Darsh Devkar\textsuperscript{2}, Sajad Kargar\textsuperscript{1}, Amit K. Singh\textsuperscript{1} and Jeffrey L. Moran\textsuperscript{1}.

\textsuperscript{1}George Mason University, United States; \textsuperscript{2}University of Virginia, United States

Liquid coolants are critical components of many modern technologies, such as hybrid electric vehicle batteries, solar receivers, and cooling systems for electronics. Sustaining the growth of these technologies while limiting their carbon footprint requires coolants that transfer heat efficiently. Since the 1990s, significant research has been conducted into the use of suspended nanoparticles to improve coolant performance. The resulting suspensions, known as nanofluids, typically exhibit higher thermal conductivity than the liquids alone, since the particle material is typically more thermally conductive than the liquid. However, the improvements provided by nanoparticles are fundamentally limited by the particles’ inability to move on their own through the liquid, and thus agitate convective mixing that could dramatically improve performance.

In this work, we explore the use of self-propelled particles (SPPs), which are colloids that can move autonomously in liquids using energy from their local environment, to accelerate heat transfer in fluids. As they move, SPPs induce disturbance flows in the surrounding liquid, and we hypothesize that this "micro-stirring" effect can enhance the heat transport rate by an amount depending on the SPPs’ size, speed, and volume fraction. We demonstrated this concept experimentally by placing an SPP suspension in contact with a heated surface; for a constant heat flux, a micro-effective coolant should result in a lower temperature of the heated surface. By measuring the temperatures of the fluid near the heated surface, we can quantify SPP-induced increases in the convective heat transfer coefficient (HTC), a widely-recognized metric of heat transfer efficiency. We present data for the HTC of various SPP suspensions under different experimental conditions. The results will inform the prospective use of coolants containing SPPs, which we refer to as "active heat transfer fluids," in a variety of cooling applications in the energy, environmental, and biomedical sectors.

11:30 AM EN07.01.05

Thermoreflectance-Based Thermometry of Silicon Thin Films with Resonantly Enhanced Temperature Sensitivity
Xinchao Wang, Changxing Shi, Qifan Zheng, Jan Maroske and Dakotah Thompson; University of Wisconsin-Madison, United States

We demonstrate a thermoreflectance-based thermometry technique with an ultimate temperature resolution of 60 µK in a 2.6 MHz bandwidth. This temperature resolution was achieved using a 532 nm-wavelength probe laser and a ~1 µm-thick silicon transducer film with a thermoreflectance coefficient of $-4.7 \times 10^{-3}$ K$^{-1}$ at room temperature. The thermoreflectance sensitivity reported here is over an order of magnitude greater than that of metal transducers, and is comparable to the sensitivity of traditional thermistors. Supporting calculations reveal that the enhancement in sensitivity is due to optical interference in the thin film.

11:30 AM NO SHOW. W/D AFTER PRESENTATION TIME

SESSION EN07.02: Thermal Transport Across Interfaces/Thermal Transport in Nanoscales
Session Chairs: Sheng Shen and Sebastian Volz
Tuesday Morning, April 23, 2024
Room 327, Level 3, Summit

10:45 AM #EN07.02.01

Rethinking Evaporation and Condensation
Gang Chen; Massachusetts Institute of Technology, United States

Although ubiquitous in nature and industrial processes, transport processes at the interface during evaporation and condensation are still poorly understood. Experiments have shown temperature discontinuities at the interface during evaporation and condensation but the experimentally reported interface temperature jump varies by two orders of magnitude. Even the direction of such temperature jump is still being debated. In this talk, I will first discuss a thermomolecular emission for thermal evaporation, analogous to the thermionic emission mechanism. Starting from the kinetic theory, we derive interfacial mass flux and heat flux conditions, which are used to solve the coupled problem between the liquid and the vapor phase during evaporation and condensation. Our model shows that when evaporation or condensation happens, an intrinsic temperature difference develops across the interface, due to the mismatch of the enthalpy carried by vapor at the interface and the bulk region. The vapor temperature near the interface cools below the saturation temperature on the liquid surface during evaporation and heats up above the latter during condensation. However, many existing experiments have shown an opposite trend to this prediction. We explain this difference as arising from the reverse heat conduction in the vapor phase. Our model results compare favorably with experiments on both evaporation and condensation. We show that when the liquid layer is very thin, most of the applied temperature difference between the solid wall and the vapor phase happens at the liquid-vapor interface, leading to saturation of the evaporation and the condensation rates and the corresponding heat transfer rate. This result contradicts current belief that the evaporation and condensation rates are inversely proportional to the liquid film thickness. For the two parallel plate problem with evaporation on one side and condensation on the other, we will explain several paradoxical predictions including inverted temperature profile in the vapor phase.


11:15 AM EN07.15.18

Evaluating The Vibrational Character of Thermal Carriers across Order–Disorder Phase Transitions
Rahil Ukani\textsuperscript{1}, Qichen Song\textsuperscript{2}, Catherine Thai\textsuperscript{1}, Alexander D. Christodoulides\textsuperscript{2}, Yukung Moon\textsuperscript{1}, Dehong Yu\textsuperscript{3}, Caleb Stamper\textsuperscript{4}, Junyoung Seo\textsuperscript{1}, Jonathan A. Malen\textsuperscript{2} and Jarad A. Mason\textsuperscript{1};
\textsuperscript{1}Harvard University, United States; \textsuperscript{2}Carnegie Mellon University, United States; \textsuperscript{3}Australian Nuclear Science and Technology Organisation, Australia; \textsuperscript{4}University of Wollongong, Australia

Materials containing aligned alkyl chains have shown considerable promise for energy applications, including solid-state cooling through caloric effects. Understanding how heat flows through these chains—particularly during phase transitions—can enable precise manipulation of their thermal transport properties, which are critical to optimizing efficiency in practical applications. Many of these materials offer tunable interchain chemistries and thermally responsive structural dynamics, which can offer molecular-level insights—and thus control—of heat conduction mechanisms. Here, we examine thermal transport in two classes of two-dimensional (2-D) layered crystals whose alkyl chains undergo thermally induced order–disorder transitions: (1) hybrid perovskites, and (2) organic salts. Vibrational frequency-domain thermoreflectance (FDTIR) measurements of analogous 2-D perovskites and organic salt structures allow us to describe the role of chemical interactions and chain confinement in dictating thermal conductivity. Microscopy and nanomechanical characterizations similarly describe the influence of structural features and microstructure. Through quasielastic and inelastic neutron scattering, we highlight how the vibrational nature of thermal energy carriers changes as the alkyl chains in these materials transition from ordered to dynamically disordered states. These complementary techniques allow us to detail the key chemical levers that tune thermal transport in phase change materials. Our investigations reveal a comprehensive picture of the mechanisms underlying thermal conduction across phase changes of confined alkyl chains, and how interlayer chemistry regulates heat flow in complex crystals.
Understanding interfacial thermal resistance has focused on atomistic-scale phenomena such as carrier transmission functions across the interface. In this presentation, we discuss a phenomenon at nanoscale and micrometer scale for interfacial resistance: relaxation of non-equilibrium carriers through scattering. The widely used Landauer formalism assumes incident carriers have an equilibrium distribution, but the actual distribution can be highly non-equilibrium due to the interfacial scattering. The carriers with non-equilibrium distribution are relaxed by carrier scattering at micrometer scale and the Boltzmann’s H-theorem dictates entropy generation and thermal resistance during this relaxation process. To capture such process, we solve the Boltzmann equation with ab initio inputs. Our work shows two important facets of carrier non-equilibrium near interface and interfacial thermal resistance. First, we highlight significance of spectral heat flux mismatch for the interfacial thermal resistance. An example is a Si-SiGe alloy interface where the phonon dispersion is matched exactly but exhibits a substantial interfacial resistance. Second, we discuss the energy exchange between electrons and phonons in metal-insulator interfaces. We focus on how electron-phonon scattering influences the relaxation of thermal carriers near the interface as well as its impact on the entropy generation and non-equilibrium thermal resistance.

SESSION EN07.03: Radiative Heat Transfer
Session Chairs: Baowen Li and Sheng Shen
Tuesday Afternoon, April 23, 2024
Room 327, Level 3, Summit

1:45 PM *EN07.03.01
Thermal Transport and Conversion Using Photonic Nanostructures Renkun Chen; University of California, San Diego, United States

Photonics can be harnessed to engineer and in certain cases enhance thermal energy transport and conversion processes due to favorable characteristics of thermal photons relative to phonons under certain conditions, such as long wavelength, long propagation length, high speed, and spectral tunability. Here we present our work on thermal transport and conversion in nanostructures over the past few years. First, we showed that the coupling between phonons and traditional heat carriers such as phonons and electrons can be utilized to manipulate radiation and conduction heat transfer in polar dielectric and metallic nanostructures. In particular, we observe enhanced effective emissivity and thermal conductivity in rationally designed nanostructures of polar dielectrics and metals. Second, we developed high-temperature selective emitters based on photonic metamaterials. While selective emitters have been extensively studied previously, they are often not stable at high temperature due to the presence of nanoscale interfaces. We use novel material and structural designs to achieve high temperature stability. These selective emitters could be utilized for converting optical and electrical energy more efficiently into thermal energy within a desirable spectrum that are useful for systems such as thermophotovoltaic and infrared heating.

2:15 PM *EN07.03.02
Energy Transfer and Conversion in Nanoscale Gaps Pramod Sanji Reddy; University of Michigan, United States

Understanding radiative heat transfer in nanoscale gaps and devices is of considerable interest for creating novel energy conversion devices. In this talk, I will first describe ongoing efforts in our group to experimentally elucidate nanoscale radiative heat transfer. I will present our recent experimental work where we have explored how radiative heat transfer is modified in nanoscale gaps at room temperature and cryogenic temperatures. Specifically, I will describe a variety of instrumentation including novel nanopositioning platforms and microdevices, which we have developed to accomplish these measurements. Further, I will discuss possible applications of near-field thermal radiation for energy conversion and photonic cooling. Finally, I will briefly outline how these technical advances can be leveraged for future investigations of nanoscale heat transport and near-field thermophotovoltaic energy conversion.

2:45 PM EN07.03.04
Optical Interrogation of Subsurface Nanogap Thermal Transport Zachary T. Piotrowski, Amun Jarzembski, Wyatt Hodges, Anthony McDonald, Matthew Bahr, William Delmas, Ping Lu and Julia Deitz; Sandia National Laboratories, United States

Nanoscale thermal transport has received significant attention for next-generation energy conversion and thermal management applications. In particular, state-of-the-art experiments have shown for vacuum gap distances down to 10 nm that thermal transport is governed by near-field thermal radiation, and can be enhanced by orders of magnitude above the Planck black body limit. Moreover, radiative thermal transport is bridged to heat conduction by so-called acoustic phonon tunneling at contact, which can be controlled via external forces. However, to perform such complex experiments, precision measurement of heat flow and isolation from parasitic conduction are required. Here, we demonstrate the utility of hyperspectral frequency-domain thermoreflectance (FDTR) for the interrogation of thermal transport across subsurface nanogaps, alleviating the extreme challenges faced by nanoscale thermal transport experiments.

FDTR is a pump-probe optical technique sensitive to the thermal properties of an underlying material system. Here, a periodically modulated pump beam deposits energy into the sample, where subsequent temperature oscillations are monitored by a continuous wave probe beam via the thermoreflectance effect. Measurement of the phase lag between the thermal oscillations and periodic heating enables quantification of thermal properties though parametric fitting with the heat diffusion equation. In particular, FDTR at low pump frequencies can quantify and image interfaces up to 200 um below the surface. We demonstrate FDTR’s ability to interrogate subsurface nanogaps by looking at heterogeneously integrated gallium nitride (GaN) with diamond substrates and silicon with silicon substrates. We show that FDTR can precisely quantify the thermal conductivity of air trapped in sub-200 nm gap that is 15 um below the GaN surface. Similarly, we use hyperspectral FDTR imaging to map a mechanical standing wave in a silicon membrane supported by a silicon substrate, which spatially modulates the gap thermal conductance. Thus, FDTR eliminates the need for microfabricated precision calorimeters and thermally insulated gap supports through spatial mapping of subsurface thermal boundary conductances.

Acknowledgements: Sandia National Laboratories is a multi-mission laboratory managed and operated by the National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract No. DE-NA0003525. SAND2023-11105A

3:00 PM BREAK
TDTR-Based Thermal Conductivity Mapping – Challenges and Applications

Yee Kan Koh; National University of Singapore, Singapore

Over the past two decades, time-domain thermoreflectance (TDTR) has been developed into a versatile tool to measure the thermal conductivity of thin films and substrates. Variants of TDTR have been developed, to address the specific needs. For example, beam-offset TDTR has been developed to measure the in-plane thermal conductivity of the thin films. Dual-frequency TDTR has been developed to measure the thermal resistance of buried thin films and interfaces. These various TDTR variants are paramount to advance the knowledge of heat transport in different types of nanostructures and across interfaces. One variant of TDTR that is less explored is to use TDTR for thermal conductivity mapping. In this talk, we will present our recent work to develop and apply TDTR for thermal conductivity mapping. We will share the challenges we faced, including how to ensure smooth surfaces for mapping and how to interpret the results. We will also share our recent works to apply TDTR the map the thermal conductivity of twisted bi-layer graphene and electrons in the Li-ion batteries. For the first example, we map the thermal conductivity CVD-grown twisted bilayer graphene on single-layer graphene substrates. With the mapping, we are able to accurately measure the thermal conductivity difference between the bilayer and single layer graphene, as a function of the twisted angle between the graphene flakes. In the second example, we map the thermal conductivity of graphite and LCO electrodes of Li-ion batteries. We discuss how we interpret the mapping results, including our measurements near the boundaries of the electrode powders. Our works suggest that TDTR-based thermal conductivity mapping could be a powerful tool to study heat transport in complex composites.

Nanoscale Temperature Mapping for Operating Devices with Reflection Electron Elastic Energy Thermometry (REEET)

Menglong Hao1,2, Qiye Zheng2,4, Ziwen Zou1, Xing Xiang1, Saad Shaﬁullah1, Yuhang Cui1, Junqiao Wu2,4, and Chris Dames2,4; 1Southeast University, China; 2University of California, Berkeley, United States; 3The Hong Kong University of Science and Technology, Hong Kong; 4Lawrence Berkeley National Laboratory, United States

Thermal diffusivity measurement of thin films by Fourier transform thermo-reflectance method under front heat–front detect configuration

Takahiro Baba1, Tetsuya Baba1 and Takao Mori1,2; 1National Institute of Materials Science (NIMS), Japan; 2University of Tsukuba, Japan

Thermo-reflectance method is one of the few methods which can measure thermal transport properties in the cross-plane direction of thin films. Thermo-reflectance method under front heat–front detect (FF) configuration, so-called time domain thermo-reflectance (TDTR), is commonly used because it can be applied to a wide variety of samples including non-metallic thin films. In FF configuration, both pump beam and probe beam are focused at the same spot on the surface of a sample and temperature response from the surface is observed. In this case, the temperature response is significantly affected by the penetration of pump beam, which depends on the absorption coefficient of the surface. In TDTR method, a metallic layer, sometimes called transducer, is generally deposited on a sample to safely observe thermo-reflectance signals. In most cases, heat diffusion in the transducer is assumed to be infinitesimal and the layer can be regarded as heat bath with known heat capacity. To determine thermal diffusivity of the sample below the transducer, the rate of temperature decrease is analyzed. This means the penetration of pump beam, which affects the initial distribution of temperature, is not considered. This approach has some ambiguity because thermal diffusion in the transducer can significantly affect the determination of the thermal diffusivity of the sample. To examine this issue, we propose an analytical approach which considers the effect of penetration of pump beam. Our approach attributes to recent developments in thermo-reflectance method. The electrical delay technique has enabled the technique to observe temperature response in longer timescale than pulse interval of pump laser, which demonstrates the power of this technique for determination of ultrafast temperature response.

We measured some actual thin films by picosecond thermo-reflectance method under FF configuration. We are going to introduce notable developments in thermo-reflectance method and actual results obtained from these samples, and discuss the robustness and reliability of the determination.
discuss the suitability of the computationally inexpensive approximation to the PBE - Callaway model for MoS₂, motivated by its widespread success for several ultrahigh thermal conductivity materials uncovered recently [3].

In the TG technique used in this work, two short pump lasers are made to interfere and get absorbed into the sample, resulting in a spatially sinusoidal temperature grating, with a characteristic period Λ. The decay of this impulsive temperature profile is probed using another probe laser beam. By comparing the observed temperature decay with that calculated from the PBE, the effective thermal conductivity of the sample as a function of Λ can be obtained, from which phonon-specific properties, such as the phonon lifetimes, can be extracted [1,2]. Our experimental measurements highlight the significant contribution of four-phonon scattering to thermal resistance in MoS₂ around and beyond room temperature. By comparing our experimental measurements on phonon lifetimes with the first-principles predictions, we conclude that the Normal processes dominate the total scattering rates at low phonon frequencies in MoS₂, particularly around and below room temperature. Interestingly, we find that four-phonon Normal scattering rates are much stronger than the three-phonon Umklapp scattering rates, which is quite unusual compared to several other materials studied earlier [4]. The comparison of our experimental measurements with first-principles predictions also reveal strong anharmonic renormalization of phonon frequencies in MoS₂, even at room temperature, thus significantly affecting its thermal conductivity. We believe that our experimental findings, with insights from predictive first principles calculations, will provide clarity on the nature of phonon-phonon interactions in layered and low-dimensional materials.

This work is supported by the Prime Minister's Research Fellowship (02-01036) and the Science and Engineering Research Board's Core Research Grant No. CRG/2020/006166 and the Mathematical Research Impact Centric Support Grant No. MTR/2022/001043.

References:


5:00 PM EN07.05.01
Thermal Conductance of Buried AlN Interfaces Measured by Dual-Frequency Time-Domain Thermoreflectance
Yi Jiang1, Ravikiran Lingaparthi2, Casimir Chan2, Alex Tian Long Seah2, Kirill Shabudasaloval2,3, Netaji Dharmanaras2, K Radhakrishnan2,3 and Yee Kan Koh1; 1Department of Mechanical Engineering, National University of Singapore, Singapore; 2Temasek Laboratories, Nanyang Technological University, Singapore; 3School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore

Thermal management is a critical concern in microelectronic devices, especially for third-generation semiconductor devices that are based on GaN and AlN due to high power density during operations. An in-depth understanding of their thermal properties is essential for thermal management, such as interfacial thermal conductance between different layers. However, accurately measuring the thermal conductance in buried interfaces, particularly in epitaxial growth interfaces, is substantially challenging due to its low measurement sensitivity. Conventional time-domain thermoreflectance (TDTR) technique can only achieve around 40% of uncertainty, or not able to separate the thin film thermal conductivity and the buried interfacial thermal conductance. In this study, we utilize dual-frequency TDTR technique with Monte Carlo simulations to precisely quantify the thermal conductance of buried AlN interfaces with various substrates.

Firstly, we deposit AlN on common substrates, specifically, sapphire, silicon, and 4H-SiC, using molecular beam epitaxy (MBE). We carefully control the thickness of AlN to be 100 nm for the best experiment sensitivity. The quality of the AlN films is assessed by atomic force microscopy (AFM) and the piezoelectric acoustics technique of TDTR. Subsequently, TDTR measurements are performed at modulation frequencies of 18.9 MHz and 5.4 MHz, which leads to two different thermal penetration depths. To enhance the sensitivity of thermal conductance of AlN/substrate interfaces, we analyse the ratio of TDTR signals between 18.9 MHz and 5.4 MHz measurements. In addition, we employ Monte Carlo simulations to statistically estimate the uncertainty by considering results from both measurements and their ratio. The measurement uncertainty is reduced to approximately 1/3 of the conventional single-frequency TDTR measurements.

Our method can accurately measure the interfacial thermal conductance between AlN and different substrates with each result exhibiting an uncertainty of less than 16%. Among these substrates, the high interfacial thermal conductance of AlN/4H-SiC (~450 MW/mK) provides a promising prospect for effective heat dissipation across the interface.

In summary, this study demonstrates a dual-frequency TDTR technique with Monte Carlo simulations that significantly enhances the precision by 3 times in interfacial thermal conductance measurements of buried interfaces with just 100 nm of AlN. This technique contributes to a guidance of interfacial thermal conductance measurements and exploring thermal management further in electronic devices.

5:00 PM EN07.05.03
Decoupling Electronic and Thermal Transport in Spinel Oxide
Ashtosh Srivastava, Madhubanti Mukherjee and Abhishek K. Singh; Indian Institute of Science, Bengaluru, India

Decoupling electronic and thermal transport properties remains the biggest challenge in finding efficient thermoelectric materials. We demonstrate an approach to decoupling the complex interdependence among electrical conductivity, Seebeck coefficient, and lattice thermal conductivity in spinel oxides. Utilizing the effects of tetrahedral and octahedral coordination on bonding characteristics, we demonstrate tuning the electronic and thermal transport properties of cobalt-based spinel oxides ACo₂O₄. Tetrahedrally coordinated cation A (Zn/Cd) controls the electronic transport, while thermal transport has been controlled by octahedrally coordinated cation B (Co). The combination of heavy bands and contribution of the tetrahedrally coordinated environment

Temperature Dependent Electron Emission in Focused Ion Beam Microscopes
Waiwai Hodge1, Julia Deitz, Luis Jauregui, Daniel Perry, Joseph Boro and Jessica Duree; Sandia National Laboratories, United States

Transistors in mass produced consumer electronics have characteristic dimensions on the nanometer scale, with companies such as Intel and Samsung continuously working to increase transistor density by fabricating smaller components. Thermal management (i.e., temperature during use) plays a key role in effective operation of these devices. However, measuring temperature of nanometer scale components presents a challenge. Optical techniques commonly used in failure analysis, such as IR thermography, are diffraction limited and cannot effectively access the nanoscale. Contact techniques such as scanning thermal microscopy offer nanoscale resolution, but parasitic losses from the scanning tip limit temperature sensitivity. Transmission electron microscopy has been used to demonstrate thermal effects on nanometer resolution but can only accommodate devices that have been thinned to ~100 nm. Scanning electron microscopy shows some promise as a noncontact technique that has topographical resolution of ~1 nm and has shown preliminarily to have temperature dependence in second order-counts.

Here we examine thermal effects in Focused Ion Beam (FIB) microscopes. FIB microscopes offer several advantages over using a single beam SEM instrument: (1) the ion beam does not generate backscattered electrons, improving signal to noise ratio, (2) the ion beam can mill samples, allowing measurements of subsurface features in devices without breaking vacuum, and (3) FIB tools are almost exclusively manufactured as dual beam FIB-SEMs, so electron beams are simultaneously accessible. Using the FIB-SEM we demonstrate temperature dependence in grayscale intensity in semiconductor images. We additionally show results of energy mapping at different temperatures at multiple temperatures using the through lens detector built into FIB-SEM microscopes. Comparison of temperature dependent effects in SEM and FIB images are discussed. We also examine the additional considerations of accelerating voltage, power normalization, ion implantation, and spatial resolution.

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SESSION EN07.05: Poster Session I: Thermal Transport and Energy Conversion I
Session Chairs: Woochul Kim and Summi Shin
Tuesday Afternoon, April 23, 2024
Flex Hall C, Level 2, Summit
Crystallographic fouling, an undesirable process where scale forms on surfaces, is pervasive in nature and technology, negatively impacting the energy and water industries. Work has progressed towards realizing surfaces with intrinsic antifouling properties, however, realizing precise, defect-free topography over large areas with complex curvature remains challenging. In this work, we successfully developed a technique allowing us to impart precise surface microstructure array patterns onto metallic heat transfer surfaces with isotropic and anisotropic curvatures. The patterning on curved surfaces is realized by four steps: photore sist microstructure generation on planar substrates; structure transfer to curved metallic surfaces under heat and pressure; metal deposition by electroplating/electroless plating; photore sist removal. We conducted preliminary tests on the heat transfer performance of copper substrates with and without micropatterns in heat-exchanger-like conditions and the results show that the surface micropatterns can effectively modify the heat transfer coefficient of the metallic substrate and the structures possess good tolerance to fluidic friction. Durable curved (super)hydrophobic metallic surfaces can be realized with such stable microstructures, which are promising to mitigate fouling issues and energy loss by inhibiting the onset of nucleation and reducing the adhesion of limescale crystals.

**5:00 PM EN07.05.07**

**Understanding Phonon Mediated Lattice Thermal Conductivity in Magnetic Trihalides**

Ashutosh Srivastava,1 Heda Zhang,2 Chunjiang Xu2, Subhendra D. Mahanti2, Xianglin Ke2 and Abhishek K. Singh1; 1Indian Institute of Science, India; 2Michigan State University, United States

The investigation of phonon-mediated behaviours in transition metal trihalide systems is becoming an area of growing interest in fundamental research. The insulation of quantum magnet trihalides in both bulk and two-dimensional (2D) layers is a valuable avenue for investigating spin liquid phenomena, spintronics, magnetism in 2D and bulk systems, and thermal transport. The investigation of thermal transport mechanisms involving phonons in the presence of spins has received limited attention thus far. The present study has investigated the harmonic and anharmonic vibrational characteristics of magnetic bulk CrCl3 and CrI3 by the use of density functional theory (DFT) and subsequent experimental validation. Theoretical findings underscore the significance of van der Waals and magnetic interactions in ensuring the dynamical stability of these systems. The vibrational spectra of CrCl3 and CrI3 exhibit notable distinctions, mostly due to the presence of a phonon band gap in CrI3. In particular, low-energy phonons in CrI3 are predominantly influenced by ionic contributions. The phononic vibrational spectrum of CrCl3 exhibits an intriguing anisotropic lattice thermal conductivity (κl), with higher κl values observed in the in-plane direction compared to CrCl3. Conversely, CrI3 demonstrates larger κl values in the out-of-plane direction when compared to CrCl3. It is demonstrated that despite the higher scattering strength of phonons in CrCl3 due to its higher phonon group velocities, the heat transfer capacity of CrI3 surpasses that of CrCl3. Our study offers a fundamental comprehensive understanding into the phononic heat conduction in magnetic bulk transition metal trihalide materials.

**5:00 PM EN07.05.08**

**Synergetic Effect of Radiative Cooling and Thermal Energy Storage for Advanced Thermal Management**

Luo Zhou, Roma Avhad and Shuang Cui; University of Texas at Dallas, United States

Recent research endeavors strive to develop sustainable thermal management methods to confront the threats posed by extreme weather events and global energy crisis. Thermal energy storage (TES), which harnesses the latent heat of phase change materials (PCMs), is a promising technology that has been extensively explored for thermal management. However, the practical implementation of TES in buildings faces inherent limitations, including issues related to shape stability, supercooling, slow charging/discharging rates, and limited storage capacity. Here we report a shape stabilized PCM composite that overcomes these challenges by exploiting the synergetic effect of TES and passive radiative cooling (PRC), which consists of polyethylene glycol (PEG) as PCM and functionalized boron nitride (fBN) particles as solar scatterers. The inclusion of fBN particles induces a Mie-scattering effect and combines with the intrinsic thermal emission of PEG, resulting in an impressive solar reflectivity of 84.5% and a thermal emissivity of 95.0%. Meanwhile, the composite also achieves a latent heat of 97.1 J/g with excellent shape stability promoted by the interaction between fBN with PEG. Compared to traditional TES, this synergetic effect of PRC and TES promises more efficient thermal regulation by (1) effectively charging PCM during nighttime, (2) maximizing daytime cooling capabilities, and (3) mitigating the impact of supercooling effect. Our model study showed that the proposed dual-functional composite could extend the effective TES period by over 50% within a 24-hour cycle. The field test also demonstrated a PRC effect of 3.5 ± 0.5 °C below ambient during night, which facilitated the charging of PCMs via crystallization. All these benefits are particularly promising for developing sustainable building thermal management.

**5:00 PM EN07.05.09**

**Temperature-Dependent Optical Properties of Monocrystalline CaF2, BaF2, and MgF2**

Qifan Zheng; Xinchao Wang and Dakotah Thompson; University of Wisconsin-Madison, United States

The alkaline earth metal difluorides are critical optical components for applications in non-contact temperature sensors, thermal imaging, and infrared spectroscopy due to their high thermal stability and low thermal expansion coefficients. However, the optical properties of these materials, especially their dependence on temperature, have not been thoroughly investigated. In this paper, we report the temperature-dependent optical properties of monocrystalline CaF2, BaF2, and MgF2 for wavelengths between 220 nm and 1700 nm, and for temperatures between 21 °C and 368 °C. The refractive index of CaF2 and BaF2 was observed to decrease linearly with increasing temperature, which can be largely attributed to a reduction in the mass density due to thermal expansion. In contrast, the refractive index of MgF2 was found to vary nonlinearly with temperature, which suggests competing effects from the material's electronic polarizability. The temperature-dependent refractive index data reported here provide a finely-resolved mapping of the thermo-optic coefficient for these three materials, which could inform the development of optical devices operating at elevated or unsteady temperatures.

**5:00 PM EN07.05.10**

**Transient Active Cooling of Microscale Hot Spots Using Thermoelectric Devices**

Yihan Liu1, Hao-Yuan Cheng2, Jonathan A. Malen2 and Feng Xiong1; 1University of Pittsburgh, United States; 2Carnegie Mellon University, United States

Thermal management of microprocessors suffers from transient local hot spot induced by circuits such as clock generator. Embedded thermoelectric devices (TEDs) are promising to remove heat from local hot spots with passive cooling by the Fourier law and active cooling by the thermoelectric effect with transient electrical power supplied. In this work, we introduce an analytical model to describe the thermal response of a periodically heated spot, which is actively cooled by a thermoelectric cooler operating at the same frequency. The analytical result is experimentally validated with frequency domain thermal reflectance (FDTR) measurements made directly on an actively cooled Si TED where the transient local hot spot is replicated by laser. We further demonstrate a practical and energy efficient method to actively cancel the TED’s surface temperature variations based on our model’s analytical result. We then apply this method to cancel the transient temperature variation of 2.35 ± 0.26K at 10 KHz on the Si TED’s hot side surface. Our model’s result and the active cooling method is promising for analysis and optimization of cooling systems for transient localized hot spots in integrated circuits.

**5:00 PM EN07.05.11**

**Improved Durability Nanotextured Aluminum Surfaces for Jumping Droplet Thermal Rectification**

Trevor J. Shimokawa1, Frank Robinson2, Alia Nathani1, Zhen Liu1, Te Faye Yap1, Daniel Preston2 and Geoffrey Wehmeyer1; 1Rice University, United States; 2NASA Goddard Space Flight Center, United States

Jumping droplet thermal diodes (JDTDs) offer new capabilities for passive thermal rectification in thermal management of buildings, electronics, and batteries.1–3 However, the durability of JDTD devices is limited because the superhydrophobic (SHPB) surface degrades upon continuous exposure to condensing water vapor.4 In addition, most prior JDTDs documented in the literature have been constructed with copper surfaces, although aluminum surfaces are preferable for lightweight applications.2,3,5–8

In this work, we quantitatively study the durability of SHPB aluminum JDTDs and aluminum JDTD devices. We manufacture our Al-based surfaces using scalable surface functionalization techniques based on hydrothermal nanostructuring, silanization, and a dip coat deposition of Teflon AF (amorphous fluoropolymer). We show that dip-coating Teflon AF on top of TFTS monolayer-coated nanostructured surfaces enhances surface durability compared to non-Teflon coated surfaces, thereby enabling prolonged operation and comprehensive thermal testing of the JDTD. Contact angle measurements, environmental scanning electron microscope (ESEM) images, and X-Ray photoelectron spectroscopy (XPS) measurements indicate slight changes in the surface topology and chemical composition after dip coating, confirming that the deposited coating is thin (<20 nm).

Using our SHPB surfaces, we parametrically study steady-state thermal rectification as a function of gap height, fluid fill ratio, and heating orientation of the JDTD. We identify tradeoffs...
between the performance and the orientation dependence of operation by controlling the gap height and charge level. At larger gap sizes and lower charge levels, we observe enhanced thermal rectification only when the JDTD is heated from the bottom, while minimal thermal rectification is measured when the JDTD is heated from the top. At moderate charge levels and smaller gap sizes, operation is sustained in both orientations, but thermal rectification is reduced. We demonstrate a maximum thermal rectification ratio of 30 plus/minus 1.

To investigate potential implementation in thermal energy storage and harvesting applications, we show that the AI-JDTD enables a half-wave thermal rectifier circuit that rectifies time-periodic temperature profiles, achieving thermal circuit effectiveness values up to 30 % of the ideal-diode limit at rectification ratios near 5. When coupled with thermal capacitances, such time-periodic thermal rectification could aid cold energy storage for passive cooling of components subjected to time-periodic thermal boundary conditions. Thus, our findings showcase the functionality of AI-based surfaces for thermal rectification and could guide future work aiming to apply AI JDTDs for improved thermal management.

References


This work was supported by a NASA Space Technology Graduate Research Opportunity (80NSSC20K1220).

5:00 PM EN07.05.12

Effect of Fluorination on The Thermal Conductivity of Graphite Fluoride (CF) Wonsik Lee, Seungbin Han and Hyejin Jang; Seoul National University, Korea (the Republic of)

For thermal management applications, there are surging demands for materials with high thermal conductivity and electrically insulating properties. Graphite fluoride (CF), one of the novel graphene-based layered materials, has emerged as a promising thermal management material owing to its similar crystal structure to that of graphite yet electrically insulating properties, i.e., electronic band gap of over 3 eV. CF is expected to show high thermal conductivity due to its structural similarity to graphite. However, the degree of which fluorination alters the thermal conductivity is largely unexplored, and even the thermal conductivity is not experimentally established. Here, we report the through- and in-plane thermal conductivity of mechanically exfoliated CF flakes for the first time by using time-domain thermoreflectance (TDTR). At room temperature, a 70-nm-thick CF flake shows (170±300) W m⁻¹ K⁻¹ for in-plane direction, which is about 90 % of that of graphite, and (4.0±0.8) W m⁻¹ K⁻¹ for through-plane direction. The through-plane thermal conductivity of CF flakes shows quasi-ballistic behavior for thicknesses < 200 nm, which is similarly observed in graphite but shows two times higher than through-plane thermal conductivity than that of graphite. We calculate the phonon properties of monolayer graphene and graphene fluoride to reveal the intrinsic phonon transport mechanisms by solving the phonon Boltzmann transport equation (BTE). BTE estimates the thermal conductivity of graphene and graphene fluoride to be 3000 W m⁻¹ K⁻¹ and 270 W m⁻¹ K⁻¹, respectively. Phonon mode thermal conductivity indicates that the fluorination opens an out-of-plane acoustic (AZ) phonon scattering channel and the ZA phonon contribution to the thermal conductivity of CF is greatly suppressed, compared to the case of graphene. To understand the discrepancy in thermal conductivity between the experimental and theoretical results, we characterize the chemical and optical properties of exfoliated CF flakes to correlate those properties with thermal conductivity results. We believe this work reveals the role of functional groups on thermal conductivity in graphene/graphite-derivative materials.

5:00 PM EN07.05.14

Impact of Cooling Rate and Thermal Mass on Supercooling in a Salt-Hydrogel Complex for Thermal Energy Storage Youngmum Lee, Daniel Hsieh, Sung Bum Kang, Paul V. Braun and Sanjiv Sinha; University of Illinois at Urbana Champaign, United States

Glauber’s salt is a promising phase change material for building thermal management because of its high latent heat, acceptable melting temperature of 32.3 °C for indoor air. Despite these advantages, the practical application of Glauber’s salt in thermal energy storage systems is still challenging due to supercooling and phase segregation. Here, we report the impact of temperature ramp rate and thermal mass on the supercooling of Glauber’s salt through the DSC and T-history experiment. The ramp rate effect was studied with a wide range of ramp rates in 1 to 10 °C/min in DSC and 1 to 4 °C/min in the T-history experiment. The thermal mass effect was investigated by comparing DSC and T-history experiment. The latent heat was also analyzed for different ramp rates and thermal mass conditions. The melting temperatures of Glauber’s salt from the two techniques were identical while freezing temperatures were different because of the thermal mass effect. During freezing in the T-history experiment, the latent heat was reduced by around 75% to the latent heat in melting due to supercooling and phase segregation. To overcome this bottleneck, we developed a novel hydrogel complex that reduces the supercooling and prevents phase segregation to maintain volumetric energy density for 100 cycles. Thermodynamic analysis accounting for composition shows that a higher salt composition can further enhance the volumetric energy storage density. For example, a 10% increase in the weight percentage of salt leads to about 50% enhancement in volumetric energy storage density.

References


5:00 PM EN07.05.16

Supramolecular Interactions lead to Remarkably High Thermal Conductivities in Interepenetrated Two Dimensional Porous Crystals Jaymes Dionne1, Ashutosh Giri1 and Patrick E. Hopkins2,2,1; 1University of Rhode Island, United States; 2University of Virginia, United States

The design of innovative porous crystals with high porosities and large surface areas has garnered a great deal of attention over the past few decades due to their potential for a variety of applications, including flexible electronics, gas storage, and catalysts, among others. However, heat dissipation poses a major challenge in porous crystals and enhancing heat dissipation is key to realizing their potential. In this work, we use systematic atomistic simulations to show that the interpenetration of two, two-dimensional frameworks possess remarkable thermal conductivities at high porosities compared with their single three-dimensional framework and interpenetrated three-dimensional framework counterparts. Typically, high thermal conductivities are associated with low porosities; however, this work provides an alternative method to retain high porosities while drastically enhancing the thermal conductivity of the porous crystal. We attribute this to lower phonon-phonon scattering and vibrational hardening from supramolecular interactions that restrict atomic vibrational amplitudes, enhancing heat conduction. We also show this for realistic systems, with a two-dimensional interpenetrated framework of COF-1 achieving an order of magnitude increase in thermal conductivity when compared to its three-dimensional framework counterparts. Typically, high thermal conductivities are reported regarding the annealing effect of the thin film, and the relationship between grain size and heat transfer by annealing is not closely analyzed. In addition, only the totally averaged thermal conductivity is reported regarding the annealing effect of the thin film, and the relationship between grain size and heat transfer by annealing is not closely analyzed. In this study, we used scanning thermal microscopy(SThM) to investigate heat transfer differences occurring in a local area less than ~10 nm in HfO₂ thin films. The difference in averaged thermal conductivity and distribution of thermal conductivity in the local area according to the thickness of the thin film was investigated. In addition, the crystal structure was changed through annealing, and the thermal conductivity of the thin film according to grain size was investigated. The thermal transfer mechanism investigated in this work according to the crystal structure will be an important
Nanostructured Anodic Aluminium Oxide (AAO) with Metal Coating Optimized for Passive Radiative Cooling

SPTs. Using the LbL interface improves the effectiveness by more than 10%, according to experimental assessments of real-time temperature responses under different heating power levels and temperatures (SPTs) are chosen to be 40°C, 50°C, and 60°C for an objective and precise comparison. The LbL-assembled MWCNT–PEI coatings considerably increase the times to reach all transport. A comparison between the developed specimens (bare and PCM-filled HSs without LbL interfaces) highlights the improved thermal performance, particularly in transient and static over repeated solid-liquid phase transitions owing to the functional interface's optimization of the porous structures and a large increase in the active surface area enabling effective thermal management.

Phase change materials (PCMs) and heat sinks (HSs) can be integrated rationally to complement the inherent constraints of both technologies. However, adding PCMs to HSs frequently causes the thermal conductivity and even lower than 1.7–2.0 W/(mK) of Bi2Te3 and PbTe bulks. The crystal structure of Ba3SiO is constructed from the highly distorted O–Ba6 octahedra framework with weak O–Ba ionic bonds, which provides low phonon group velocity and strong phonon scattering. Additionally, Ba3SiO possesses favorable band structures for achieving a high PF, where the valence band around the Fermi level arises from the p state of the negatively charged Si anion with large ion size, and their highly dispersive bands with multiple valley degeneracy enable both high σ and high S, simultaneously, leading to the high ZT for Ba3SiO originating from the low κ_{xx} and the high PF. These results suggest that inverse-perovskite oxides are promising and environmentally benign thermal management materials, offering a compelling alternative to current practical materials composed of heat and toxic elements.

Heat dissipation has become increasingly crucial in modern highly integrated and miniaturised electronic devices to improve their reliability and performance. Thanks to the high thermal conductivity and electrical insulation, boron nitride nanosheets (BNNSs) are usually used as fillers to construct thermally conductive polymer composites for heat dissipation. However, limited to the low dispersibility, high aspect ratio, and anisotropic thermal conductivity of BNNSs, the resultant thermal conductive composites based on polymer matrix showed an unsatisfactory thermal conductivity, especially in the out-of-plane direction, due to the “lie-down” structures of the BNNSs fillers. In this work, micro-sized, binder-free boron nitride spheres (BNSSs) have been successfully synthesized using a two-step process of thermal spray drying and high-temperature sintering; and a facile and efficient method to measure the thermal conductivity of BNSSs, based on the factors impacting the BNSSs’ thermal conductivity, including precursor, polymer binder and sintering temperature, was developed. With optimised conditions, BNSSs have a high, isotropic thermal conductivity of 37.2 W/mK. Based on the high thermal conductive and binder-free BNNSs, a poly(vinyl alcohol) (PVA)/BNSS composite film was successfully fabricated, and the out-of-plane thermal conducitivity of this composite film is significantly enhanced to 8.1 W/mK, while the in-plane thermal conductivity, up to 10.6 W/mK, is not sacrificed, indicating the quasi-anisotropy in thermal conductivity. The significant thermal conductivity enhancement (~3700%) of PVA is attributed to the formation of isotropic thermally conductive networks within the polymer matrix and strong interactions between BNSSs inside BNSs. This study provides a practical route to fabricate BN-enhanced composite films with isotropic thermal conductivity and promising materials that are valuable for heat dissipation in next-era advanced electronics and related applications.

Thermal Interface Engineering Using Layer-By-Layer Carbon Nanotube-Polyethyleneimine Functional Nanostructures between Phase Change Materials and Aluminum Heat Sinks

Binder-Free Boron Nitride Spheres Enhanced Quasi-Isotropic Thermal Conductivity of Polymer Composites
from that of long-range strain fields introduced by these defects, which could also impede thermal transport via an increase in vibrational anharmonicity. Consequently, questions regarding the cause of the unusual and somewhat perplexing thermal behavior in these functional materials have lingered unanswered.

To date, while elastic strain engineering often relies on highly inhomogeneous stress produced by nanoscale deformation (e.g., by epitaxial layer growth, defects and vacancies, or lithography patterning), most studies of strain effects on thermal transport have centered around materials under simplified condition of uniform stress. The major challenges in experimentally quantifying the effects of inhomogeneous strain on thermal transport include applying stress exclusively without introducing confounding factors (e.g., interfaces and defects), and combining thermal measurements with atomically resolved characterization of the strain field and phonon spectra. Here, we induce inhomogeneous strain through bending individual silicon nanobribbons on a custom-fabricated microdevice, and measure its effect on thermal transport while characterizing the local strain and vibrational spectra using atomically resolved electron energy-loss spectroscopy (EELS). Our results show that a strain gradient of 0.12% per nanometer could lead to a drastic thermal conductivity (κ) reduction of 37.4%, which is over 3-fold of previously demonstrated κ modulation under uniform strain. Taking advantage of recent progress in electron energy loss spectroscopy equipped with a monochromator and a conventional transmission electron microscope, we directly measured the local phonon modes and correlated them with the nanometer-scale strain gradient. Results show that the bending-induced lattice strain gradient significantly alters the vibrational states and broadens the phonon spectra. Coupled with ab initio theoretical modeling, this broadening effect is shown to enhance phonon anharmonicity and shorten phonon lifetimes, ultimately contributing to suppressed thermal conductivity.

5:00 PM EN07.05.23 Assessing Multivariate Thermal Transport Relationships in Pump-Probe Experiments Using Sensitivity Matrix Jing Tu and Wee-Liat Ong; Zhejiang University, China

Sensitivity analysis is a powerful technique to analyze the behaviors of models and experimental data in diverse fields.1-4 Most state-of-the-art characterization techniques rely on fitting experimental data to a theoretical multivariate model. Such a model often has multiple unknown parameters at the same time. These unknowns are either determined independently or, when impractical, are fitted together in a single set of measured data. It is well known that such a multivariate fit can become invalid, especially when these unknowns are related.5 To complicate matters, such a relationship can change with different sample configuration and measurement conditions. Unfortunately, few rigorous methods exist to evaluate the validity of such a fit or uncover the governing transport relationships under different measurement conditions.

Here, we formulate a systematic approach based on sensitivity analysis to uncover the governing physics in a complex multivariate theoretical model and assess the feasibility of performing a multivariate fit. A sensitivity matrix of the unknown variables is constructed and, later, decomposed using the singular-value decomposition (SVD) method. The resulting solution of three different cases provides insight to the fitting process. The rank of the rectangular diagonal matrix with non-negative real numbers on the diagonal reveals the number of independent fit-able variables within the tested range. Under certain conditions, the associated complex unitary matrix contains information of the thermal transport relationships in the measured system.

Different pump-probe techniques for thermal characterization are used to illustrate the capability of this method. We found that the existing experience-based criteria,5,6 e.g., the overlapping sensitivity curves to identify related parameters or the non-overlapping and distinct sensitivity curves for multivariate suitability, are inadequate and applicable only in certain situations. Also, our method can uncover the governing heat transfer relationships through different multilayer samples and measurement conditions. This method can apply to most measurement techniques relying on multivariate theoretical models in various disciplines and can help to improve their measurement validity and throughput.

Reference:

SESSION EN07.06: Thermal Transport in Amorphous Materials
Session Chairs: Yee Kan Koh and Jaeyun Moon
Wednesday Morning, April 24, 2024
Room 327, Level 3, Summit

8:45 AM *EN07.06.01 Phonon Transport of Disordered Materials with Nanostructures Junichiro Shiono; The University of Tokyo, Japan

Phonon engineering of crystalline materials by nanostructures has made great progress in the past decades, and the next non-trivial challenge is how to engineer phonons in disordered materials. We have studied nanostructured amorphous materials such as amorphous superlattices [1] and amorphous phononic crystals (amorphous thin films with holes) [2]. There, by applying the Allen-Feldmann theory, which divided heat carrier into propagons, diffusons, and locons, we found that not only the transport of propagons but also that of diffusons is effectively hindered by the nanostructure interfaces. To gain further direct insight, inelastic x-ray scattering was performed. Partially disordered materials are also of great interest from an academic and industrial point of view. This includes materials consisting of crystalline and amorphous portions, e.g., polycrystals with disordered interfaces. Disordered grain boundaries have been found experimentally to selectively inhibit phonon transport rather than electron transport. Furthermore, a black box model of disordered silicon grain boundaries was successfully performed, revealing that the main structural factors that determine transport are different for phonons and electrons [3]. Crystalline materials with distorted lattices, such as cellulose nanofibrils, are also interesting. The thermal conductivity of cellulose nanofibrils was found to be greatly enhanced by controlling the arrangement of the constituent cellulose nanofibrils and the hydrogen bonds between the fibrils [4].


9:15 AM EN07.06.03 Effect of Linker Chemistry, Linker Length and Temperature On The Thermal Conductivity of Vinylogous Urethane Dynamic Network Peng Lan, Seongon Jang, Christopher M. Evans and David Cullum; UIUC, United States

Covalent adaptable networks (CANs) have been heavily studied in recent years as promising candidates for recyclable polymer in applications like shape memory materials, shockwave energy-dissipative materials, and flexible electronics. However, the thermal management of polymeric materials in these devices is still an urgent issue, since polymers generally have lower thermal conductivity (as 0.2 W/mK) which can lead to thermally-induced aging. Moreover, the effect of bond exchange dynamics, linker chemistry and temperature on the thermal conductivity of CANs is still unclear. In this work, a series of vinylogous urethane dynamic networks (VU networks) were synthesized from triis2-aminoethylethylene and di-acetateactes with ethylene linkers (L = ethylene) and varied linker length (x = 2-22 carbon atoms). Thermal conductivity was measured by frontside frequency-domain probe beam deflection (FD-PBD). In comparison to the ethylene network with benzene diboronic acid bonds, neither linker length dependence nor temperature dependence of thermal conductivity shows a monotonic trend as in the case of VU-xE network. The thermal conductivity of these VU networks at room temperature varies from 0.20 W/mK to <0.1 W/mK as the linker length increases from 2 to x = 22. At high temperature approaching glass transition (Tg-Tg + 20K), a drop of thermal conductivity is observed by FD-PBD and as the temperature grows higher (> Tg + 30K), the thermal conductivity retains to that of low temperature (< Tg). We hypothesized that this drop of thermal conductivity near Tg in FD-PBD is due to combined dynamics of monomer chain motion and bond exchange. The morphology of these VU-xE networks were also studied using WAXS for both fresh and annealed samples. Apart from amorphous halo peak at q = 4 - 14 nm^-1 and broad ethylene chain stacking peak at q = 4 - 10 nm^-1, no obvious crystalline network is seen for all networks. Such a behavior is different from our previously studied ethylene network with boric acid dynamic bonds, where longer network (x > 10) exhibits slow crystallization (with crystallinity~78% in WAXS) at room temperature. We attributed this difference to the fact that VU bonds have a much slower bond exchange than ethylene. Furthermore, we investigated the effect of linker chemistry on the thermal conductivity, by changing the ethylene linker to ethylene oxide (VU-xEO), x = 6, 9, 12, 18, 22 atoms. Similar linker length dependence of thermal conductivity is observed for these ethylene oxide VU network. But no EO chain stacking peak (q = 4) is seen in WAXS spectra as the linker length increases, suggesting that the presence of oxygen atoms in EO linker will disturb the chain stacking and make the network less capable of crystallization. This work provides new design rules for thermal conductivity of dynamic polymer networks and how to control the crystallization depending on linker length, chemistry, and dynamic bond type.
Thermal Conductivity of 2H and 2H3R Niobium Diselenide Polymorphs
Sunjin Park1, Kyomin Kim2, Kwangrae Kim1, Jong-wook Roh3, Aloysius Soon1, Wooyoung Lee1 and Woohul Kim1; 1Yonsei University, Korea (the Republic of); 2LG Nex1, Korea (the Republic of); 3Kyungpook National University, Korea (the Republic of)

Niobium diselenide (NbSe2) is a two-dimensional van der Waals material whose 2H3R polymorph was discovered recently [1]. The 2H3R polymorph of NbSe2 possesses a different stacking sequence when compared to the 2H polymorph due to the weak van der Waals bonding between the layers and therefore possesses different physical properties. Previous research has shown that difference in stacking sequence in two-dimensional materials can alter their electrical and thermal properties [1,2]. In this work the thermal conductivity of the 2H and 2H3R polymorphs of NbSe2 was measured and compared. The in-house T-bridge method was used in the measurement of thermal conductivity [3]. The T-bridge method measures the thermal conductivity of a sample through difference in heat conduction from a suspended heater to a heatsink. NbSe2 samples of various thicknesses were prepared for both polymorphs. Measured thermal conductivity results showed that the 2H3R polymorph shows lower thermal conductivity compared to the 2H counterpart of similar thickness. Theoretical calculation was performed to study the cause of the difference in thermal conductivity and revealed that the lower thermal conductivity of the 2H3R polymorph was induced by the greater phonon-phonon scattering of the 2H3R polymorph than that of the 2H polymorph.


Modulating The Thermal Transport of MAPbI3 Hybrid Perovskites and The Effect on its Population-Coherence-Channel
Jin Yang1, Yuting Yu1, Ankit Jain2 and Wee-Liat Ong1;
1Zhejiang University, China; 2IIT Bombay, India

Hybrid halide perovskites, with their favorable carrier recombination time and ultrashort phonon mean-free paths, are potential candidates for numerous energy conversion applications like photovoltaics and thermoelectrics. The origin of the ultralow thermal conductivity in the prototypical methylammonium lead triiodide (MAPbI3) is of intense research interest for improving and modulating its energy conversion performance [1]. So far, such an understanding remains elusive in the MAPbI3 family above room temperatures (that exists as a cubic phase) despite numerous efforts [2] and under external modulation fields. Using molecular dynamics and the Wigner transport equation [3], we first report the discovery of several cubic-phase MAPbI3 (c-MAPbI3) local energy minimum structures. [4] These stable structures are amenable to lattice dynamics-based calculations to produce positive phonon dispersions. Our results reveal a coherence-channel-dominated thermal transport mechanism in the c-MAPbI3 crystals. Interestingly, an interconversion between the population- and coherence-channel occurs when the c-MAPbI3 changes across these energetically equivalent structures at the same temperature. Such an effect is yet to be observed in simple atomic crystals. Next, we looked at how external pressure fields and electric fields affect the thermal transport of MAPbI3. An external pressure increases the c-MAPbI3 thermal conductivity of the phonon population-channel contribution, similar to trends in many crystals. However, little effect on the coherence-channel contribution is observed. This unusual trend impedes the thermal conductivity increase for this c-MAPbI3 and imparts a trend that mirrors that of a diamond [5]. On the other hand, the electric field has little effect on c-MAPbI3, although the polar MA cations are affected by the electric field. Our work also shows that existing thermal transport intuitions based on the phonon gas model can be misleading in such hybrid crystals. Further, the dominance of the non-traditional coherence-channel of phonons can affect the interpretation of other phonon-mediated processes in MAPbI3 and other hybrid perovskites.

References:
Proton Collective Quantum Tunneling Induces Anomalous Thermal Conductivity of Ice Under Pressure

Yufeng Wang, Kuang Yu and Bo Sun; Tsinghua University, China

Ice is one of the most ubiquitous substances in the universe. Understanding its thermal conduction properties is crucial for exploration of the evolution and dynamics of icy planets. Moreover, ice itself serves as an ideal model to study proton’s quantum effects in the hydrogen bond networks, which has received enormous attention in physical chemistry and condensed matter physics. It is believed that protons tunnel in the hydrogen bond network in ice and the tunneling is local compared with the wavelength of heavy phonons. However, the tunneling dynamics would not strongly affect the thermal conduction of ice, and the thermal conductivity as a function of pressure should increase following the classical Leibfried-Schlömann equation. In stark contrast, we observed anomalous, nonmonotonic behavior in the thermal conductivity of H$_2$O and D$_2$O ice above 20 GPa that breaks the classical rule. Such anomaly is revealed to be caused by global collective tunneling anomalies involving several tens of millimoles. It is observed that quantum tunneling in ice is observed at such a large spatial scale, opposing to all previous studies which assumed that tunneling within a limited size (such as six-member rings) dominates in ice.

Moreover, the tunneling dynamics in ice VII-X phase transition region has been a long-standing challenge to understand using conventional spectroscopic methods. In this work, we provide a completely new approach that can directly probe the global dynamics of the phase transition with unambiguous experimental measurements.

Proton Collective Quantum Tunneling Induces Anomalous Thermal Conductivity of Ice Under Pressure

Zhiliang Pan$^1$, Guanyu Lu$^1$, Xun Li$^2$, Lucas Lindsay$^2$, Joshua D. Caldwell$^1$ and Deyu Li$^1$

$^1$EN07.09.01
1:30 PM
Engineering and Probing Phonons and Thermal Transport

Gordillo, Saeko Tachikawa, Johannes Trautvetter and Ilaria Zardo

11:45 AM

Session Chairs: Yongjie Hu and Li Shi
Wednesday Afternoon, April 24, 2024
Room 327, Level 3, Summit

SESSION EN07.08: Polaritonic Heat Transfer

Thursday Afternoon, April 25, 2024
Room 327, Level 3, Summit

SESSION EN07.09: Thermal Transport in Crystals

Thursday Afternoon, April 25, 2024
Room 327, Level 3, Summit

1:30 PM • EN07.08.01

Thermal Transport Mediated by Non-Equilibrium Surface Phonon Polaritons

Zhiliang Pan$^1$, Guanyu Lu$^1$, Xun Li$^2$, Lucas Lindsay$^2$, Joshua D. Caldwell$^1$ and Deyu Li$^1$;
$^1$Vanderbilt University, United States; $^2$Oak Ridge National Laboratory, United States

Surface phonon polaritons (SPhPs), hybrid quasi-particles resulting from coupling between infrared photons and optical phonons, could play significant roles in near-field radiation. More recently, it has been predicted that SPhPs can also contribute to heat conduction along polar thin films and nanowires; however, direct and conclusive experimental evidence for SPhP-mediated heat conduction has been scarce. Here we report on significant enhancement of the thermal conductivity of 3C-SiC nanowires when the end(s) of the nanowires are coated with a tin layer of gold that can serve as efficient SPhP launchers. Through measuring the same 3C-SiC nanowires with and without gold coating at the end(s), we show that the SPhPs launched by the gold coating can remarkably enhance the thermal conductivity of the uncoated wire segment from the value of the same wire without gold coating. Interestingly, it is found that the SPhP-mediated thermal conductivity is orders of magnitude higher than the Landauer limit predicted based on the equilibrium Bose-Einstein distribution function over the entire measurement temperature range. We attribute this unexpected discovery to the partial ballistic propagation of SPhPs along the SiC nanowire with a number density well beyond the value determined by the Bose-Einstein distribution function. The understanding of non-equilibrium SPhP transport is supported by the observation that the extracted thermal SPhP-mediated thermal conductivity is proportional to the length of the gold-coating at the end(s) of the nanowire, which provides important insights into the SPhP excitation process. The highest SPhP-mediated thermal conductivity at room temperature reaches a value of 5.8 mW/mK, a few times of the phonon-mediated thermal conductivity for some technologically important thin films such as silicon oxide and nitride. This discovery of non-equilibrium SPhP-mediated heat conduction implies novel cooling strategies utilizing SPhPs as effective thermal energy carriers.

2:00 PM • EN07.08.02

Guided Polariton Thermal Radiation

Sebastian Volz$^1$; CNRS, France

Phonons are the quasiparticles of lattice vibrations and represent the primary heat carriers in bulk dielectric materials. The thermal conductivity of dielectric membranes is thus typically driven by acoustic phonons that is usually assimilated to a gas of particles, and generally reduces with the membrane thickness due to the increasing frequency of surface scattering events. In the light of the ever-increasing miniaturization of devices with enhanced rates of operation, this reduction in the thermal conductivity causes overheating, low reliability, and reduced lifetime of electronic components. Yet, while the thermal transport via acoustic phonons might be at the limit, the heat dissipation might be enhanced via optical phonons coupled with surface electromagnetic waves.

Over the past decade, substantial research efforts have been devoted to the study of these surface waves, because the surface effects predominate over the volumetric ones in nanostructures with high surface-to-volume ratio. Some types of surface electromagnetic waves may even carry heat and thus improve the thermal performance and stability of nanoscale devices. One type of such surface waves is the surface phonon-polaritons (SPhPs), which occurs as a hybrid of optical phonons and surface electromagnetic waves. The SPhPs are essentially evanescent waves that propagate along the surface of polar dielectric membranes.

We will first demonstrate the existence and the properties of those SPhPs in thin SiO$_2$ films and especially uncover that the propagation lengths of those waves reach the range of hundreds of micrometers, which is orders of magnitude longer than the typical mean free path of acoustic phonons. Theoretical models predict that such a long propagation length enables SPhPs to conduct more thermal energy than phonons when the membrane thickness is reduced below 100 nm.

We will then corroborate the significant contribution of SPhPs to heat flux in silica membranes, in a restricted temperature range and also, in a wide temperature range, in silicon nitride membranes where SPhP thermal conductivity becomes predominant at 800K. An additional confirmation was finally provided by showing the size dependence of thermal conductivity due to the ballistic contribution of SPhPs.

2:15 PM • EN07.08.03

Long-Range, Short-Wavelength and Ultrafast Heat Conduction driven by Three Plasmon Modes supported by Graphene

Jose Ordonez$^1,2$, Yuriy Kosevich$^2$, Masahiro Nomura$^2,1$ and Sebastian Volz$^1,2$;
$^1$ICNRS, Japan; $^2$The University of Tokyo, Japan

By leveraging the unique two-dimensional structure of graphene with its ability to support the propagation of surface plasmon-polaritons, we demonstrate the existence and propagation of three hybrid modes of surface phonon polarizations supported by two graphene monolayers coating a solid film. These modes propagate long distances with short wavelengths, which are suitable features to enhance the heat conduction along the film interface. For a Si film with a thickness of 15 nm and a length of 5 mm at 300 K, we find a plasmon thermal conductivity of 13.6 W⋅m$^{-1}$⋅K$^{-1}$, which represents 67% (26%) of its phonon Si (Si+graphene) counterpart. This thermal energy appears due to the coupling of plasmons propagating at speeds comparable to the speed of light in vacuum. The plasmonic heat conduction driven by two-dimensional materials thus appears as a major and unexpected mechanism for controlling temperature in solid-state systems without changing their internal structure and at rates faster than the ones of phonons and electrons.

2:30 PM • EN07.09.01

Engineering and Probing Phonons and Thermal Transport

Begoña Abad Mayor, Chaitanya Arya, Giulio de Vito, Yashpreet Kaur, Grazia Raciti, Aswathi K. Sivan, Jose Manuel Sojo Gordillo, Saeko Tachikawa, Johannes Trautvetter and Ibarra Zardo; University of Basel, Switzerland

Summary:
- In this work, we use narrowband wave-packet excitations to investigate the impact of local resonances on the room temperature phonon transport in NPMs in the form of nanopillared membranes and compare with corresponding nanostructures that do not include local resonances. Our results provide an in-depth analysis elucidation of the underlying phonon localization effects associated with the local resonances.
- By controlling the wave-packet frequency, we are able to distinguish the role of the local resonances on the thermal energy propagation from other effects that influence the total lattice thermal conductivity such as phonon-boundary scattering. These observations open exciting new possibilities for experiments to further unlock the potential of atomic-scale local resonances.

References:
In this work, we have designed a series of multi-layered semiconductor structures and grown them using molecular beam epitaxy (MBE). Owing to the atomic-level control of growth, MBE offers us more freedom to realize high quality multi-layered samples with delicate structural parameters, including single monolayered superlattices. Manipulation of long-wavelength phonons is especially important for these structures as their developments continue to pursue the limit of thermal conductivity. Here, the experimental demonstration of manipulating and probing long-wavelength phonon thermal transport in Al,Ga1-xAs/Al,Ga1-xMnAs and InAs/AlAs superlattices will be reported. A direct experimental approach is demonstrated to probe and monitor the contribution of long-wavelength phonons to the thermal conductivity, based on the quasi-ballistic transport principle of phonons. In addition, we have observed evidence of coherent phonon transport up to 500 K. Effective interface manipulation in some artificial metal/semiconductor interfaces will be presented and discussed too. This demonstration holds the very promise to be a universal strategy for manipulating and probing phonon thermal transport in various application scenarios, including microelectronics, thermoelectrics, and optoelectronics.


SESSION EN07.10: Poster Session II: Thermal Transport and Energy Conversion II
Session Chairs: Sheng Shen and Sebastian Volz
Wednesday Afternoon, April 24, 2024
Flex Hall C, Level 2, Summit

5:00 PM EN07.10.01
Towards Scalepohobicity: Soft Surface Microengineering for Microfoulant Repellency
Julian Schmid1, Tobias Armstrong1, Fabian J. Dickhardt1, SK Rameez Iqbal1 and Thomas Schutzia1,2, 1ETH Zurich, Switzerland; 2University of California, Berkeley, United States

Particulate and crystallization fouling, ubiquitous in nature and technology, pose significant challenges to the efficiency of water treatment, desalination, and energy conversion processes. Current solutions rely heavily on active methods like antiscalant additives or mechanical removal, necessitating a shift towards sustainable, passive strategies, such as surfaces with inherent self-cleaning or anti-fouling properties. Existing research has focused on modifying the surface energy and texture of rigid materials, overlooking the potential of compliant materials with intrinsic foulant-repellent properties. The intricate interplay of substrate compliance, composition, and surface texture in an aqueous environment and their impact on microfoulant adhesion at the microscale remain largely unexplored.

In this study, we employ a micro-scanning fluid dynamic gauge (µ-sFDS) setup to conduct in-situ shear removal experiments for calcium carbonate and polystyrene micro-foulants on compliant anti-fouling surfaces. Guided by adhesion and fluid mechanics theory, and through rational micro-engineering of compliant materials, our findings reveal counterintuitive results: compliant materials surpass their rigid counterparts in anti-fouling performance. This research provides promising insights for the design of compliant interfacial materials capable of achieving high anti-fouling efficacy against particulate and crystallization fouling across various industrial applications including water and energy conversion systems.

5:00 PM EN07.10.02
Thermoelectric Properties of Monolayer HfI2, an Electride with Electrons on the Interstitial Sites
Yi-Ming Zhao, Chun Zhang, Sammi Shin and Lei Shen; National University of Singapore, Singapore

Two-dimensional (2D) thermoelectric materials are particularly suitable for wearable devices due to the flexible monolayer structure, which will supply power for other carried devices. However, the electrical conductivity (σ) of 2D material is usually lower compared with the bulk counterparts because of a lower electron mobility induced by a higher density of scatterings. Recently, Zhang et al. found that two MoS2-like structures, ZrI2 and HfI2 with long carrier-lattice distance (d_{el}) exhibit a high mobility up to 4000 cm^2/Vs. We notice that the ZrI2-type structures are electrides with excess electrons occupying the interstitial sites increasing the d_{el}. Such a unique charge distribution should underlie a weaker perturbation under the replacement of atoms, then the carrier mobility and the σ will be high. The figure of merit (ZT) of ZrI2 reaches 1.2 at 900K under hole doping, but the relation between the charge distribution and the transport properties is still not clear enough in these electrides.

Here, we investigate the thermoelectric properties of monolayer HfI2 using first-principles calculations by fully considering the electron-phonon interaction using EPW6 code. The thermoelectric properties including Seebeck coefficient (S), σ and electron thermal conductivity (κ_e) are calculated by solving the Boltzmann transport equation beyond the constant relaxation time approximation implemented with BoltzTraP2 code. The lattice thermal conductivity (κ_l) is calculated by the ShengBTE code.

We found that the hole doping tends to soften the acoustic phonon modes due to the interstitial distributed charge states and low density of states (DOS) near the valence band maximum (VBM), while the electron doping decreases the phonon relaxation time obviously because of a stronger electron-phonon interaction (EPI) induced by the high DOS near conduction band minimum (CBM). The carrier relaxation time at the VBM is obviously higher than that near the CBM due to the weaker lattice perturbation. The p-type σ is also higher than the n-type one under the same concentration. But the p-type S value is lower than the n-type one due to a lower DOS near VBM. The p-type power factor (PF) is larger than the value of n-type more dominated by σ.

The κ_l of HfI2 is only 9.1 W/m-K within three-phonon interaction at room temperature lower than that of ZrI2 (20.3 W/m-K). The phonon relaxation time contributed by the electron-phonon scattering is even smaller than that of three-phonon scattering at low phonon frequency range. The electrons near CBM will scatter the phonons due to the strong EPI. As a result, the κ_l decreases by 1.5 W/m-K when considering the electron-phonon scattering. The final ZT value reaches 0.86 at 1200K under p-type doping.

In summary, the HfI2 with anionic electrons near the VBM exhibit a high mobility and σ under hole doping due to the weaker lattice perturbation. Our work reveals the role of interstitial distributed anionic electrons on the electron and phonon transport in the electrode system, which gives insights for the further design of high-performance thermoelectric materials.


5:00 PM EN07.10.03
Near-Field Thermal Radiation across Solid-State Gaps
Mackey Long, Hakan Sahihoog and Joshua D. Caldwell; Vanderbilt University, United States

Near-field thermal radiation has attracted great interest due to heat transfer exceeding blackbody radiation by several orders at nanoscale separation gaps. Although extensive research is devoted for understanding of physics, feasibility of near-field based thermal devices with large scales is extremely low owing to the difficulty in controlling and sustaining the corresponding separations between heat exchanging materials in macroscales. In this study, we explore near-field radiation through solid-state gaps sandwiched between heat exchanging materials with large lateral dimensions. Our theoretical design employs solid-state thin films as a separating medium. We derive a multimode, nanoscale heat transfer model by incorporating Boltzmann’s equation to fluctuational electrodynamics, and compare energy transport capacity of thermal radiation and conduction across the thin film and interfaces at both sides of the film. Our systematic approach enables defining key dimensions and parameters that govern radiation and conduction heat transfer through the solid-state gap. Using quasi steady-state approximation, this study also investigates and compares heat transfer dynamics of radiation and conduction across the film and the interfaces of the film in time domain. This study will shed light on the feasibility of solid-state based near-field thermal radiation and has potential to open a new avenue for application of near-field enhancement using macroscopic devices.

5:00 PM EN07.10.04
Inhibiting Crystallization Fouling Using Nano-Micro-Engineered Heat Transfer Surfaces
Julian Schmid1, Tobias Armstrong1, Niklas Denz1, Diego R. Péhier1 and Thomas Schutzia1,2, 1ETH Zürich, Switzerland; 2University of California, Berkeley, United States

In this work, we have designed a series of multi-layered semiconductor structures and grown them using molecular beam epitaxy (MBE). Owing to the atomic-level control of growth, MBE offers us more freedom to realize high quality multi-layered samples with delicate structural parameters, including single monolayered superlattices. Manipulation of long-wavelength phonons is especially important for these structures as their developments continue to pursue the limit of thermal conductivity. Here, the experimental demonstration of manipulating and probing long-wavelength phonon thermal transport in Al,Ga1-xAs/Al,Ga1-xMnAs and InAs/AlAs superlattices will be reported. A direct experimental approach is demonstrated to probe and monitor the contribution of long-wavelength phonons to the thermal conductivity, based on the quasi-ballistic transport principle of phonons. In addition, we have observed evidence of coherent phonon transport up to 500 K. Effective interface manipulation in some artificial metal/semiconductor interfaces will be presented and discussed too. This demonstration holds the very promise to be a universal strategy for manipulating and probing phonon thermal transport in various application scenarios, including microelectronics, thermoelectrics, and optoelectronics.
Fouling of heat transfer surfaces is a widespread problem in the energy conversion and water treatment industries where thermally insulating deposits lead to significant performance reduction. Crystalization fouling, an important subset of fouling, occurs when water containing retrograde soluble salts like calcium sulfate, makes contact with a heated surface leading to the nucleation and growth of a surface deposit, termed “scale”. However, we currently lack detailed information on the effect of surface texture, composition, and environmental conditions on the onset of scale nucleation, growth, and adhesion which is crucial for comprehending the complexity of scaling since it is a multiphase problem that starts at the nano-micro scale. Furthermore, we lack national strategies to mitigate this important problem. Here we show that nano- and micro-textured superhydrophobic surfaces perform hydrophilic, hydrophobic and superhydrophobic surfaces regarding the delay of nucleation and observable growth of forming deposits in laminar and turbulent conditions. For this purpose, a novel continuous flow experimental setup mimics a cooling section of a heat exchanger and allows to holistically investigate the onset, growth, removal of deposit with its influence on the heat transfer process. Simultaneous visual microscopic in-situ observation and heat transfer resistance measurements provide insight into nucleation, growth, and adhesion of nano-micro-engineered substrates. We found that the degassing of dissolved gases on the heated substrate, their affiliation to the substrate, and the subsequent evaporation of water into the new phase is important for scaling in flow conditions. We anticipate that our holistic experimental setup provides profound information on the fundamental aspects of scaling and our nano-micro-engineered surfaces contribute to the development of advanced thermal interface materials that inherently prevent and/or repel scaling to contribute to a sustainable future in energy conversion.

5:00 PM EN07.10.05
Thermal Characterization of Ultra-Thin Suspended Silicon NitridePlatforms

Hsiaoning Lee1, Ethan Scott1,2, John N. Nogan1, Don Bethke1, Peter A. Sharma2, Tsu-Ming Lu1 and C. Thomas Harris1; 1Sandia National Laboratories, United States; 2University of Virginia, United States

Silicon nitride is widely used in the microfabrication of thermal sensors due to its favorable material properties. While numerous studies have leveraged thin silicon nitride membranes for highly sensitive thermal measurements, there have been limited reports on concerning membranes and platforms with thicknesses well below 100 nm. Herein, we report on the development of low-stress, suspended platform devices designed to facilitate the thermal characterization of membranes spanning a thickness range from 120 nm down to less than 10 nm. Depending upon the membrane thickness, we observe a substantial reduction in the thermal conductivity from 2.4 W m⁻¹ K⁻¹ to 1.2 W m⁻¹ K⁻¹ near room temperature. These platforms in this low thickness regime can significantly enhance the performance of devices requiring thermal isolation, such as bolometers, calorimeters, and gas sensors.*

This work was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. DOE, Office of Basic Energy Sciences, user facility. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE’s National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.

5:00 PM EN07.10.06
Super-Resolution Thermometry via Computational Correction to Overcome Diffraction Limit

Edward D. Walker and Thomas Beechem; Purdue University, United States

A computational enhancement is proposed, allowing for the realization of optical thermometry at spatial resolutions beyond the diffraction limit. Since the temperature measurement is a weighted average over the beam spot, the spot needs to be much smaller than the region of interest for accurate measurements. If it is too large, averaging creates a smoothing effect, flattening the measured profile. The simple solution is to somehow focus the beam in order to create a smaller spot size. However, there is a limit to how a beam of a given wavelength of light can be focused, known as the diffraction limit. For a diffraction limited system, then, there is a minimum temperature profile that is resolvable. To counter this, the relationship between the true profile and the flattened profile needs to be put into the form of an integral equation, whose solution is the “true” profile. This equation takes a form that is similar in structure to problems in fields such as electromagnetism, image processing, and heat conduction. By studying how these fields approach the problem, their solutions can be used to create a set of corrective methods to undo the smoothing effect. Applying these to existing Raman systems allows for accurate measurements at scales up to 5x smaller than currently possible, improving spatial resolution without changing the underlying hardware.

5:00 PM EN07.10.07
Reversible PolymersPolymerization for Compact Thermochemical Energy Storage Systems

Mayur S. Prabhudesai, Meyesiva Veerabagu, Paul V. Braun and Sanjiv Sinha; University of Illinois at Urbana Champaign, United States

Thermal energy storage (TES) can be an effective alternative to electrochemical batteries in applications where the end usage is primarily heat. Within TES, thermochemical energy storage (TCS) based on reversible chemical reactions have been demonstrated for high-temperature applications via gas-gas or solid-gas reactions based on ammonia, sulfuric acid, limestone, etc. However, the development of these inorganic systems is limited by material degradation with cycling, hysteresis losses, and complex equipment and operation. Recent studies have explored organic reactions that operate in a homogeneous phase for low to medium temperature TCS applications. With significant advances in chemically recyclable polymers, we investigate here the polymerization/depolymerization chemistry of ε-caprolactone/polyepsilon-caprolactone as a viable candidate for TCS. This chemistry is advantageous from an applications perspective due to a simple operation as a closed system and a broad range of charge/discharge temperatures suitable for water heating (100 – 200 °C). Preliminary studies confirm high conversion in the forward direction (polymerization) and selective formation of the monomer in the reverse direction. We find the heat of reaction obtained from DSC experiments (~140 J/g) to be consistent with prior literature values. We discuss ongoing experiments to optimize the monomer yield during depolymerization and to quantify heat of polymerization (storage capacity) using a laboratory-scale reactor. This work advances the usage of organic compounds for TES applications and could form the basis for further identification of similar chemistries.


5:00 PM EN07.10.08
A Personal Cooling Garment with Flexible Thermoelectric Devices and Heat Sinks

Ethan Sun1,2, Tianshi Feng2 and Renkun Chen2; 1The Bishop's School, United States; 2University of California, San Diego, United States

Global warming is causing more intense, more frequent, and longer periods of extreme heat events, which have caused numerous diseases and, in some cases, fatalities, among patients, the elderly, and outdoor workers such as those in the agriculture and construction sectors and firefighters. A lightweight personal cooling garment could be a game-changing solution to protect at-risk populations and enhance their comfort and performance. However, today’s personal cooling garments are not adequate as they are often too bulky and heavy, have limited cooling duration, and have no or limited temperature controllability. Hence, there is a strong need for a personal cooling garment with effective cooling, adjustable temperature, lightweight, is flexible & wearable, consumes less power (high coefficient of performance), and has low cost. Here we present our work on a personal cooling garment with flexible thermoelectric devices and heat sinks. This work leverages our earlier concept of developing flexible thermoelectric devices using high-performance rigid thermoelectric pillars. Here, we integrated individual thermoelectric devices into a flexible garment with the hot side cooled by flexible heat sinks. The garment is optimized with a finite element model for minimal weight. The performance of the garment under various heat flux levels and environmental temperatures was characterized. The results show that the garment can deliver high-flux cooling in a hot environment with high coefficient of performance (COP > 1.). The technology and performance of this garment are also discussed.

5:00 PM EN07.10.09
Identifying Molecular Scale Interactions of Nucleating Agents with Salt Hydrates for Thermal Energy Storage Applications

Mayur S. Prabhudesai, Sung Bum Kang, Youngmun Lee, Daniel Hsieh, Jay M. Taylor, Paul V. Braun and Sanjiv Sinha; University of Illinois at Urbana Champaign, United States

Losalt based thermoelectric materials are of interest as a method to mitigate and time-shift thermal load peaks and hence reduce energy demands for heating and cooling buildings. Notably, Glauber’s salt (CaSO₄·2H₂O) is attractive as a phase change material (PCM) for building applications because it has a melting point near room temperature (i.e., 32.4 °C), a large heat of fusion and energy density, and is low cost (~$100/ton). However, there are several known limitations to using GS as a PCM, such as incongruent melting, high degree of supercooling, and formation of other hydration states, which renders GS unsuitable for practical use. Inorganic crystals acting as nucleating agents can avoid some of these issues with GS [1]. Understanding nucleation behavior through typical calorimetry experiments offers limited insight into the molecular-scale mechanisms. Here, we report isothermal titration calorimetry [2] to investigate the interactions between sodium sulfate salt and an organic nucleating agent - glycerine. Our experiments provide qualitative and quantitative understanding of how glycerine interacts with sodium sulfate across
highly accurate machine learning interatomic potential (MLIP) for Sr$_2$Si$_{1-x}$Ge$_x$ disordered alloys. This MLIP is created through a machine learning technique trained on first-principles density determining the optimal alloy ratios through first-principles calculations can be quite challenging because disordered effects require a large supercell in the computations. Here, we introduce a calculations. To improve thermoelectric performance, the common practice involves alloying to reduce lattice thermal conductivity and enhance the Seebeck coefficient. Nevertheless, Yingru Song

Molecular Aspect Ratio Effect on Axial Thermal Transport in Solution-Spun Carbon Nanotube Fibers

This work is supported by India's Science and Engineering Research Board through the Core Research Grant No. CRG/2020/006166 and the Mathematical Research Impact Centric Support in the research areas of developing robust, efficient computational tools for materials discovery.

Understanding thermal behavior in two dimensional (2D) materials is important for advancing nanoelectronics and thermoelectric applications, as these materials can exhibit exceptionally tunable thermal conductivities. Especially, emerging 2D materials like Silicene, Arsene, Bismuthene and Antimonene are necessary as they find applications in a wide range of electronic and thermal devices. In this work we perform molecular dynamic simulations to understand thermal transport of these 2D nanomaterials and their corresponding nanotubes using equilibrium molecular dynamics with the Green-Kubo formalism. We utilize our in-house Tersoff models optimized against different polymorphs across local and global properties. Also, we present the impact of understanding the phonon dispersion predictions made by these models on thermal conductivities.

Thermal Transport in 2D Materials Using Tersoff Interatomic Potentials Adil Muhammed$^{1,2}$, Subramanian Sankaranarayanan$^{1,2}$, Aditya Koneru$^{1,2}$, Kiran Sasikumar$^3$ and Partha Sarathi Dutta$^{1,2}$, $^1$University of Illinois Chicago, United States; $^2$Argonne National Laboratory, United States; $^3$Avant-Garde Materials Simulation, Germany

Unusual thermal transport phenomena such as the hydrodynamic and Poiseuille phonon flow arise out of strong coupling among phonons in certain solid-state crystalline materials, and find applications in thermal cloaking and shielding of semiconductor devices and in the development of low thermal noise detectors. The linearized Peierls-Boltzmann equations (LPBE), which form a set of multi-dimensional and coupled differential equations, govern the coupled dynamics, transport and equilibration of phonons in these systems. Hence, solving the LPBE is a crucial step towards discovering new materials that display these unusual, yet technologically important phenomena.

However, predictive solutions of the LPBE including lower-order interactions among three phonons and higher-order interactions among four phonons with $ab$ initio inputs from density functional theory, which will serve as search tools for new materials, have been computationally intractable until recently [1, 2]. Even considering these recent advances, the computational cost due to the high dimensionality of the LPBE, large number of phonon polarization for the materials with complex crystal geometries and the need to resolve highly localized, temporally evolving interactions among phonons makes these conventional methods unsuitable for the rapid search of new materials that show exceptional hydrodynamic phonon transport.

To overcome this problem, here we develop a neural network scheme to solve the steady-state and the transient LPBE, which enables rapid convergence of the steady-state solution of the LPBE and allows for computationally efficient high temporal resolution of localized interactions among phonons under transient transport conditions, which is particularly important to search for materials with strongly hydrodynamic phonon flow. We show that, for materials with complex crystal structures beyond the cubic geometry such as bulk MoS$_2$, graphite, w-GaN and MoS$_2$, where hydrodynamic transport is possible at cryogenic conditions, the neural network scheme significantly outperforms the conventional iterative solution of the LPBE under both steady-state and transient conditions. Our findings highlight the computational advantages of adopting this new neural network-based first principles solver for the LPBE, which can have significant impact in the research areas of developing robust, efficient computational tools for materials discovery.

This work is supported by India's Science and Engineering Research Board through the Core Research Grant No. CRG/2020/006166 and the Mathematical Research Impact Centric Support Grant No. MTR/2020/001043. The presenter also acknowledges the Infosys Young Investigator award for support.


Phonon Thermal Transport in Semiconductors Studied Using a Neural Network Assisted Solution of The Peierls-Boltzmann Equation

Phonon Thermal Transport in Semiconductors Studied Using a Neural Network Assisted Solution of The Peierls-Boltzmann Equation

Navaneetha Krishnan Ravichandran; Indian Institute of Science, India

Neat, densely packed, and highly aligned carbon nanotube fibers (CNTF) have appealing room-temperature axial thermal conductivity (κ) and thermal diffusivity (α) for applications in lightweight axial heat spreading or flexible thermal connections. Although increasing the molecular aspect ratio (i.e., ratio of nanotube length to nanotube diameter) of the constituent single-wall and few-wall carbon nanotubes (CNTs) is expected to improve and by reducing the number of interfaces along the axial direction per unit length, no prior work has quantified the molecular aspect ratio effect on thermal transport for solution-spun CNTF. Here, we perform self-heated steady-state and three-omega thermal measurements at room temperature on suspended CNTF in vacuum. The CNT molecular aspect ratios range from 960 to 5600, as quantified by rheological measurements of liquid crystalline CNT solutions. The thermal measurement results show that increases from to with increasing . The axial electrical conductivity also increases from to with increasing , and the Wiedemann-Franz law predicts the electronic contribution to is for the highest sample. CNTF made with increasing volume fraction of constituent high- and low- CNTs generally fall within typical macroscopic rule-of-mixtures bounds for and . The thermal diffusivity scales with , leading to a sample-averaged volumetric heat capacity of $1.5\pm0.1$. Thus, this work shows that increasing the molecular aspect ratio enhances and of solution-spun CNTF, motivating further investigation into thermal transport mechanisms and applications of carbon nanotube fibers.

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Bioengineering a Reversible Thermal Conductivity Switch in Tandem Repeat Proteins

Emma Tieran, John Tomko, Benjamin Allen, Melik Demirel and Patrick E. Hopkins
1University of Virginia, United States; 2Tandem Repeat Technologies, Inc, United States; 3The Pennsylvania State University, United States

The reversible regulation of heat transport within a material provides the user the ability to control its temperature as well as that of its surroundings. To achieve this nanoscale regulation, a material must be able to switch between thermally conductive and insulative states. In recent years it has been shown that thin films of certain tandem repeat proteins can achieve this thermal switch by simply hydrating and dehydrating the film. One material that is able to serve as a thermal switch is a synthetic bio-polymer whose sequence is inspired by those found in squid ring teeth (SRT). These SRT bio-polymers consist of repeating amorphous and crystalline domains which rely on hydrogen bonding and other intermolecular forces to retain their folded conformation. The addition and removal of water to these films will enhance or disrupt the intermolecular forces, thus encouraging or inhibiting the transport of heat.

In these experiments, we used time-domain thermoreflectance (TDTR) to monitor the thermal conductivity switch of SRT thin films under varying hydration conditions. TDTR is an optical pump-probe technique for measuring thermal conductivity of nanoscale material systems, where a low power "probe" beam monitors the change in reflectivity of a material modulated by a delayed "pump" laser. By applying an analytical solution to the heat conduction equation, we calculate thermal conductivity and other thermal properties of the material. We show that by modifying the composition of the hydrating solution, we are able to obtain a thermal conductivity switch ratio of four between ambient and hydrated states.

5:00 PM EN07.10.20

Anti-Environmental Aging Passive Daytime Radiative Cooling Paint

Jianjie Song and Xu Deng; University of Electronic Science and Technology of China, China

Passive daytime radiative cooling technology presents a sustainable solution for combating global warming and extreme weather, with great potential for diverse applications. The key characteristics of this cooling technology are the ability to reflect most sunlight and radiate heat through the atmospheric transparency window. However, the required high solar reflectance is easily affected by environmental aging, making the cooling ineffective. We demonstrate a facile strategy to use titanium dioxide nanoparticles, with UV resistance, forming hierarchical porous morphology via evaporation-driven assembly, which guarantees a balanced anti-soiling and high solar reflectance, rendering anti-aging cooling paint (AACP) based coatings. We challenged the AACP coatings against simulated 3 years of natural soiling and 1 year of natural sunshine, and found that the solar reflectance only declined by 0.4% and 0.5% compared with the un-aged ones, barely affecting the cooling performance. Our AACP is scalable and can be spray coated on desired outdoor architecture and container, presenting promising SDR, promising for real-world applications.

8:30 AM *EN07.11.01

Physics-Informed Neural Networks for Solving Phonon Boltzmann Transport Equation

Tengfei Luo, Jiahang Zhou and Ruiyang Li; University of Notre Dame, United States

The phonon Boltzmann transport equation (pBTE) has been proven to be capable of precisely predicting heat conduction in sub-micron electronic devices. However, numerically solving pBTE is extremely computationally costly due to its high dimensionality, especially when phonon dispersion and time evolution are considered. In this study, we use physics-informed neural networks (PINNs) to solve pBTE for multiscale non-equilibrium thermal transport problems both efficiently and precisely. In particular, a PINN framework is devised to predict phonon energy distribution by minimizing the residuals of governing equations, boundary conditions, and initial conditions without the need for any labeled training data. With phonon energy distribution predicted by the PINN, temperature and heat flux can be obtained thereby. In addition, geometric parameters, such as characteristic length scale, are also considered as a part of the input to PINN, which makes our model capable of predicting heat distribution in different length scales. Furthermore, 1D to 3D heat conduction problems are studied under our PINN framework, and the results show excellent agreement with numerical and FEM solutions. Moreover, our PINN framework has proved to be far more efficient compared to existing pBTE numerical solvers. With superiorly high efficiency and accuracy, the proposed method shows great promise for practical applications, such as thermal design and thermal management of microelectronic devices. Besides pBTE, we have also extended the applicability of the PINN framework for models of coupled electron-phonon (e-ph) transport. e-ph coupling and transport are ubiquitous in modern electronic devices. The coupled electron and phonon Boltzmann transport equations (BTEs) hold great potential for the simulation of thermal transport in metal and semiconductor systems. However, solving the BTEs is often computationally challenging due to their high dimensional complexity and widespread heat carrier properties, hindering large-scale thermal modeling at the device level. In this work, we present a PINN framework for solving the coupled electron and phonon BTEs. Instead of relying on labeled data, the proposed framework directly learns the spatiotemporal solutions (i.e., the electron and phonon distribution functions) within a parameterized complexity by enforcing physical laws. The efficacy of this framework is demonstrated through its ability to accurately resolve temperature profiles in low-dimensional thermal transport problems and visualize the ultrafast electron and phonon dynamics in laser heating experiments on thin metal films. The results indicate that our approach can accurately describe non-equilibrium e-p energy transfer with improved efficiency, opening new avenues for the predictive design and optimization of micro- and nanostructures.

9:00 AM EN07.11.03

Screening Ultrawide Thermal Conductivity from 150,000 Crystals by Sub-Trillion-Scale Atomic Data Integrated Deep Learning Approach

Ming Hu; University of South Carolina, United States

Existing machine learning potentials for predicting phonon properties of crystals are limited to either small amount of training data or a material-to-material basis, primarily due to the exponential scaling of the number of atomic species or elements. This renders high-throughput infeasible when facing large-scale new materials. Unlike previous machine learning models with inherently limited training on small data and global properties, we develop Elementary Spatial Density Neural Network Force Field (Elemental-SDNNFF) with abundant atomic level environments as training data. Benefiting from this innovation, we integrate ~50 atomic data to train a single deep neural network without increased expensive ab initio simulations. The effectiveness and precision of the Elemental-SDNNFF approach is demonstrated on a set of 150,000 inorganic crystals spanning 63 elements in the periodic table by prediction of complete phonon properties. Our algorithm achieved a competitive force root mean square error of about 40 meV/Å and a speed-up of 3 - 4 orders of magnitude in comparison to first principles. Self-improvement schemes such as active learning and data augmentation techniques are also incorporated allowing human-free refinement of the force accuracy on arbitrary combinations of chemistries. Deep insight into the ultrawide lattice thermal conductivity (<1 W/mK) of predicted structures are gained by p-d orbital hybridization analysis and charting the thermal conductivity data in the bonding-antibonding map, which offers a quick approach for future screening of crystals with strong intrinsic phonon anharmonicity. Our model also quantitatively reveals the transition between off-diagonal coherence and diagonal populations and identifies the distinct crossover from particle-like to wave-like heat conduction. Our algorithm is promising for accelerating discovery of novel phononic systems for emerging applications, such as heat dissipation in electronics, optoelectrics, and coherent phonons for quantum information technology.

9:15 AM EN07.11.04

Advancing Thermal Management in Buildings Globally: Machine Learning-Optimized Dynamic Window Materials

Yuan Gao, Jacob Jonsson, Charlie Curcija, Simon Vidanovic and Tianzhen Hong; Lawrence Berkeley National Laboratory, United States

Dynamic window materials represent a significant advancement in energy-efficient building technology, offering a promising approach to intelligent thermal management and energy conversion in architectural applications. Leading active areas of interest in dynamic window research include hydrogels, passive radiative cooling materials, dynamic devices based on reversible metal electrodoposition. These cutting-edge materials are capable of dynamically altering their optical and thermal properties in response to external environmental variations, thereby efficiently managing light and heat transfer within buildings. However, dynamic window materials face significant challenges in their development and application. First and foremost, these materials are often optimized based on specific weather conditions rather than a comprehensive, global spectrum. Achieving continuous optimization on a global scale proves to be difficult due to the immense volume of calculations required. This lack of universal optimization may limit their efficiency across diverse climate zones. Furthermore, there is a noticeable gap in the presence of robust indicators to quantify the dynamic performance of these materials. This void in performance metrics poses a challenge, as without clear quantification, it becomes difficult to determine the true value of these windows, especially since their dynamic features may be superfluous in certain climatic conditions.

To address these issues, we proposed novel indicators to evaluate the necessity level of using dynamic windows in buildings for different climates. We use thermochromic (TC) materials as examples to demonstrate this concept for passive dynamic windows. Through an unprecedented global-scale analysis, we executed more than 2.8 million simulations across over two thousand global locations covering most of the Köppen climate classifications in the world. A typical commercial office space, which is adapted from Department of Energy's prototype building model, is used for EnergyPlus simulation in this study. Beyond typical office space, whole commercial and residential buildings are also used for analysis. World heatmaps of indicators for dynamic...
Recent advances of atomistic modeling techniques have shown remarkable accuracy while predicting heat transport mechanisms in isolated nanoscale systems, such as thin films with confining surfaces, single solid-solid interfaces between materials with different degrees of crystallinity or disorder. Heat is mostly carried by phonons in semiconductors and insulators. When the system size becomes comparable to the characteristic lengths of phonons, heat conduction is affected by phonon confinement and enhancement of scattering due to boundaries, interfaces, and various defects. Phonon confinement results in localization of modes in spatial regions. The effect of scattering mechanisms on phonon transport properties could also be highly varied. The thermal transport properties of nanoscale systems that include multiple confining surfaces, interfaces, and materials with different degrees of crystallinity or disorder, is far from understood.

The computational costs of atomistic approaches prohibit us to explore the complete structural parameter space of large systems, that influence phonon transport. The state-of-the-art (SoA) deeply sub-scaled 100-nanometers transistors are heterogeneous structures that include nm-scale crystalline semiconductors, disordered dielectric materials and metals, within confining interfaces. The confined geometry results in a net increase of the power density within the structures. The associated self-heating accelerates the defect generation mechanisms leading to decline of performance and reliability issues. The SoA thermal models of microelectronic circuits utilize continuum level models to predict the temperature distribution in the structures, even after 40+ years of being declared outdated. The models also incorporate input from non-continuum models that are better suited to describe the physics at smaller length scales. However, the transistor-level thermal properties are often approximated from the bulk thermal properties or computed using effective models. The effective models include several parameters that need to be calibrated using measurement data. The calibrated parameters may not even accurately represent behavior in dynamic operating conditions. The heat transfer in nm-scale systems can be drastically different from their bulk counterparts. The effective models do not include these details and as a result, cannot explain thermal bottlenecks or runaways or reveal any mitigation strategies. A predictive thermal model must consider the effects of confinement to accurately predict temperatures and identify thermal bottlenecks. In the past decades, algorithmic improvements, and dramatic increase of computing power, have enabled rigorous techniques such as molecular dynamics (MD) simulations to accurately model heat transport in finite systems, with disordered components and interfaces. MD simulations implicitly capture the full dynamics of anharmonic interactions and do not make any assumptions about scattering mechanisms. In this talk, I will discuss how we use atomistic modeling approaches combined with machine learning methods to predict thermal properties of sub-10-nm confined geometry field effect transistors and other complex devices.

11:00 AM EN07.12.02
Monte Carlo - Finite Element Mixed Model for Heat Transport on Electronic Devices at The 20 nm Scale F. Xavier Alvarez, Jordi Tur and Albert Beardo Ricol; Univeritat Autonoma de Barcelona, Spain
Simulation of the thermal evolution of actual electronic devices is a very challenging topic. Heat transport at the nanoscale does not behave as in the macroscale [1-2]. This is a problem for engineers, as they cannot predict the thermal response of their devices with accuracy.

In the last years, the Kinetic Collective Model (KCM) has been used to develop a finite element tool to describe the thermal evolution of electronic devices with great accuracy using the Gayer and Krumhansl hydrodynamic equation. The results obtained from this approach fit extraordinarily to experiment with characteristic scales up to 400 nm using only ab initio parameters [1-2], but for smaller devices, effective values for the parameters are required. In that situations, some corrections are required in order to predict the experiments.

We present the Higher Order Perturbation (HOPE) an improvement of the KCM-hydrodynamic approach [4-5]. This new method allows to obtain a full predictive finite element model for thermal transport at the 20nm scale. The model is obtained from the split of the Boltzmann Transport Equation (BTE) in two terms, a first one that describes the hydrodynamic behavior and a second one with the residual terms that describes the evolution of the perturbations of higher order. From the solution of the residual term using a Monte Carlo approach we derive a boundary correction term that modifies the hydrodynamic boundary conditions. With this correction, the applicability of our finite element tool is significantly improved. We compare the results obtained from our simulations with experimental data of devices in the 200-20 nm range.

Bibliography

11:15 AM EN07.12.03
Study of Interfacial Thermal Resistance of Heterostructures Using Machine Learning (ML)-Molecular Dynamics Tianli Feng; University of Utah, United States
Diamond, as an ultra-wide bandgap semiconductor, holds significant potential in many cutting-edge applications from electronics, nanotechnology, biosensors and quantum information processing, owing to its ultra-high thermal conductivity and mobility. The interfacial thermal conductance between diamond and metals is crucial for the thermal management of diamond-based electronic devices and determines the maximum working temperature. However, current knowledge about the metal/diamond thermal interfacial transport is still very limited. There is no reliable interatomic potential between metals and diamond. In this work, we train machine learning interatomic potentials at the interface based on density functional theory (DFT) calculations. The accuracy of the potential is validated against DFT calculations. Using the potentials, we conduct MD simulations to obtain the interfacial thermal conductance. Different surface terminations of diamond have been studied. The results from this research should have significant contribution to improved understanding of interfacial thermal properties, which is key to developing new diamond-based electronics devices.
Finding amorphous polymers with higher thermal conductivity (TC) is technologically important, as they are ubiquitous in a wide range of applications where heat transfer is crucial. While TC is generally low in amorphous polymers, it can be enhanced by selecting them to strain since it facilitates the alignment of polymer chains. However, using the conventional Edsallson approach, the discovery of polymers that may have high TC after strain can be time-consuming and lack guarantee of success. In recent years, machine learning approaches have shown promise in the prediction of polymer properties with high accuracy and efficiency. In this work, we employ an active learning scheme to speed up the discovery of amorphous polymers with high TC under strain. Polymers under strain were simulated using molecular dynamics (MD), and their TCs were calculated using the non-equilibrium MD method. A Gaussian Process Regression (GPR) model is then trained using these data. The GPR is used to screen the PolyInfo database, and the predicted mean TC and uncertainty are used towards an acquisition function to recommend new polymers. The TC results of these selected polymers are then labeled using MD simulations and the obtained data are incorporated into the training set, initiating a new iteration of the active learning cycle. Over a few cycles, we identified more strained polymers with significantly higher TC than the original dataset, and the results offer valuable insights into the structural characteristics that contribute to enhanced energy conversion from a physical perspective.

**Active Learning Exploration of Thermally Conductive Polymers Under Strain** Renzhang Zhang, Jiaxin Xu, Hanfeng Zhang and Tengfei Luo; University of Notre Dame, United States

Thermal Conductivity and Elastic Modulus in Two-Dimensional Hybrid Metal Halide Perovskites: From a Molecular Engineering Perspective Ankit Negi1, Liang Yan2, Cong Yang1, Yeonju Yu3, Subhransu Mukherjee1, Andrew Comstock1, Ziqi Wang1, Dali Sun1, Harald Ade1, Qing Tu3, Wei You2 and Jun Liu1; 1North Carolina State University, United States; 2University of North Carolina at Chapel Hill, United States; 3Texas A&M University, United States

Device-level implementation of soft materials demands a comprehensive understanding of their thermal conductivity and elastic modulus to mitigate thermo-mechanical challenges and ensure long-term stability. Thermal conductivity and elastic modulus are usually positively correlated in soft materials, such as amorphous macromolecules, which poses a challenge to discover materials that are either soft and thermally conductive or hard and thermally insulative. Here, we show an anomalous correlation of thermal conductivity and elastic modulus in two-dimensional (2D) hybrid organic-inorganic perovskites (HOIPs) by employing the molecular interaction between organic cations. When replacing the organic cation from a softer alkyl ligand to a more rigid aryl ligand, we find that the elastic modulus increases but thermal conductivity decreases, which provides a route to engineer thermal conductivity and elastic modulus independently. We further conducted molecular dynamics simulation to understand the molecular interactions and this anomalous dependence. Introducing chirality into the organic cation induces a unique molecular packing, leading to the same thermal conductivity and elastic modulus regardless of the composition for all half-chiral 2D HOIPs. This finding provides substantial leeway for further investigations in chiral 2D HOIPs to tune opto-electronic properties without affecting the thermal and mechanical stability.

**Understanding Effects of Gas Molecules on Thermal Transport in Metal–Organic Frameworks** Yukvang Moon, Rahil Ukani, Qichen Song, Joy Cho and Jarad A. Mason; Harvard University, United States

Metal–organic frameworks (MOFs)—porous crystals composed of metal nodes and organic linkers—are promising materials for a wide range of applications, notably in gas storage and separations. Despite ultrahigh porosities, large internal surface areas, and highly tunable structures, realizing the full potential of MOFs has been hindered in part by their inadequate thermal properties. MOFs typically possess low thermal conductivities (< 2 W m⁻¹ K⁻¹), which can dictate gas adsorption dynamics under practical loading rates. While it has been suggested that the presence of gas molecules within the pore can impact the propagation of phonons, it has been challenging to experimentally examine the effects of interactions at the pore wall. Recent studies have sought to measure the thermal conductivities of various MOFs, and molecular dynamics simulations have been employed to elucidate the factors governing their intrinsic transport properties, but the microscopic mechanisms underlying the effects of adsorbates remain underexplored. Here, we present experimental investigations of thermal transport in zeolitic imidazolate framework-8 (ZIF-8) under systematically varied gas environments. We employ the frequency-domain thermoreflectance (FDTD) technique to probe thermal conductivity in single crystals of ZIF-8 with chemically diverse gas adsorbates. This approach enables us to investigate how the interaction energies between gas molecules and the pore walls influence transport pathways along the porous framework. Our FDTD measurements reveal that gases with higher adsorption capacity, such as CO₂, result in a notable decrease in the thermal conductivity of ZIF-8 compared to adsorbates with a lower adsorption capacity such as N₂. Additionally, variable-temperature FDTD measurements provide unique insights into the kinetics of gas molecules confined within the pores of ZIF-8. Our research illuminates the dynamic interplay between gas adsorption and the thermal properties of ZIF-8, offering new mechanisms to chemically modulate thermal transport in porous materials systems.

**Anomalous Thermal Transport of Two-Dimensional Materials in Contact with Metal due to Complex Phonon Scattering** Jei Sun, Bin Xu, Rulei Guo and Junichiro Shiomi; Tokyo University, Japan

Heat dissipation is paramount in the realm of modern electronics, encompassing chips and wearable devices, whose typical candidates are the two-dimensional (2D) materials due to their superior intrinsic electrical, optical or phonon properties. However, these materials are seldom found in a freestanding state when integrated into devices, often integrated with crystalline semiconductors, Kirchoff or flexible Phynics. Thermal management strategies for such devices typically rely on a macroscopic perspective, which may lack phonons. By combining the techniques of machine-learning-based interatomic potentials within DFT-level quality, together with the theory of phonon coherence and scattering from different orders, the heat transport of the 2D materials combined with substrates are investigated. Contrary to conventional expectations of hindered thermal transport, our findings reveal that the thermal conductivity of graphene remains invariant when placed on a substrate. This invariance is attributed to the suppression of four-phonon scattering, a consequence of symmetry-breaking effects. The more intriguing phenomenon is the observed enhancement of thermal conductivity when germanene is placed on the substrate. This outcome defies expectations and can be attributed to the competing mechanisms: increased third-order anharmonicity and decreased fourth-order anharmonicity. Besides, an increase in coherent phonon transport due to the reduced disparities in the frequencies of various phonon modes also accounts for the enhanced thermal transport. In conclusion, our study has unveiled both the invariant and enhanced heat transport in 2D materials when combined with substrates. This investigation, driven by the microscopic phonon transport theorem, offers a fresh perspective on heat dissipation in electronic devices.

**Unlocking Rayleigh's Law Limit of Thermal Transport for Extremely Low Thermal Conductivity by Materials Informatics** Meng An, Wenyang Ding, Jianguo and Junichiro Shiomi; The University of Tokyo, Japan

Engineering materials with extremely low thermal conductivity are crucial and desirable for many applications such as thermal management of electronic devices, thermal insulation and thermoelectric conversion. Recently, two-dimensional (2D) materials with heteroatoms from multiple distinct materials blocks show excellent properties and are considered as the promising candidates for constructing integrated circuits and quantum computers. However, Rayleigh's law implies that acoustics phonons, which carry most of the heat, are insensitive to scattering by atomic-scale defects. Therefore, realizing low thermal conductivity of lateral heterostructure with complex composition and diverse arrangement remains challenging due to the high degree of freedom and complex objectives. Herein, we develop a hybrid materials informatics approach which combines the variational autoencoder and Bayesian optimization to design two-dimensional patterned graphene/h-BN lateral heterostructure with extreme low thermal conductivity. With only several hundred training data sets, new structure with extremely low thermal conductivity can
be quickly determined in a compressed latent space by calculating far less than 0.0001% of the total candidate structures, which greatly decreases the design period and cost. More interestingly, the thermal conductivity of newly obtained structure is much lower than that of randomly arranged graphene/h-BN lateral heterostructure, where the extracted phonon relaxation time of newly obtained structure from phonon energy spatial density are calculated to demonstrate the validity of Rayleigh's law. Finally, the mode-resolved atomic Green's function (AGF) method was utilized to calculate the phonon modal transmission of newly obtained structure and analyze the elastic phonon scattering behavior. This study not only can be easily extended to other thermal conduction metamaterials with higher dimensional features but would be beneficial to screening the phonon transport mechanism of two-dimensional heterostructures with multiple thresholds of thermal conductivity.

2:45 PM EN07.13.05
Tailoring Thermal Conductivity Anisotropy Using Ion Beam Modification

Marat Khafizov, Vinay Chauhan, Hao Ma, Zilong Hua, Azat Abdulahaev, Shadman S. Priam, Saqeb Adnan, Erika Nosal, Michael Manley, Zhandos Utegulov, Lingfeng He, and David Hurley; 1The Ohio State University, United States; 2Oak Ridge National Laboratory, United States; 3Idaho National Laboratory, United States; 4Nazarbayev University, Kazakhstan; 5North Carolina State University, United States

We demonstrate utilization of energetic particle to introduce few nanometer-sized features in crystalline solids leading to changes in thermal transport. This integrated analysis includes ion irradiation, microstructure characterization using transmission electron microscopy, measurement of thermal conductivity tensor using spatial domain thermoreflectance, and modeling of thermal conductivity accounting for observed nanostructure. In cubic CeO2 bombarded with 2 MeV protons faulted dislocation loops are formed. These loops have long range strain field resulting in significant reduction of thermal conductivity. Aligned ion tracks in Al2O3 generated by bombardment with 167 MeV xenon ions modify its thermal conductivity anisotropy, where thermal conductivity along direction perpendicular to ion exhibits larger conductivity reduction compared to direction parallel to the channels. Lastly, we show modification of conductivity anisotropy in hexagonal delta-phase U-Zr alloy, caused by formation of platelet nanoprecipitates. For the latter case, the anisotropic modification is also observed in phonon lifetimes measured using inelastic X-ray scattering.

3:00 PM BREAK

SESSION EN07.14: Thermal Transport Modulation
Session Chairs: Taeyong Kim and Jun Liu
Thursday Afternoon, April 25, 2024
Room 327, Level 3, Summit

3:30 PM EN07.14.02
Reversible and High-Contrast Thermal Conductivity Switching in a Flexible Covalent Organic Framework Possessing Negative Poisson’s Ratio

Sandin Thakur and Ashutosh Girri; University of Rhode Island, United States

The ability to dynamically and reversibly control thermal transport in solid-state systems can redefine and propel a plethora of technologies including thermal switches, diodes, and rectifiers. Current material systems, however, do not possess the swift and large changes in thermal conductivity required for such practical applications. For instance, stimuli responsive materials, that can reversibly switch between a high thermal conductivity state to a low thermal conductivity state, are mostly limited to thermal switching ratios in the range of 1.5 to 4. Here, we demonstrate reversible thermal conductivity switching with an unprecedented 18× change in thermal transport in a highly flexible covalent organic framework with revolving imine bonds. The pedal motion of the imine bonds are capable of reversible transformations of the framework from an expanded (low thermal conductivity) to a contracted (high thermal conductivity) phase, which can be triggered through external stimuli such as exposure to guest adsorption and desorption or mechanical strain. We also show that the dynamic imine linkages endow the material with a negative Poisson’s ratio, thus marking a regime of materials design that combines low densities with exceptional thermal and mechanical properties.

https://doi.org/10.1039/D3MH01417G

3:45 PM EN07.14.03
Thermal Rectification Mediated by Polaritonic Heat Conduction

Sichao Li and Sunmi Shin; National University of Singapore, Singapore

The pursuit of advanced thermal management solutions for applications spanning electronics, buildings, and energy conversion/storage has intensified with the exploration of thermal nonlinear elements for advanced thermal management. We construct proof-of-concept thermal circuits to demonstrate that these nonlinear thermal devices enable thermal logic operations, passive heat flow routing, and duration (0.5 year) storage. We discuss the rationale behind the design of nanostructured heat channels and thermometers, showcasing their critical role in realizing asymmetric transmittance of quasi-ballistic heat transport.

4:00 PM EN07.14.04
Thermal Transistor and Thermal Regulator Devices Utilizing Temperature-Dependent Magnetic Forces

Lorenzo Castelli, Ajay Garg, Qing Zhu, Trevor J. Shimokusu, Pooja Sashital and Geoffrey Wehmeyer; Rice University, United States

Switchable and nonlinear thermal devices are enabling technologies for applications ranging from waste heat scavenging to solid-state cooling and battery thermal management. Existing high-performance passive switching devices operating near room temperature rely primarily on thermal expansion to open or close gaps between surfaces; however, many thermal expansion switches have substantial thermal hysteresis and/or require large device thicknesses. Here, we demonstrate passive thermal switching with several devices that use temperature-dependent magnetic forces to make and break mechanical contact between thermally conductive elements. Our devices rely on the reversible paramagnetic/ferromagnetic phase transition of the magnetically soft material gadolinium, which has a convenient Curie temperature near 20°C for room temperature switching. We use this magnetically-actuated mechanism to construct a thermal regulator, which is a two-terminal device in which the steady-state thermal conductance can be passively tuned between an ON or OFF value by the temperature of the control thermal terminal. We also demonstrate the first reported thermal transistor, which is a three-terminal device in which the temperature at the gate terminal controls the source-drain heat flow in a manner that leads to heat flow switching and amplification.

The thermal regulator displays an average thermal switch ratio of 34 (uncertainty ±30, −13) in vacuum with switching temperatures near 20°C and a 5°C thermal hysteresis. The magnetic actuation mechanism leads to relatively low thermal hysteresis and smaller thicknesses (~2 cm) as compared to the prior thermal expansion demonstrations. Similarly, the thermal transistor displays an average source-drain thermal switch ratio of 109 (uncertainty ±62, −38) in vacuum with switching gate temperatures near 25°C and a 7°C thermal hysteresis. The thermal transistor displays measured heat flow amplifications near 30, meaning that a small gate heat flow can drive a larger source-drain heat flow, and has characteristic thermal time constants ranging from 4 to 17 minutes. We quantify the durability and performance of both devices over >1000 cycles and find that the regulator switch ratio decreases by a factor of four after cycling and long-duration (0.5 year) storage. We construct proof-of-concept thermal circuits to demonstrate that these nonlinear thermal devices enable thermal logic operations, passive heat flow routing, and temperature regulation capabilities. Thus, our demonstrations of passive heat switching using a magnetic thermal regulator and thermal transistor will motivate further research implementing nonlinear thermal elements for advanced thermal management.

This work was supported by an Early Career Faculty grant from NASA’s Space Technology Research Grants Program (Grant #80NSSC20K0066), by a NASA Space Technology Graduate Research Opportunity (Grant # 80NSSC20K1220), and by a grant from the Welch Foundation (Grant No. C-2023).

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4:15 PM EN07.14.05
Asymmetric Thermal Transport and The Influence of Contact Resistance in Telesopic Nanowires

Yashpreet Kaur1, Saeko Tachikawa2, Jose Manuel Sojo Gordillo1, Milo swinkels1, Matteo Camponovo1, Anna Fontcuberta i Morral2, Riccardo Rurai2 and Ilaria Zardo3,1; University of Basel, Switzerland; 2EPFL, Switzerland; 3ICMAB-CSIC, Spain

Heat dissipation has become a critical problem in the performance of electronic devices, thus reducing their lifespans [1]. To cope with this, researchers are using several approaches like thermoelectric generators, coolers, thermal diodes, heat guides, and more [2]. A thermal diode works as a rectifier, allowing the flow of heat preferentially in one direction. In our current research, we have studied telesopic nanowires for their thermal transport and rectification capabilities [3].

A telesopic nanowire is a quasi-one-dimensional structure with a thick and a thin part having diameters of 300 and 90 nm, respectively, with a transition region in between. The GaAs telesopic nanowires are grown by MBE technique using the VLS mechanism [4]. Thermal conductivity measurements of one-dimensional (1D) structures were conducted using thermal bridging technique [5]. Thermal rectification ratios of up to 8% were measured as a function of applied temperature bias.

Further, the temperature jump at the contacts is extracted using Raman thermometry [6] while applying different temperature biases. In numerous instances within the literature, this crucial contact contribution tends to be overlooked despite its substantial influence on the determination of thermal properties. In our case, a thermal contact resistance of (2.71 ± 0.43) × 10⁻⁸/K/W was estimated and compared to reference homogeneous nanowires. This enables a correct estimation of the rectification from the nanostructure. The thermal mapping along the nanowire axis was also done to extract the thermal conductance of the corresponding thick and thin parts.

These results underscore the significance of accounting for thermal contact resistance in accurately characterizing the thermal properties of nanowire-based systems. Moreover, this is the first experimental study on telesopic nanowires indicating rectification and an important contribution towards the development of thermal circuit elements.


SESSION EN07.15: Poster Session III: Thermal Transport and Energy Conversion III
Session Chairs: Jaeyoung Moon and Sunmi Shin
Thursday Afternoon, April 25, 2024
Flex Hall C, Level 2, Summit

5:00 PM EN07.15.01
Low-Dimensional Heat Conduction in Surface Phonon Polariton Waveguide

Yu Pei; Li Chen, Wonjae Jeon, Zhaowei Liu and Renkun Chen; UCSD, United States

Heat conduction in solids is governed by Fourier's law, describing a diffusion process primarily driven by phonons and electrons with short wavelengths and mean free paths. Non-Fourier heat conduction, observed in exotic systems, remains elusive in typical solids. Surface phonon polaritons (SPhPs) are evanescent surface waves resulting from the collective oscillation of atoms on the surface of polar dielectric materials. They couple thermal phonons and optical phonons, potentially contributing significantly to heat conduction, particularly in nanostructures with diminished volumetric heat conduction by phonons and electrons. Unlike thermal radiation, SPhPs carry a high energy flux along the solid surface, acting as thermal waveguides. Surface phonon polaritons (SPhPs) offer a promising avenue for extraordinary heat transfer due to their longer wavelength and propagation length. However, their low energy flux has hindered direct observation of SPhP-mediated heat conduction.

Here, we demonstrate direct observation of enhanced thermal conductivity mediated by SPhPs in SiO2 nanoribbon waveguides. To distinguish SPhPs from phonons, the waveguide cross-section must be reduced. However, this introduces challenges related to wave leakage and inefficient coupling with thermal reservoirs. Our study addresses these challenges by designing nanoribbon waveguides of SiO2 with controlled SPhP mode size and efficient coupling to thermal reservoirs using an absorber. We directly observe an increased thermal conductivity in these waveguides, surpassing the limit of phonon thermal conductivity by up to 34%. Moreover, we observe non-Fourier behavior in SPhP thermal conductance over 50-100 μm distances at room and high temperature, indicating the unique characteristics of phonon heat conduction. Our work represents the first direct observation of enhanced thermal conductivity mediated by SPhPs and provides insights into the potential of manipulating heat conduction beyond traditional limits. These findings open up new possibilities for engineering thermal transport in various applications.

5:00 PM EN07.15.03
Nanoscale Thermal Transport in SiC: Effects of Inter-Grain Misorientation, Grain Size and Crystal Anisotropy

Omid Farzadian, Yanwei Wang and Zhanded Uteguulov; Nazarbayev University, Kazakhstan

Detailed understanding of the thermal transport across grain boundaries (GBs) and nano-size grains in nanocrystalline thermal functional materials is essential for optimizing their performance across variety of advanced energy applications [1,2]. This study aims at elucidating the nature of inter-grain heat transport as well as spatially-resolved thermal conductivity inside small grains by controlling the misorientation tilt angle θ, grain sizes D and crystal anisotropy to advance our fundamental insight into thermal transport in nanocrystalline materials.

For a detailed atomistic treatment of interfacial heat transport across GBs in SiC bi-crystals, non-equilibrium molecular dynamics (NEMD) simulations are employed. We focus on the (hk0) {001} family of symmetrical tilt GBs, where {001} represents the tilt axis, (hk0) signifies the GB plane with tilt angle θ. The primary interest in structural analysis of GBs revolves around uncovering the atomistic configuration that represents the lowest energy state for a specific θ, commonly referred to as the ground-state structure. To discern this equilibrated state for each GB, we employ an optimization procedure involving the conjugate gradient (CG) method [3,4].

To examine the heat propagation behavior across these GBs, a temperature gradient is imposed on both ends of the SiC structure. It is anticipated that κ of nanocrystalline material will be significantly lower than that of the bulk single crystal due to the presence of thermal resistance at the GB interfaces, defined as the Kapitza resistance R. The variation of R with θ across individual GBs is studied with minimized GB energy. Observed asymmetry in R with respect to θ = 0 degrees is due to two dissimilar atoms (Si and C) present in the lattice.

Moreover, we employ perturb MD [3] to compute spatially-resolved anisotropic local thermal conductivities in SiC by varying D and θ. It was explored that the intra-grain κ decreases with the reduction of D and also varies with the rise of θ in the cross-GB and along-GB directions. The κ remains relatively uniform within the grain interiors but decreases near the GB plane. It should be noted that this reduction is more significant in larger grains than in smaller ones. This observed phenomenon is discussed in terms of the enhanced phonon scattering in the nanoscale vicinity from GBs, phonon mean free paths, interatomic interaction within a diatomic SiC crystalline lattice across the GBs connecting grains misoriented from each other at various tilt angles directly affecting inter- and intra- grain phonon-mediated heat transport.

References:

5:00 PM EN07.15.04
Theory of The Soret Effect in Liquids and Solids

Patrick K. Schelling; University of Central Florida, United States

The Soret Effect, also known as thermodiffusion, is the flow of matter in response to externally applied heat sources. This effect is important in a number of applications including crystal growth and analysis interactions between biomolecules, and may present opportunities for guided materials synthesis using temperature gradients. While this effect has been known for some time, predictive models and microscopic understanding have been lacking. We have recently demonstrated that the Soret effect is closely connected to the response of a system to the internal stresses induced by a heat source. In particular, as a system approaches mechanical equilibrium, density gradients develop, and the difference in response to these density gradients is...
exhibits a density of 0.2 g/cm³, thermal conductivity of 0.03 W/(mK), and compressive strength of ~1 MPa at 10% strain. This example of the quick development of efficient sustainable manufacturability of wood-based thermal insulation materials by eliminating solvents from the fabrication process. Performance characterization of wood waste-based thermal insulation foam through a rapid hot-pressing technique, demonstrating significant product tunability, manufacturing scalability, and time- and cost-efficiency. This method significantly improves the manufacturability of wood-based thermal insulation materials by eliminating solvents from the fabrication process. Performance characterization of wood waste-based thermal insulation foam exhibits a density of 0.2 g/cm³, thermal conductivity of 0.03 W/(mK), and compressive strength of ~1 MPa at 10% strain. This example of the quick development of efficient sustainable manufacturability of wood-based thermal insulation materials by eliminating solvents from the fabrication process. Performance characterization of wood waste-based thermal insulation foam through a rapid hot-pressing technique, demonstrating significant product tunability, manufacturing scalability, and time- and cost-efficiency. This method significantly improves the manufacturability of wood-based thermal insulation materials by eliminating solvents from the fabrication process. Performance characterization of wood waste-based thermal insulation foam exhibits a density of 0.2 g/cm³, thermal conductivity of 0.03 W/(mK), and compressive strength of ~1 MPa at 10% strain. This example of the quick development of efficient sustainable manufacturability of wood-based thermal insulation materials by eliminating solvents from the fabrication process. Performance characterization of wood waste-based thermal insulation foam through a rapid hot-pressing technique, demonstrating significant product tunability, manufacturing scalability, and time- and cost-efficiency. This method significantly improves the manufacturability of wood-based thermal insulation materials by eliminating solvents from the fabrication process. Performance characterization of wood waste-based thermal insulation foam exhibits a density of 0.2 g/cm³, thermal conductivity of 0.03 W/(mK), and compressive strength of ~1 MPa at 10% strain.

Wood, a renewable resource with passive carbon sequestration abilities, has a history of use within construction materials because of its cheap, abundant, and sustainable nature; however, natural wood’s low porosity makes it an unfit candidate for readily producible and highly efficient thermal insulation materials, leading to a high overall thermal conductivity (> 0.1 W/(mK)).

Wood, a renewable resource with passive carbon sequestration abilities, has a history of use within construction materials because of its cheap, abundant, and sustainable nature; however, natural wood’s low porosity makes it an unfit candidate for readily producible and highly efficient thermal insulation materials, leading to a high overall thermal conductivity (> 0.1 W/(mK)).

Thermoelectric Properties of Stressed p-Doped Polycrystalline Hollow Nanotubes

Thermoelectric Properties of Stressed p-Doped Polycrystalline Hollow Nanotubes Jose Manuel Sojo Cordillo1, 2, Yashepree Kaur1, Saeko Tachikawa2, Giulio de Vito4, Alex Morata2 and Ilaria Zardo1; 1University of Basel, Switzerland; 2Catalonia Institute for Energy Research - IREC, Spain; 3National Institute of Advanced Industrial Science and Technology - AIST, Japan

Thermoelectric generators have the potential to efficiently convert waste heat into valuable electrical power. However, conventional thermoelectric materials face limitations in terms of efficiency, scarcity, high cost, and scalability, impeding their widespread adoption. Nanoelectronic techniques have emerged as a promising solution to enhance the thermoelectric properties of abundant and inexpensive materials like silicon. The integration of these nanomaterials on a large scale, necessary for efficient waste heat recovery, remains a significant challenge.

Recently, a novel class of nano-enhanced materials in the form of extensive, paper-like fabrics composed of nanotubes has been developed, offering a cost-effective and scalable approach to thermoelectric power generation [1]. However, the fundamental properties of the building blocks of these fabrics, namely the p-type silicon nanotubes, have not been individually investigated to date. This study conducts electrothermal measurements using microfabricated suspended nitride membranes to characterize the thermoelectric properties of these nanotubes, including the electrical and thermal conductivity as well as the Seebeck coefficient. Furthermore, Raman thermography is employed in order to account for the effects of thermal contact resistance in the thermal conductivity measurement. Raman spectroscopy is also used to examine the residual mechanical stress in the nanotubes and investigate its relationship with the observed thermoelectric properties. A network model is proposed to link the macroscopic thermal properties of the fabrics with those of the nanotubes. Additionally, the study investigates the light absorption within these hollow structures. Finally, the effects of SiGe alloy on the properties of the nanotubes are compared and discussed.

By understanding the interplay between the morphology, structure, and thermoelectric properties of the nanotubes, a pathway can be established for the development of more mechanically stable and efficient fabrics, with the potential for commercializing waste heat recovery through this technology.

References:
Unveiling High-Order Phonon Physics: High-Pressure Thermal Transport in Extreme Materials

Sumeet Li1, Zhaowu Qin1, Huan Wu1, Man Li1, Martin Kunz2, Ahmet Alatas3, Abby Kavner1 and Yongjie Hu1; 1University of California, Los Angeles, United States; 2Advanced Light Source, Lawrence Berkeley National Laboratory, United States; 3Advanced Photon Source, Argonne National Laboratory, United States

High pressure provides a new dimension for exploring the transport physics and properties of materials. Over the past century, tremendous efforts have been made to study thermal transport under high pressure. However, the first-principles phonon theory for understanding thermal transport under high pressure has been rarely applied. Here, for the first time, we studied high pressure transport in silicon and identified high order anharmonic behaviors beyond the classical textbook understanding. We conducted in-situ experiments, incorporating thermal transport, vibrational spectroscopies, and synchrotron X-ray experiments. These measurements were juxtaposed with first-principles calculations, shedding light on the microscopic dynamics underlying heat transfer. Our finding uncovering high-order anharmonic behaviors beyond traditional comprehension based on classical physics. Our development enables new research platforms and provides fundamental insights into thermal transport under extreme conditions. Reference: S. Li, Z. Qin, H. Wu, M. Li, M. Kunz, A. Alatas, A. Kavner, Y. Hu, "Anomalous thermal transport under high pressure in boron arsenide," Nature 612, 459 (2022). https://www.nature.com/articles/s41586-022-05381-x

5:00 PM EN07.15.15
Thermal Boundary Conductance at High Temperatures Sameer Khan and Richard B. Wilson; University of California, Riverside, United States

Understanding the physics of thermal boundary conductance is essential for thermal management of semiconductor devices. Thermal boundary conductance at high temperatures has been shown to depend on atomic scale details like interfacial bonding, interfacial roughness, and interfacial layers. The intrinsic vibrational properties of the materials at the interface also affect thermal boundary conductance2. Surprisingly, only a few experimental studies of thermal boundary conductance at high temperatures exist. This prevents testing of theories for how inelastic processes contribute to thermal conductance2-3. Inelastic processes at the interface between dissimilar materials are expected to be most important, and more noticeable at high temperatures. In this study, we present results of time domain thermoreflectance (TDR) measurements of thermal boundary conductance for nitride-metal/group-IV-semiconductor interfaces between 80 and 800 K. The nitride-metals (TiN and HfN) and group-IV-semiconductors (Ge, Si, SiC, and diamond) have systematic differences in bulk vibrational properties. By comparing the conductance vs. temperature of these systems, we determine the effect of vibrational similarity on inelastic scattering processes. We show that the average probability for interfacial energy transmission increases significantly with temperature by comparing the measured conductance values to theoretical predictions for the elastic and inelastic limits of the conductive interface. In diamond systems, the transmission probability of thermal energy triples from 20% at 300 K to 60% at 900 K. Our findings fill an important gap in the literature for how interfacial conductance evolves at high temperatures, and tests burgeoning theories for the role of inelastic processes in interfacial thermal transport. References


5:00 PM EN07.15.17
Manipulation of Near-Field Radiative Heat Flow via Mid-Infrared Plasmonic Coupling Saman Zare1, William D. Hutchins2, Maxwell Tolchin2, Angela Cleri2, Mingze He3, Joshua D. Caldwell3, Jon-Paul Maria2 and Patrick E. Hopkins1; 1University of Virginia, United States; 2The Pennsylvania State University, United States; 3Vanderbilt University, United States

With the continuous reduction in the size of electronic devices to the nanoscale, it becomes imperative to gain a deep understanding of heat transport mechanisms at these levels. In recent years, breakthroughs in nanotechnology and radiative engineering have introduced thermal radiation as a promising mechanism to tailor both the magnitude and direction of heat transfer. The use of metamaterials enhances our capability to manipulate radiative heat transfer in nanoscale systems, particularly in the context of near-field radiation, which can significantly exceed the blackbody limit even at multiple orders of magnitude. Heat transport in the near field of metamaterials depends on their geometry, optical properties of the constituent materials, and interfacial properties. By fine-tuning interfaces in and/or metamaterials, we can manipulate heat flux, and facilitate an augmented flow of radiative heat from specific spectral modes into bulk heat carriers. One proposed way to tune this flow is by capitalizing on the hybridization of resonant modes in plasmonic materials. Highly doped cadmium oxide (CdO) is poised as an exceptional candidate for that purpose as it allows for high electron mobilities while maintaining dielectric properties mechanically. Also, sub-wavelength films of CdO support epsilon-zero plasmons in the mid-infrared range of the spectrum. Most importantly, it has been shown that carefully constructed multilayers of CdO with varying carrier densities exhibit tunable hyperbolic plasmonic dispersion properties, allowing for carrying heat across interfaces at a significantly higher rate than conduction. In this research, we conduct experimental investigations into the interactions between hyperbolic plasmon-polaritons (HPPs) within a layered hyperbolic metamaterial (HMM) and ENZ modes within a doped CdO thin film. Our approach involves employing a unique ultrafast pump-probe technique that enables the precise detection of heat transfer modes with sub-picosecond temporal resolution. This technique relies on a wavelength-tunable mid-infrared probe pulse, allowing us to directly interface with plasmonic heat carriers, thereby providing a direct assessment of the thermal transport properties of the HMM. Furthermore, we explore the impact of the MgO dielectric gap positioned between the HMM and ENZ layers on the efficiency of near-field coupling between HPP and ENZ modes via far-field sensing. Additionally, we demonstrate the capability of tuning the near-field radiative heat transfer by introducing a dielectric spacer in an HMM/ENZ structure. Our results provide a new path for novel designs of plasmonic devices with far-reaching applications in tailored thermal emission and thermal management of microelectronics.

5:00 PM EN07.15.19
High Temperature Thermal Conductivity Measurement Using Two-Color Thermal Imaging Hao-Yuan Cheng, Alexander Myers and Jonathan A. Malen; Carnegie Mellon University, United States

This research explores measuring the thermal conductivity of various materials at high temperatures (up to 4000 K). We use the two-color thermal imaging technique with a commercial color camera to measure the temperature distribution on a sample heated by the high-power laser heat source of a Directed Energy Deposition (DED) additive manufacturing machine. The thermal conductivity of various semiconductor materials has been measured using this technique, including silicon, gallium arsenide, and silicon carbide. The technique relies on the measurement of the temperature difference between two surfaces using two color channels, allowing for the determination of the thermal conductivity of the material. This method has been validated using high-temperature standards and has been shown to be a reliable technique for measuring thermal conductivity at high temperatures. This research is important for the development of high-temperature electronic devices and thermal management solutions. The two-color thermal imaging technique allows for high spatial and temporal resolution, making it suitable for applications in the field of thermal management and materials science. This research presents a novel approach to measuring thermal conductivity at high temperatures, which has the potential to revolutionize the field of thermal management and materials science. The results of this research will be useful for the design and development of high-temperature electronic devices and thermal management solutions. The two-color thermal imaging technique is a versatile tool for measuring thermal conductivity at high temperatures, and it has the potential to be applied in various fields, including materials science and engineering.

5:00 PM EN07.15.20
Determination of Thermal Conductivity in Metals Under High Temperature and Pressure: A First Principles Study Pravin Karna1, Oleg Prezhdo2, Patrick E. Hopkins3 and Ashutosh Gir1; 1University of Rhode Island, United States; 2University of Southern California, United States; 3University of Virginia, United States

Metallic structures find applications across a wide range of challenging environments, including situations involving high temperatures and pressures like nuclear reactors, plasmonics, pressure calibrators, and interconnects. These metals exhibit distinct properties when subjected to extreme conditions, which might not be apparent under ambient conditions. We employ first principles calculations to investigate the interaction between electrons and phonons in these conditions for various metals: free-electron metal (Al), noble metals (Au, Ag, Cu), and a transition metal (W). This analysis reveals how these metals respond to extreme conditions and sheds light on their thermal and electrical characteristics in such environments. Our calculations encompass the thermal conductivity of these metals under extreme conditions, factoring in both electron-phonon and electron-electron interactions. Furthermore, by computing the spectrally resolved electron-phonon coupling parameter at high pressures, we calculate the contribution of different phonon modes in scattering with electrons. This research offers valuable insights into the processes of electron-phonon scattering under high pressures, uncovering a new realm of electrical and thermal transport properties in metallic materials.

5:00 PM EN07.15.21
Effect of Interface Curvature at The Axial Junction in Silicon-Germanium (Si-Ge) Nanowires Orelawo A.O. Adejina and Laura de Sousa Oliveira; University of Wyoming, United States

Due to a wide array of potential applications, such as thermal management, thin-film technologies, microelectronics, and semiconductor and optical devices, thermal transport in silicon-based nanowires is of significant interest. The interface curvature, in particular, plays a crucial role in determining the thermal transport properties of these nanowires. In this study, we investigate the effect of interface curvature on the thermal transport properties of Si-Ge nanowires. By using a first principles-based approach, we calculate the thermal conductivity of Si-Ge nanowires with different interface curvatures. Our results show that the interface curvature significantly affects the thermal conductivity of these nanowires. This finding has important implications for the design and optimization of Si-Ge nanowires for various applications, including thermal management and microelectronics. The study also highlights the importance of considering interface curvature in the development of nanowire-based devices. This research provides valuable insights into the factors that influence thermal transport in Si-Ge nanowires and paves the way for the development of new materials and devices with improved thermal properties.
germanium (Si-Ge) materials, including nanowires, is an area of continued interest. Thermal transport in small-scale heterogeneous systems is controlled by interfacial thermal resistance but the relative contributions of different transport mechanisms (e.g., elastic and inelastic phonon scattering) remain elusive. Our work is expected to further our understanding of phonon thermal transport and the role of boundary scattering at the interfaces of low-dimensional materials. The curvature and sharpness of the interface at the heterojunctions in Si-Ge nanowires depend on their growth environment. Herein, we evaluate the effect of interfacial curvature at the axial junctions in Si-Ge nanowires. We employ the non-equilibrium molecular dynamics (NEMD) Muller-Plathe method (with the Tersoff potential) to model thermal transport in nanowires with lengths between 100 nm and 1.3 μm and varying interfacial curvatures. Boundary resistance is probed for directional transport between both Si and Ge and Ge and Si. We have observed an overall weak dependence of thermal conductivity on curvature, and that the effect of curvature on thermal transport is dependent on nanowire length. The evolution of the wave-packet kinetic energies during the course of a simulation provides a more comprehensive picture of the wave behavior of phonons across the Si-Ge interface.

5:00 PM EN07.15.02
High Thermal Conductive Liquid Crystal Elastomer Nanofibers
Jingxuan Wang1, Yue Wen1, Duo Pan2,2, Shulang Lin1, Chinappan Amutha1, Qiguang He1, Chunli Liu2, Zhifei Huang1, Shengqiang Cai3, Seeram Ramakrishna1 and Summi Shin1; 1National University of Singapore, Singapore; 2Zhejiang University, China; 3The Chinese University of Hong Kong, Hong Kong; 4University of California, San Diego, United States

Liquid crystal elastomers (LCEs), consisting of polymer networks and liquid crystal mesogens, show reversible phase change induced by thermal stimuli. However, the kinetic behavior is limited by the inherently low thermal conductivity of polymers. Transforming amorphous bulk into fiber-like forms enables us to enhance the thermal conductivity by aligning polymer chains. Rigid networks of crosslinked polymer have challenged to fabricate nanofibers of it while the existence of the crosslinks in LCEs is crucial to shape reversible transformation of the elastomers. In this study, hydrodynamic alignment was employed to orient the LCE domains assisted by controlled in-situ crosslinking. A drag force was applied to a suspended individual single polymer fiber anchored to a micro-thermometer device. This process remarkably cuts down the fiber diameter to sub-microns. We explored the highly enhanced thermal conductivity of LCE nanofibers (~100 nm in diameter) which is one order of magnitude higher than that of bulk counterpart. To further elucidate the size-effect on heat transfer in LCE fibers, temperature-dependent analysis was made with various diameters of LCE fibers.

5:00 PM EN07.15.22
Unlocking Enhanced Thermal Conductivity in Polymer Blends through Active Learning
Jinxin Xu and Tengfei Luo; University of Notre Dame, United States

Polymers play a integral role in various applications, from everyday use to advanced technologies. In the era of machine learning (ML), polymer informatics promises to become a valuable tool for efficiently designing and developing polymeric materials. However, the focus of polymer informatics has predominantly centered on single-component polymers, leaving the vast chemical space of polymer blends relatively unexplored. This study employs a high-throughput molecular dynamics (MD) simulation approach combined with active learning (AL) to uncover polymer blends with enhanced thermal conductivity (TC) compared to the constituent single-component polymers. Initially, TC values for about 600 amorphous single-component polymers and approximately 200 amorphous polymer blends with varying blending ratios are determined through MD simulations. The optimal representation method for polymer blends is also identified, which involves a weighted sum approach that extends existing polymer representation from single-component polymers to polymer blends. An AL framework, combining MD simulation and ML models, is employed to explore the TC of an unlabeled dataset comprising approximately 550,000 potential polymer blends. The AL framework proves highly effective in accelerating the discovery of high-performance polymer blends for thermal transport. Additionally, we delve into the relationship between TC, radius of gyration (Rg), and hydrogen bonding, highlighting the roles of inter- and intra-chain interactions in thermal transport in amorphous polymer blends. A significant positive association between TC and Rg improvement and an indirect contribution from H-bond interaction to TC enhancement are revealed through a log-linear model and odd ratio calculation based on the polymer blend dataset, emphasizing the impact of increasing Rg and H-bond interactions on enhancing polymer blend TC.

8:30 AM *EN07.16.01
Si-Based Planar-Type Thermoelectric Generators over 1 μWcm⁻²K⁻²
Masahiro Nomura; The University of Tokyo, Japan

Thermoelectric energy harvesting is one of the key technologies for carbon neutrality. This talk introduces recent advances in Si-based thermoelectric generators (TEGs) and we demonstrate a planar-type double-cavity Si TEG with phononic nanostructures based on a phonon-engineered design. The planar-type device was fabricated in an SOI wafer with CMOS and MEMS processes to largely integrate the device. By using phononic nanostructures and three-dimensional thermal design, we achieved over 100 mWcm⁻² output power density at a temperature difference of lower than 10 K. We fabricated the Si TEG in an SOI wafer with a 1.1-μm-thick n-type poly-Si device layer and a 1.5-μm-thick BOX layer. The phononic crystal (PnC) structures are an array of circular holes with a period of 300 nm and a neck size between 8 and 100 nm. It was designed to reduce the thermal conductivity of poly-Si by considering the phonon mean free path spectrum. The cap wafer is designed for efficient cooling of the device. This double-cavity thermal design leads to a high-power density of the device. We found that more than 30% of the temperature difference between the upper and bottom of the device was applied in the thermoelectric material thanks to the careful thermal design of the double cavity structure. This thermal design is an important key factor, as well as the ZT of the thermoelectric material. Our TEG showed the output power density of more than 100 μWcm⁻² at a lower than 10 K temperature difference between the devices (a few Kelvin in thermoelectric material). The obtained normalized performance of over 1 μWcm⁻²K⁻² is, to our knowledge, the highest-performing planar-type Si thermoelectric generator reported to date.

9:00 AM *EN07.16.02
Geometric Design and 3D Printing of Thermoelectric Materials and Devices
Jae Sung Son1, Seungjin Choo1, Jungsoo Lee2, Seong Eun Yang2 and Keonkuk Kim2; 1Pohang University of Science and Technology, Korea (the Republic of); 2Ulsan National Institute of Science and Technology, Korea (the Republic of)

Heat is omnipresent in natural and artificial environments, more than 60% of which is dissipated. Thermoelectric (TE) power generation can provide a unique solution to convert this dissipated, wasted heat into useful energy, that is, electricity. The performance of thermoelectric modules, typically composed of cuboid-shaped materials, depends on both the materials’ intrinsic properties and the temperature difference created. Despite significant advancements in the development of efficient materials, macroscopic thermal designs capable of accommodating larger temperature differences have been largely underexplored because of the challenges associated with processing bulk thermoelectric materials. At this moment, three-dimensional (3D) printing technology can maximize the flexibility in the design and fabrication of TE modules into more efficient structures. Herein, we present the design strategy for various thermoelectric materials for enhancing power generation performances using a combination of finite element modeling and 3D printing. The macroscopic geometries are designed and realized by the 3D printing technology, leading to significant enhancements in the temperature difference within devices and the resulting output powers. The proposed approach paves the way for designing efficient thermoelectric power generators.

9:30 AM EN07.16.03
All-Silicon Micro-Thermoelectric Generator for IoT Applications
Jose Manuel Sojo Gordillo1,2, Denise Estrada-Wiese3, Alex Rodriguez-Iglesias3, Marc Salleras3, Alex Morata2, Albert Tarancón2 and Luis Fonseca3; 1University of Basel, Switzerland; 2Catalonia Institute for Energy Research, Spain; 3Institute of Microelectronics of Barcelona, Spain

In the next decade, a digital revolution will be held over the expansion of the Internet of Things (IoT), involving the deployment of trillions of nodes in multiple locations. The exponential growth of this kind of wireless devices represents a major challenge in terms of their energy supply [1]. Among the available environmental sources, heat can be harvested by means of thermoelectric devices [2]. This work presents a new generation of densely packaged all-silicon microthermoelectric generators (μTEGs) with planar architecture.

Optimized p-doped silicon nanowires with 80 ± 30 nm in diameter are epitaxially integrated as dense arrays into these generators for an improved performance [3]. A procedure to reliably place a heat sink on top of the devices, boosting the fraction of external thermal gradient captured by the thermoelectrically active nanowires, is described. These improvements boosts the generated voltage up to six times with respect to that of a bare μTEG, leading to output powers well within the range of IoT needs (10-100 μW/cm²). Specifically, the μTEG on top of a heat source above
200°C and under still air convection conditions generates more than 10 μW/cm². When exposed to the same temperatures and to an airflow of 1.3 m/s (equivalent to a light breeze) the power density increases above 80 μW/cm².

Moreover, a long-term stability study running the device in load matching conditions for a period of 1000 h does not show degradation below 200°C. Finally, the suitability of connecting the μTEG with the current state of the art DC-DC converters is discussed, showing how eventual transients in real operation conditions could allow the device to reach the required cold start-up voltages.

Overall, the results shown here demonstrate the readiness of the presented μTEG as a valid power source for IoT applications at the microscale.

References


9:45 AM EN07.16.04

Geometric Thermoelectricity (GTE) - Towards "Junction-Less" Unconventional Thermoelectric Devices Oleg V. Kolosov1, Alexandros El Sachat2, Charalambos Evangeli1, Sergio Gonzalez-Munoz3, Peng Xiao4, Elisa Castanon3, Edward McCann5, Matthew Hamner6, Johanna Zultak6, Olga Kazakova7 and Roman Gorbachev8; 1Lancaster University, United Kingdom; 2NCSR "Demokritos", Greece; 3IICN2, Spain; 4The University of Manchester, United Kingdom; 5National Physical Laboratory, United Kingdom

Traditionally, thermoelectric (TE) phenomena require junctions between two dissimilar materials to either generate the current when opposing junctions are held at two differing temperatures (Seebeck effect) or to cool and heat the opposing junctions when the external current is applied (Peltier effect). The two materials must have a different thermoelectric (Seebeck) coefficient, S (defined as the voltage per temperature difference, θT), in order to observe each Seebeck or Peltier effect. Nevertheless, the recently discovered phenomenon of “Geometrical Thermoelectricity”, GTE [1] indicated that a nanoscale constriction (of the order of 50-200 nm) in the monolayer of two-dimensional material (2DM) graphene on the insulating SiO2/Si substrate acts as de-facto different material with the different Seebeck coefficient, changing the Seebeck coefficient solely by geometrical patterning and allowing to create TE devices out of a single material [2], avoiding the need for another material and a junction between two materials.

Here we investigate the origin of the GTE phenomenon using a well-defined structure of graphene encapsulated between hexagonal boron nitride (hBN) layers with the insulating constrictions (flat-taper/flat-flat/taper-flat) and under different polarity of the carriers using the back-gating. By using Scanning Thermal Gate Microscopy (STGM) [3] we developed the Seebeck coefficient on the distance of less than 20 nm, whereas the modification of the Seebeck coefficient is extended to the distances larger than 500 nm, suggesting the characteristic TE modification length is linked with the charge carriers.

In summary, we conclusively linked the GTE phenomenon to the geometrical factors and demonstrated that such an effect is present in other 2D materials such as dichalcogenides SnSe2. We also showed the one can create large areas of multilayer 2D material building de-facto a new material with different TE properties while preserving its heat transport performance, paving the way for the much broader applications of GTE effect for the nanoscale and microscale cooling, heat manipulation and TE energy generation.

10:00 AM BREAK

10:30 AM #EN07.16.05

Unusually Large Anomalous Nernst Effects in Partially-Crystallized Ferromagnetic Metallic Glasses Hyeonju Jin and Hyun-Woo Lee; Pohang University of Science and Technology, Korea (the Republic of)

Nernst effect is a well-established thermoelectric effect where electrons traveling along the direction of a temperature gradient are deflected by the Lorentz force into the transverse direction perpendicular to both temperature gradient and applied magnetic field. As a result, a finite electric field develops along the transverse direction. In magnetic and topological materials, such transversal deflection occurs owing to different mechanisms classified into intrinsic and extrinsic origins, and the phenomenon is called the anomalous Nernst effect (ANE). Recent studies reported that a large ANE arises in materials possessing a large Berry curvature near the Fermi level. Since its origin is intrinsic electronic band topology, such a large ANE is observed in specific crystalline orientations which requires the consistency of the crystal structure. Contrary to the growing research interest in discovering new materials with large Berry curvatures, much less attention has been paid to extrinsic aspects of ANE.

In this talk, we show that unusually large ANE can be obtained even in amorphous ferromagnetic metals, when the degree of disorder within the materials is properly controlled. By applying high-speed FIB milling of arrays of holes of about 50 nm in diameter in a thick 50 nm layer of 2D material SnSe2 using the varying pitch, density and ordering, showing that it is indeed possible to create multi-μm size areas of material with a very different Seebeck coefficient. By combining STGM with scanning thermal microscopy (SThM) [4] we found that the holes modify the heat transport on the distance of less than 20 nm, whereas the modification of the Seebeck coefficient is extended to the distances larger than 500 nm, suggesting the characteristic TE modification length is linked with the charge carriers.

Moreover, we explored whether GTE can be used for modification of the Seebeck coefficient in the area of 2D material rather than for a single point (nanoscale constriction). We performed the FIB milling of arrays of holes of about 50 nm in diameter in a thick 50 nm layer of 2D material SnSe2 using the varying pitch, density and ordering, showing that it is indeed possible to create multi-μm size areas of material with a very different Seebeck coefficient. By combining STGM with scanning thermal microscopy (SThM) [4] we found that the holes modify the heat transport on the distance of less than 20 nm, whereas the modification of the Seebeck coefficient is extended to the distances larger than 500 nm, suggesting the characteristic TE modification length is linked with the charge carriers.

Acknowledgement

This work was supported by Samsung Research Funding & Incubation Center of Samsung Electronics under Project Number SRFC-MA2002-02 and by the National Research Foundation of Korea (NRF) grants funded by the Korea government (MSIT) (NRF-2022M3C1A3091988) and by the Ministry of Education, Science and Technology (RS-2023-0052296).

11:00 AM #EN07.16.06

Advanced Energy Materials and Devices for Low-Grade Heat Harvesting and Flexible Thermal Sensing Dongyan Xu; The Chinese University of Hong Kong, Hong Kong

With the recent advance of the internet of things, wearable technology, and soft robotics, there is great interest to develop low-cost energy harvesting devices for converting low-grade heat into electricity and flexible sensors for artificial thermal sensation. In this talk, I will share our recent research efforts in these directions through exploring three effects: (1) thermoelectric effect; (2) thermogalvanic effect; and (3) thermodiffusion effect. Specifically, we developed flexible micro thermoelectric generators (TEGs) with high power density and light weight by integrating pulsed electroplating with microfabrication processes. Compared to traditional electron-based thermoelectric materials, redox couples and ionic thermoelectric (ITE) materials using ions as charge carriers can achieve much larger thermopowers typically on the order of mV/K. Recently, we report polarized electrolytes consisting of I- /I3- redox couple, methylcellulose (MC), and KCl with ultrahigh thermopowers of 8.18 mV/K for n-type and 9.62 mV/K for p-type. Thermoresponsive MC enables polarization switching from n-type to p-type above the gelation temperature, while the giant thermopowers mainly come from the thermogalvanic effect of the I- /I3- redox coupled enhanced synergistically by MC and KCl. We also developed an iTE hydrogel with a thermopower of 24.17 mV/K and flexible thermal sensor arrays for human-machine interaction.

11:30 AM EN07.18.06

Thermal Characterization of GeTe PCM based Reconfigurable Devices Zexiao Wang, Xi Liu, Hyeonggyun Kim and Sheng Shen; Carnegie Mellon University, United States
Energy harvesting systems based on triboelectric nanomaterials are in great demand, as they can provide routes for the development of self-powered devices which are highly flexible, stretchable, mechanically durable, and can be used in a wide range of applications. Ultrasound was used to deliver mechanical energy through skin and liquids and demonstrated that a thin film device can be applied to the skin. The results showed that the device can harvest energy from ultrasound waves and could be used in various applications such as powering medical devices.

**Triboelectrics and Tribovoltaics for Energy Harvesting**

**1:45 PM**

**Dynamically Tunable Solid-State Thermal Energy Storage** Shuang Cui,1,2 and Judith Vidal, Ph.D2; 1The University of Texas at Dallas, United States; 2National Renewable Energy Laboratory, United States

Thermal energy storage (TES) utilizing phase-change materials (PCMs) holds substantial promise in various applications, such as climate control in buildings and thermal management for electronics and batteries. A critical challenge in the design of TES applications is the limited tunability of the operating temperature, especially for the near-ambient applications. The phase change temperature of the PCM, however, can be controlled through the introduction of electric fields. This work reports on the design and experimental validation of a dynamically tunable solid-state TES device, allowing thin and flexible device fabrication. The device is fabricated and experimentally tested. The steady-state temperature response of the TES device is measured through a thermal mapping system, proving the potential of such devices for various applications.

**Dynamically Tunable Solid-State Thermal Energy Storage**

**2:15 PM**

**Nanophotonic Devices with Tunable Optical Response** Sungsik Kang,1,2,3,4 and Sung Bum Kang; 1Yonsei University, Korea (the Republic of); 2Pontifícia Universidade Católica do Rio de Janeiro, Brazil; 3National Renewable Energy Laboratory, United States; 4University of Illinois at Urbana-Champaign, United States

Nanophotonic devices with adjustable optical response can be achieved through phase change materials (PCMs) such as Germanium Tellurium alloy (GeTe). GeTe can be rapidly melt-quenched or annealed between amorphous and crystalline states with large contrast of electrical and optical properties, making it a good candidate for reconfigurable electromagnetic devices, optical devices, and memory devices. However, challenges exist on the thermal aspect of GeTe PCM, where the cooling rate high as 1 K/ns from the melting point of 1000 K is required for quenching process. The stringent thermal requirements possess high demands on both heating power and heat dissipation ability. Currently, several different heating approaches are adopted to achieve phase change in GeTe based nanophotonic devices, including hot plate, pulsed laser, and integrated electrical heater. However, reversible switching of GeTe covering a large area remains difficult, and the device-level understanding of the thermal and electrical properties is still elusive for the GeTe reconfigurable devices.

In this work, device level thermal modelling is conducted for a representative GeTe switching heater device, which includes a Si substrate, an AlN insulation layer, an electrical heater made from tungsten, an Al2O3 separation layer, and the GeTe phase change material on top. Frequency domain thermoreflectance (FDTD) method is adopted for thermal characterization, where the thermal properties of a multi-layered structure can be determined through pump-probe laser heating and curve fitting to an analytical heat conduction model. The most thermally sensitive material parameters, including thermal conductivity and heat capacity of Si, AlN, and GeTe layers, as well as the thermal boundary resistance between Si and tungsten heater, are characterized through FDTD with delicately designed multi-layered samples.

Based on the thermal measurement results, an actual GeTe switching heater device was designed with 8-unit heater layout covering the phase change region of 25±12.5 μm². A finite element model is established for the heater device to predict the steady state and transient thermal responses. To validate the thermal measurement results and the finite element model, the heater device is also fabricated and experimentally tested. The steady state temperature response of the TES device is measured through a thermal mapping system, proving the potential of such devices for various applications.

**Moisture-Capturing Hydrogels and Their Applications** Sung Bum Kang,1,2,3 and Sung Bum Kang; 1Yonsei University, Korea (the Republic of); 2National Renewable Energy Laboratory, United States; 3University of Illinois at Urbana-Champaign, United States

Moisture-capturing hydrogels have emerged as promising low-cost sorbent materials for applications including thermal management, thermal energy storage, and atmospheric water harvesting. Despite extensive efforts in the synthesis of novel hydrogels, there is a large knowledge gap between the synthesis variables and the material properties, which hinders the design of properties and system-level optimization. In this work, we develop physics-based models to predict the properties of moisture-capturing hydrogels from their composition. We develop and experimentally validate thermodynamic models that accurately predict the water uptake and absorption enthalpy as a function of humidity as relevant hydrogel synthesis variables are changed. We also develop mass transport models, using a convection-limited transport description, that accurately predict experimental absorption and desorption speeds. This work represents a major step in the design of moisture-capturing hydrogels, enabling application optimization for high performance thermal management of electronics, buildings, and people, heat storage, and atmospheric water production.

**Hydrogel-Salt Hydrate Composite for Highly Stable Heat Energy Storage with Reduced Supercooling** Sung Bum Kang,1,2,3 Youngmoon Lee, Wonsik Eom, Wuchen Fu, Mayur S. Prabhudesai, Daniel Hsieh, Sameh Tawfick, Nenad Miljkovic, Sanjay Sinha and Paul V. Braun; University of Illinois at Urbana-Champaign, United States

Phase change materials (PCM) have potential for use in thermal energy storage in buildings, medical devices, and water heat pumps. Sodium sulfate hydrate (SSD) is appealing due to its high energy storage capability and affordability. However, SSD has issues including high supercooling (>15°C) and low thermal cyclic stability. In this study, we introduced an ionically and molecularly nucleating agent that decreases the supercooling temperature to under 2°C. When this SSD was combined with a hydrogel, it maintained its thermal energy storage capacity for over 100 cycles without any decline. The success is attributed to the polymer confining the SSD crystals, preventing large-scale phase separation, and the nucleating agent which resulted in nucleation of many small SSD crystals at small undercoolings rather than a small number of larger crystals. As a proof-of-application, we synthesized this composite at a kg scale and demonstrated its properties in a close to real-world demonstration.

**3:00 PM BREAK**
Energy-efficient thermal management for buildings is one of the keys to our sustainable future, as the demand for thermal comfort has increased swiftly under the impact of extreme weather. Tremendous research endeavors have been reported in recent decades, striving to tackle thermal management tasks using sustainable methods such as radiative cooling, evaporative cooling, and smart window. Thermal energy storage (TES), which utilizes latent heat of phase change materials (PCMs), also received emerging interest for its ability in mitigating temperature fluctuations and sustaining thermal comfort without extra energy input. However, practical implementation of PCMs is constrained by cost, shape stability, and energy density. Here we report an inorganic PCM composite based on sodium sulfate decahydrate (SSD). In contrast to most organic PCM, SSD has an ultralow cost ($1.60$/kWh) and high energy density (254 J/g), making it a promising PCM for building thermal management. To address the intrinsic limitations of SSD in shape stability and phase separation, we introduced another low-cost hydrogel, i.e., poly (acrylamide-co-acrylic acid), to encapsulate SSD through swelling. In particular, we optimized hydrogel composition by exploring the hydrolysis effect, and achieved a swelling ratio of 29.96 g/g in 70 wt% SSD solution. The obtained phase change hydrogel exhibited a melting latent heat of 133.32 J/g with melting temperature of 32.84 °C, while withholding excellent shape stability after 500 hundreds thermal cycles. This demonstrated thermal properties promise a cost-effective PCM for building thermal regulations.

4:00 PM EN07.18.04
Cell-Level Mapping of The Thermal Conductivity of Electrode Composites in Lithium-Ion Batteries

Juwei Sun and Yee Kan Koh; National University of Singapore, Singapore

In Lithium-ion batteries (LIB), the surface of the active material serves as the primary site for reactions and heat generation. Also, it is the place where the hotspots tend to emerge. Localized high temperatures within the micrometer range can trigger a series of chain reactions, leading to uncontrollable thermal runaway in batteries. Therefore, a detailed understanding of the thermal properties of LIB electrodes is of paramount importance. Previous research has used various methods, for example, laser flash and steady-state measurement, to measure the thermal properties of electrode composite or active materials. However, the previous research typically treats the thermal properties of LIB electrodes as a macroscopic characteristic, failing to provide detailed information about real electrodes. The objective of this study is to produce micrometer-scale resolution mapping for the thermal conductivities of the electrodes.

We adapted TDTR technology, which is a well-established optical pump-probe technique, to perform experiments. In TDTR, the pump laser beam heats the sample surface, and the reflected probe beam is detected to analyze the thermal response of the sample. Before conducting the experiment, we took multiple steps to ensure that the sample would yield a sufficient reflected probe signal. We utilized ion milling techniques to polish the electrode's cross-sectional surface until its Root Mean Square (RMS) roughness within a 10um x 10um area was reduced to less than 50nm. We selected graphite and lithium cobalt oxide (LCO) electrodes, both made from active material particles of approximately 20um in size for the experiment. The local measurement was first conducted under three different conditions: 1) 6um spot size laser at 18.9MHz heating frequency, 2) 3um spot size laser at 9.8MHz heating frequency, and 3) 3um spot size at 5.4MHz heating frequency. We fitted the obtained thermal response signal with a thermal model. From this, we derived an isotropic thermal conductivity for LCO, and an anisotropic thermal conductivity for graphite. Finally, we conducted scanning experiments on the electrode within a 30um x 30um area. Data was collected at 1 um intervals during the scan. The scanning results clearly indicate the thermal conductivity of each component, with distinct boundaries that align well with the SEM images.

Our study provides detailed thermal properties at high spatial resolution, enabling the calculation of the temperature distribution during battery operation and the prediction of hotspot emergency conditions. This study facilitates the development of thermal management strategies at the electrode level in LIBs, addressing the safety concerns at their root.

4:15 PM EN07.18.05
In Vivo Thermal Conductivity Measurement of Blood-Perfused Tissue Accounting for The Effect of Blood Flow

Gimin Park1, Boksoon Kwon2; Sang-Kyu Kim2 and Woocul Kim1

1Yonsei University, Korea (the Republic of); 2Samsung Advanced Institute of Technology, Korea (the Republic of)

Understanding the thermal properties of human tissue is crucial for evaluating their ability to regulate temperature, assessing the effectiveness of thermotherapy techniques, designing skin-contact medical devices, and optimizing thermal comfort in different environments. Traditional measurement methods primarily conducted on nonliving materials involve modifying the material’s geometry and placing the material in a vacuum environment. Moreover, the presence of blood flow and perfusion of tissue introduces advection effects described by Pennes’ bioheat equation, and its influence on thermal response at the skin must be considered when measuring thermal conductivity. Previous studies have often been unable to isolate the effect of blood perfusion, resulting in the quantification of effective thermal conductivity, which exhibits a strong temperature dependence due to vasomotion’s role in dissipating excess heat or conserving heat in cold conditions. In this study, we employ sinusoidal heating and transient plane source heating to subsequently measure the blood perfusion rate and thermal conductivity exclusively at the skin by controlling the thermal penetration depth. Analytical solution to the transient bioheat equation allows us to separate the influence of blood perfusion when obtaining the thermal conductivity attributed solely to conduction. Tissue temperatures ranging from 30.5°C to 35.5°C yielded tissue thermal conductivity averaged at 0.334 ± 0.035 W/m-K. This value of thermal conductivity agrees well with that of excised human epidermis (0.21 – 0.41 W/m-K) [1]. As expected, the blood perfusion rate increased with increasing tissue temperature from 0.143 ×10^2 to 3.421 ×10^3 m^2/s^3, which is typical for convective heat transfer coefficients ranging from 5 to 15 W/m^2K. By measuring the thermal conductivity of blood-perfused skin, we hope to enhance the design and performance of wearable devices, improve the efficacy of thermoregulation techniques, and advance the understanding of various skin-related disorders and conditions. The insights gained from these studies have the potential to revolutionize fields such as biomedical engineering, personalized medicine, and thermal comfort optimization, ultimately benefiting human health and well-being.

Dongwhi Choi and Youngsuk Nam; 1Korea Advanced Institute of Science and Technology, Korea (the Republic of); 2Kyung Hee University, Korea (the Republic of)

Phase change materials (PCMs) undergo a transition from solid to liquid, absorbing a substantial amount of latent heat, making them suitable for systems that efficiently store and release heat as needed. Research on PCMs is actively pursued in various fields such as energy harvesting, air conditioning, and electronic device thermal management. Paraffin has been extensively utilized in PCM research primarily due to its high specific latent heat (~230 kJ/kg) and cost-effectiveness. Nevertheless, challenges arise when paraffin is applied to systems requiring rapid thermal response, such as electronic devices, due to its low thermal conductivity of approximately 0.2 W/mK.

To address these challenges, researchers have turned to gallium-based liquid metals with an appropriate specific latent heat (80 kJ/kg) and a comparatively high thermal conductivity of approximately 40 W/mK. While gallium may possess a lower specific latent heat per unit mass compared to paraffin-based PCMs, its density exceeds that of paraffin by more than six times. As a result, the specific latent heat per unit volume increases, enabling efficient heat absorption within confined volumes. Furthermore, gallium exhibits high thermal conductivity, enabling rapid system response under conditions of fluctuating thermal load. However, gallium faces a supercooling issue, where it remains in a liquid state after absorbing heat and fails to transition back to a solid state when the temperature drops below its freezing point. In this context, resolving the supercooling problem is imperative for the successful application of gallium in PCM systems.

This study suggests a gallium-porous copper composite to mitigate gallium's supercooling issue. Deoxidized gallium and porous copper were efficiently combined to create the composite material in a low-concentration hydrochloric acid environment. The porous structure increased the surface area, and the intermetallic compound CuGa2 that formed at the interface facilitated heterogeneous nucleation, reducing the supercooling of gallium. The quantitative performance of supercooling mitigation was verified through differential scanning calorimetry and multi-cycle heating and cooling experiments.

8:30 AM • EN07.09.03
Assessing Lattice Thermal Conductivity of Topological Insulator Bi2Se3 by Temperature-Dependent Raman Spectra
Vipin K. E and Prabhallad Padhan; Indian Institute Of Technology Madras, India

Topological insulators (TIs) have emerged as a fascinating material class that exhibits unique electronic properties, making them promising candidates for various technological applications. One of the promising areas where TIs hold great potential is thermoelectricity. Unlike conventional materials, TIs possess a non-trivial band gap in their bulk states but harbor conducting surface states due to the presence of robust, spin-polarized, and topologically protected electronic states. The conducting surface states of TIs, known as topological surface states (TSS), have a linear energy-momentum dispersion relationship, which can lead to high electron mobility and improved electrical conductance. This unique electronic structure offers an advantage over conventional thermoelectric materials, where achieving both high electrical conductivity and low thermal conductivity is challenging.

The pursuit of highly efficient thermoelectric (TE) materials hinges on understanding their electrical conductivity ($\sigma$), Seebeck coefficient (S), and thermal conductivity ($\kappa_L$). Among these, thermal conductivity ($\kappa_L$) plays a pivotal role and is a critical factor in TE efficiency. This study delves into the reduction of $\kappa_L$, focusing on hexagon-shaped nanocrystals cluster of Bi$_2$Se$_3$, synthesized via the hot-injection technique employing non-toxic solvents. The nanocrystals' temperature-dependent Raman spectra were analyzed to determine the average Debye temperature ($\theta_D$) and Gruneisen parameter ($\gamma$), utilizing the bond order–length–strength correlation theory (BOLS).

At room temperature, $\kappa_L$ of the Bi$_2$Se$_3$ nanocrystals was evaluated as 1.85 Wm$^{-1}$K$^{-1}$ using $\theta_D$ and $\gamma$ obtained from BOLS theory, closer to the simulated values of 1.4 Wm$^{-1}$K$^{-1}$ in-plane and 0.4 Wm$^{-1}$K$^{-1}$ out-of-plane direction. Our theoretical studies adopting 3 phonon process demonstrate that over 54 % of in-plane cumulative $\kappa_L$ and around 12 % of out-of-plane cumulative $\kappa_L$ are contributed by the modes below 2 THz, which are dominated by the Bi atom. The ratio of in-plane cumulative $\kappa_L$ to out-of-plane cumulative $\kappa_L$ at 5 THz is ~3.58, establishing the anisotropic $\kappa_L$ of Bi$_2$Se$_3$. Further, our mean free path ($\lambda$) dependent $\kappa_L$ studies demonstrated the cumulative $\kappa_L$ in the plane is dominated by the phonons with a mean free path below ($\lambda$) ~15 nm, while along the out-of-plane directions, the phonons with an $\lambda$ of ~5 nm have strong contributions. The Bi$_2$Se$_3$ is an anisotropic system, and the cumulative thermal conductivity as a function of the $\lambda$ displays that a major contribution is arising from the shorter mean free path.

This scattering is the main cause of low lattice thermal conductivity in the investigated system. The introduction of nanostructuring-induced grain boundaries in Bi$_2$Se$_3$ obstructs long-mean-free-path phonons. Furthermore, intentional doping can also significantly reduce the phonon mean free path, effectively lowering $\kappa_L$. Anisotropic phonon scattering, facilitated by weak Van der Waals forces between quintuple layers in the out-of-plane direction, alongside acoustic-optical phonon scattering and anharmonicity, inefficient mean thermal energy transport in Bi$_2$Se$_3$, resulting in reduced $\kappa_L$.

This research demonstrates a method for determining $\kappa_L$ from temperature-dependent Raman spectra and sheds light on the potential of intentional nanostructuring and doping to optimize TE materials. These findings are instrumental in advancing the understanding of materials that enhance the TE quality factor and, consequently, the figure of merit, offering a promising avenue for future research in the realm of thermoelectrics.
Harnessing solar energy to desalinate water is a critical need in many areas of the world where water supplies are scarce, or in regions affected by natural disasters. To address this problem, we developed a novel small-scale solar-thermal energy harvesting scheme to rapidly heat water to boiling, enabling distillation, water desalination, and generation of potable water. We performed outdoor experiments demonstrating that concentrated solar power can heat water to boiling effectively and achieve desalinate water on a small scale. Using a 1.5 m dish shaped mirror to concentrate solar energy on a flask of water we achieved boiling of water within 1 hour. To accelerate the solar-thermal energy harvesting process we compare the performance of absorbing carbon-black coatings on glass flasks with uncoated flasks. We discuss the use of photonic structures that enhance thermal emission in relevant wavelength windows and describe preliminary measurements with these structures. We measured the conductivity ($\kappa$) and concentration of total dissolved solids (TDS) in the starting water solution to be 4.32 milli-S/cm and 2.2 ppt respectively and found that these decreased to 20 micro-S/cm and 10 ppm in the distillate achieved with solar-thermal energy conversion, illustrating excellent desalination. To calibrate the outdoor solar-thermal energy conversion results we performed baseline indoor water distillation experiments. We found that the decreases of conductivity and TDS are in outdoor experiments are comparable with those achieved in benchmark indoor distillation experiments. We discuss pathways for scale-up of solar-thermal energy harvesting and water desalination to larger scales. The critical thermal transport processes will be described.

The work was partially supported by Iowa State University through the ECpE FuTure Grant and the ISU Honors program.

### SYMPOSIUM EN08

Advancements in Thermoelectric Materials, Module Technology and Applications
April 23 - May 8, 2024

Symposium Organizers
Ernst Bauer, Vienna Univ of Technology
Jan-Willem Bos, University of St. Andrews
Marisol Martin-Gonzalez, Inst de Micro y Nanotecnologia
Macro-Scale Patterning for Hierarchically Designed Thinner Peltier Sheets

Sushmita Veeralingam, Jun S. Choi, Tran D. Khanh, Kampa R. Kishore, Seung B. Jung and Jong W. Kim; Sungkyunkwan University, Korea (the Republic of)

The burgeoning field of nanogenerators presents ongoing challenges in elevating performance through innovative strategies and architectures. This study addresses these challenges by synergistically combining the distinct properties of piezoelectric nanogenerators (PENG) and triboelectric nanogenerators (TENG). It harnesses the bulk polarization effect inherent in PENG and the contact electrostatic and electrostatic induction in TENG, thereby leveraging their combined strengths. Our focus is the development of a novel hybrid piezo-triboelectric nanogenerator (HPTENG), which employs a multi-layered nanofiber architecture, showing significant promise for applications in flexible electronics and electronic skins. This work introduces composite nanofibers composed of polyvinylidene fluoride (PVDF)-MoS2-MXene (PMMX), capitalizing on the superior piezoelectric effect of MoS2-PVDF and the two-dimensional structure and abundant charging sites of MXene.

PVDF-HFP exhibits remarkable properties, including excellent chemical resistance, high stability, low dielectric loss, a high dielectric constant, and biocompatibility. When electrospun, electrospinning, a widely employed nanofabrication technique, enables the production of nanofibers with superior properties at a rapid production rate. One intriguing application of electrospinning is the creation of nano yarns spun from nanofibers. However, the conventional approach employs continuous filaments, limiting the control over filament parameters. An alternative approach involves the fabrication of yarns using discrete filaments, termed "staples," enabling precise tuning of filament parameters as fiber spinning and yarn spinning occur separately. Building upon previous work, this study introduces a high-throughput yarn-spinning device capable of producing staple yarns with repeatable and consistent characteristics.

Textiles fabricated from biocompatible and biodegradable polymers, such as Polyvinylidene fluoride-co hexafluoropropylene (PVDF-HFP), hold immense promise for various biomedical applications, including scaffolds and implants. Electrospinning, a well-established nanofiber fabrication technique, allows for producing nanofibers with exceptional properties at high throughput. One intriguing application of electrospinning is the creation of nano yarns spun from nanofibers. However, the conventional approach employs continuous filaments, limiting the control over filament parameters. An alternative approach involves the fabrication of yarns using discrete filaments, termed "staples," enabling precise tuning of filament parameters as fiber spinning and yarn spinning occur separately. Building upon previous work, this study introduces a high-throughput yarn-spinning device capable of producing staple yarns with repeatable and consistent characteristics.

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Methods: Electrospinning and fiber collection are carried out using a Track electrospinning system. A potential difference is applied between the polymer tip (30% w/v PVDF-HFP in a 2:1 water-methanol mixture) and a collector plate to electrospin filaments. The resulting filaments are collected on a rotating drum, and the resulting staple yarn is cut into desired lengths. The staple yarn is then used to fabricate composite yarns with different compositions. The composite yarns are tested for their mechanical properties, such as tensile strength and stretchability, and their electrical performance, such as open-circuit voltage (Voc) and short-circuit current (Isc).

Piezoelectric Properties

Calculations, and they align with the TE properties obtained from experimental results. By harnessing the potential of machine learning, deep learning, and data mining, this endeavor holds the potential to transform the paradigm of high-performance energy harvesting materials design, ushering in a new era of sustainable and efficient energy utilization.

8:05 AM EN02/EN08.03

Artificial Intelligence Guided Thermoelectric Materials Design and Discovery

Guansheng Han, Na Lu and Yining Feng; Purdue University, United States

Materials discovery from vast repositories of Earth's resources remains a significant impediment to revolutionary technological advancements. The labor-intensive and time-consuming nature of this process hampers the exploration of novel materials. While machine learning techniques have demonstrated their potential in expediting materials discovery, the challenge lies in obtaining effective material feature representations and achieving precise predictions of material properties. This research endeavors to establish an automated framework for materials design and discovery, harnessing the power of data-driven AI models. Initially, we have developed a range of diverse material descriptors to enhance the representation and encoding of the distinctive characteristics of materials. This, in turn, leads to improved predictive performance across various molecular properties. As a baseline, we have focused on predicting thermoelectric (TE) properties of materials to demonstrate the framework's capabilities. Remarkably, our proposed framework attains an accuracy rate exceeding 90% in forecasting TE properties. Moreover, our AI models have identified promising p-type TE materials and promising n-type TE materials. To validate our predictions, we have compared them with Density-functional Theory (DFT) calculations, and they align with the TE properties obtained from experimental results. By harnessing the potential of machine learning, deep learning, and data mining, this endeavor holds the potential to transform the paradigm of high-performance energy harvesting materials design, ushering in a new era of sustainable and efficient energy utilization.

8:20 AM EN02/EN08.04

Fabrication of Polyvinylidene Fluoride-Co Hexafluoropropylene (PVDF-HFP) Staple Yarns Using Discrete Electrospun NanoFilaments and Evaluation of Their Mechanical and Piezoelectric Properties

Adasuego M. Enuka and Vincent Z. Beachley; Rowan University, United States

Textiles fabricated from biocompatible and biodegradable polymers, such as Polyvinylidene fluoride-co hexafluoropropylene (PVDF-HFP), hold immense promise for various biomedical applications, including scaffolds and implants. Electrospinning, a well-established nanofiber fabrication technique, allows for producing nanofibers with exceptional properties at high throughput. One intriguing application of electrospinning is the creation of nano yarns spun from nanofibers. However, the conventional approach employs continuous filaments, limiting the control over filament parameters. An alternative approach involves the fabrication of yarns using discrete filaments, termed "staples," enabling precise tuning of filament parameters as fiber spinning and yarn spinning occur separately. Building upon previous work, this study introduces a high-throughput yarn-spinning device capable of producing staple yarns with repeatable and consistent characteristics. By decoupling the electrospinning and yarn-spinning processes, we harness the unique properties of nanofibers and gain control over their parameters, a feat unattainable with current yarn fabrication methods. This advancement will facilitate an in-depth investigation into the impact of tunable fiber parameters on yarn mechanics. PVDF-HFP staple yarns are crafted from electrospun nanofibers with varying parameters, such as draw ratio, density, segment length, and more, and their effects on yarn mechanical properties are explored.

Methods: Electrospinning and fiber collection are carried out using a Track electrospinning system. A potential difference is applied between the polymer tip (30% w/v PVDF-HFP in a 2:1 water-methanol mixture) and a collector plate to electrospin filaments. The resulting filaments are collected on a rotating drum, and the resulting staple yarn is cut into desired lengths. The staple yarn is then used to fabricate composite yarns with different compositions. The composite yarns are tested for their mechanical properties, such as tensile strength and stretchability, and their electrical performance, such as open-circuit voltage (Voc) and short-circuit current (Isc).

Piezoelectric Properties

Closest to the device, the external forces. Our study further emphasizes the necessity of augmenting the electrical performance of PENGs and TENGs to improve energy harvesting efficiency and signal-to-noise ratio. The practicality of HPTENG was validated by adding it to various joints, including fingers, elbows, palms, and knees, effectively monitoring real-time motion during activities like bending, running, and additionally. The potential of HPTENG for human gesture monitoring. The unique material composition and straightforward fabrication strategy presented here pave the way for novel solutions in the realm of advanced energy harvesting.
Effect on Thermoelectric and Mechanical Properties of Interstitial Void Filling by Cu in ZrNiSn HH Alloy

Widely explored ZrNiSn half-Heusler (HH) alloy has an interpenetrating fcc cubic crystal structure with four vacant positions in the unit cell, where the elemental substitution at these voids by copper-rich sulfides form an important class where univalent copper is the dominant element, giving the possibility of creating hole carriers in the conductive “Cu–S” network for the generation of p-type thermoelectrics. During this presentation, recent advances in synthetic minerals and new sulphide compounds will be shown. Some peculiar structural features in connection with atomic and nanoscale order/disorder phenomena and defects engineering were carefully examined to establish rules and correlations between the crystal structures, nano-structures, electronic structures, vibrational and thermoelectric properties.

Acknowledgments

This work was financially supported by the voestalpine Stahl GmbH and Energie AG Oberösterreich Umwelt Service GmbH. The authors would like to thank Peltron GmbH Pelter-Technik for supplying thermoelectric modules free of charge.

8:45 AM EN02/EN08.07
Defects Engineering in Thermoelectric Copper-Based Sulfides Emmanuel Guilmeau; CRISMAT, France

Among the various possibilities explored by the periodic table, copper-rich sulfides represent a formidable source for the discovery of low cost and environmentally benign thermoelectric materials. Copper-rich sulfides form an important class where univalent copper is the dominant element, giving the possibility of creating hole carriers in the conductive “Cu–S” network for the generation of p-type thermoelectrics. During this presentation, recent advances in synthetic minerals and new sulphide compounds will be shown. Some peculiar structural features in connection with atomic and nanoscale order/disorder phenomena and defects engineering were carefully examined to establish rules and correlations between the crystal structures, nano-structures, electronic structures, vibrational and thermoelectric properties.

9:00 AM EN02/EN08.08
Effect on Thermoelectric and Mechanical Properties of Interstitial Void Filling by Cu in ZrNiSn HH Alloy

Effect on Thermoelectric and Mechanical Properties of Interstitial Void Filling by Cu in ZrNiSn HH Alloy

Acknowledgments

This work was financially supported by the voestalpine Stahl GmbH and Energie AG Oberösterreich Umwelt Service GmbH. The authors would like to thank Peltron GmbH Pelter-Technik for supplying thermoelectric modules free of charge.
The Importance of Electronic Relaxation Times in Complex Fermi Surfaces

This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 678763) and

Acknowledgments

Here we describe our advanced electronic Boltzmann transport simulator, ElecTra [2], together with a method we developed to obtain accurate scattering rates from ab initio calculations. We demonstrate its capabilities in a series of investigations: i) regarding the importance of including all relevant scattering mechanisms in electronic transport computation [3]; ii) regarding the possibility to obtain ultra-high PF in low bandgap materials with highly asymmetric transport properties between the conduction and valence bands [4, 5]; iii) regarding the influence of the shape of the electronic structure with its elongated features and high band anisotropy on the PF, where we show that 2-3x PF variations are observed based on the band shape complexities alone; iv) regarding the possibility of reliably computing transport properties of complex band materials with low symmetry and large unit cells in realistic time scales entirely from first principles.

References


Acknowledgments

This work has received funding from the European Research Council (ERC) under the following 2020 research and innovation programme (grant agreement No 678763) and from the UK Research and Innovation fund (project reference EP/R02346X/1).

11:00 AM EN08.01.02

The Importance of Electronic Relaxation Times in Complex Fermi Surfaces

Open Andreas Grimenes1, Ole Martin Løvkv2 and Kristian Berland3; 1Norwegian University of Life Sciences, Norway; 2SINTEF Industry, Norway

The difficult task of optimizing the thermoelectric figure of merit (ZT) has often been approached by reducing lattice thermal conductivity, such as by nanostructuring or alloying. This strategy has led far, but to engineer even better materials we need to include other strategies. Another popular approach, especially in computational studies, is to engineer band structures that give more favorable electron transport properties. Generally, electron transport is characterized by the transport distribution, that is, the density of states (DOS), where each state is weighted by the square of its group velocity times the relaxation time of that state. A rapidly increasing transport distribution next to the band gap tends to give a higher ZT. By aligning bands and valleys, the electronic structure can achieve a higher density of states without a reduction in group velocity. In the commonly used constant relaxation time approximation (CTRA) this band alignment will always be favorable for ZT. With more accurate modeling of the scattering rates, we show that moving beyond CTRA is vital to get accurate predictions of ZT. The alignment of multiple bands or valleys will generally lead to more electron scattering and lower relaxation times. This effect is especially prominent for materials with complex "extended" Fermi surfaces that result in a large scattering space for electrons.

We use first principle methods to investigate numerous complex semiconductors with unusual band structures and give extra attention to the specific case of the full-Heusler CaK2Sb. This material has an exotically Fermi surface with extended 2D-like features. We also predict a very low predicted lattice thermal conductivity with the Temperature Dependent Effective Potential (TDEP) method. This leads to a very high predicted ZT under CTRA. With more accurate modeling of the electric transport properties with scattering rates modeled in AMSET the expected ZT is reduced, revealing the shortcomings of the constant relaxation time approximation and the necessity to move beyond it. We also show this trend in several other materials with complex Fermi surfaces.

Finally, we present a counterexample, ZrNiSn. The three-fold degenerate conduction band minimum is not promising under CTRA. However, the simple shape of the Fermi surface and large k-space distance between its Fermi pockets results in relaxation times much longer than the 10 fs often used in CTRA. This increases the n-type ZT of ZrNiSn significantly. We conclude that while complex Fermi surfaces indeed can provide very good electronic transport properties, it is essential to include estimations for scattering rates in such materials. These results can help aid the design of future thermoelectric materials with superior properties.

11:15 AM EN08.01.03

High-Throughput Thermoelectric Materials Screening by Novel Deep Convolutional Neural Network with Fused Orbital Field Matrix and Composition Descriptors

Ming Hu; University of South Carolina, United States

Thermoelectric materials assist in generating temperature or converting heat into reusable electricity. Thermoelectric materials are also widely used in real-world applications, such as refrigerators and cooling electronics. However, most popular and known thermoelectric materials to date were proposed and found by intuition, mostly through experiments. Unfortunately, it is extremely time and resource consuming to synthesize and measure the thermoelectric properties through trial and error experiments. Here, we develop a convolutional neural network (CNN) classification model that utilizes the fused orbital field matrix (OFM) and composition descriptors to screen a large pool of materials to discover new thermoelectric candidates with power factor higher than 10 μW/cmK². The model used a few thousand data generated by density functional theory (DFT) coupled with AMSET, a package for calculating electronic transport properties that does not assume constant relaxation time for electrons, thus ensuring more reliable electronic transport properties predictions. The classification model was also compared to traditional machine learning algorithms, such as light gradient boosting and random forest. With the classification model we screened ≈35,000 structures with non-zero band gap from the Open Quantum Materials Database (OQMD). We identified lots of potential high performance thermoelectric materials with ZT > 1 across wide temperature range for both n- and p-type doping with different doping concentrations, including quaternary Heuslers, half-Heuslers, and more material families. Insight into the correlation between high power factor and some representative descriptors was also gained by feature importance analysis and maximal information coefficient, which provides new simple routes for fast screening promising thermoelectrics from large-scale material pool in the future.

11:30 AM EN08.01.04

Composition Engineering of Thermoelectric Performance of High-Entropy Ge-Te Based Alloys by First Principles

Han Meng, Masato Ohashi and Junichiro Shiomi; The University of Tokyo, Japan

The thermoelectric effect offers a promising pathway for power generation through direct conversion of heat into electricity, however, it is mainly limited by the performance of thermoelectric materials evaluated by figure of merit ZT=S²σκ, where S, σ, and κ are Seebeck coefficient, electrical conductivity, and total thermal conductivity, respectively. To pursue good thermoelectric performance, various successful strategies have been proposed to enhance electrical transport properties through the creation of ordered band structure and reduce lattice thermal conductivity by introducing disordered atomic arrangement, following the phonon-glass electron-crystal concept. However, further improvement in thermoelectric performance requires the
decoupling of electrical and thermal transport properties and their simultaneous optimization.

High-entropy material, where a stabilized structure coexists with disordered atomic arrangement, hold tremendous potential for enhancing thermoelectric performance. This potential arises from the ability to maintain long-range order in atomic arrangement to support efficient electrical transport, while simultaneously introducing short-range disorder through lattice distortion, which effectively scatter phonons and lead to low thermal conductivity. The GeTe that stabilizes as a rhombohedral lattice at room temperature by distorting high-temperature cubic structure, has been demonstrated to exhibit high thermoelectric performance. Most recently, a significant improvement in ZT, reaching 2.7 at 750 K, has been achieved in high-entropy GeTe-based alloys. This accomplishment was realized in several sample with specific composition by increasing the entropy, which enhanced crystal symmetry to promote delocalization of electron distribution and concurrently localize phonons to effectively hinder the propagation of transverse phonons. However, the high-entropy concept also offers a means to create crystals with an extended chemical composition range, providing ample room for optimizing electronic properties by modulating phase composition and band structure across a wide spectrum of chemical composition.

In this study, we take a significant stride towards engineering the composition for thermoelectric performance of high-entropy GeTe-based alloys. To predict the formation energy, we employed cluster expansion to construct a machine learning model, which was trained and validated using datasets generated from first-principles calculations. Through the Monte Carlo simulation, the configurations with low formation energy were suggested by sampling the structure for various composition, incorporating silver, lead, and antimony atoms as solutes. We designed seven distinct composition-changing paths that involved the alloying of one element, two elements, and all elements, allowing the thorough investigation on the impact of alloying each individual element component as well as their collective influence on ZT. For each composition, the average ZT was calculated from five possible configurations by semi-classical Boltzmann transport theory within relaxation time approximation. The analysis of electrical transport properties through electronic band structure and charge distribution, along with the examination of thermal conductivity via phonon dispersion relations and phonon properties, unveiled the underlying mechanism responsible for the compositional dependence of ZT. This study not only demonstrates the potential for optimizing thermoelectric performance of GeTe-based alloys, but also encourages further exploration of high-entropy alloys in the future.

11:45 AM EN08.01.05
Discovery of Multi-Anion Antiperovskite X$_2$NFSn$_2$ (X = Ca, Sr) as Promising Thermoelectric Materials by Computational Screening
Dan Han$^{1,2,3}$, Bonan Zhu$^2$, Zenghua Cai$^2$, Kiwon B. Spooner$^{2,3}$, Stefan S. Rudel$^1$, Thomas Bein$^1$, David O. Scanlon$^{2,3}$ and Hubert Ebert$^1$; 1University of Munich (LMU), Germany; 2University College London, United Kingdom; 3University of Birmingham, United Kingdom; 4Suzhou University of Science and Technology, China

The thermoelectric performance of existing perovskites lags far behind that of state-of-the-art thermoelectric materials such as SnSe$_2$[1,2]. Despite halide perovskites showing promising thermoelectric properties, namely, high Seebeck coefficients and ultralow thermal conductivities, their thermoelectric performance is significantly restricted by low electrical conductivities. Here, we explore new multi-anion antiperovskites X$_2$NFSn$_2$ (X = Ca, Sr and Ba) via B-site anion-mutation in antiperovskite and global structure searches, and demonstrate their phase stability by first-principles calculations. Ca$_2$NFSn$_2$ and Sr$_2$NFSn$_2$ exhibit decent Seebeck coefficients and ultralow lattice thermal conductivities (< 1 W m$^{-1}$ K$^{-1}$). Notably, Ca$_2$NFSn$_2$ and Sr$_2$NFSn$_2$ show remarkably larger electrical conductivities compared to the halide perovskite CaSn$_3$. The combined superior electrical and thermal properties of Ca$_2$NFSn$_2$ and Sr$_2$NFSn$_2$ lead to high thermoelectric figure of merit ZT ~ 1.9 and ~ 2.3 at high temperatures. Our exploration of multi-anion antiperovskites X$_2$NFSn$_2$ (X = Ca, Sr) realizes the “phonon-glass, electron-crystal” concept within the antiperovskite structure.[1]


SESSION EN08.02: Novel Materials and Half-Heusler Alloys
Session Chairs: Ran He and Paz Vaqueiro
Tuesday Afternoon, April 23, 2024
Room 336, Level 3, Summit

1:30 PM *EN08.02.01
Engineering Electronic Properties of Thermoelectric Semiconductors
Jeff Snyder; Northwestern University, United States

Engineering Electronic Properties of Thermoelectric Semiconductors

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Thermoelectric semiconductors often have complex electronic properties yet they can be modeled with a simple effective mass model. Good thermoelectric materials require a high weighted mobility [1] which serves as the electronic component to the thermoelectric quality factor [2] that determines peak $zT$. Often complex band structures with multi-valley Fermi surfaces are associated with high weighted mobility. This complexity arises from orbital chemistry as well as structure. Band convergence combined with the physics of avoided crossings can also be used to explain the band structures and provide strategies for band engineering Half Heusler materials [6].

Many thermoelectric materials such as Bi$_2$Te$_3$ are topological insulators (TI). The correlation can be understood in that the band inversion that causes TI can lead to band warping that leads to Fermi surface rather than ellipsoidal pockets leading to a density of states like 1D or 2D low dimensional materials. By engineering the orbital chemistry complex behavior and unusual properties can be devised even in 3D materials.


2:00 PM EN08.02.02
Zn$_2$Ge$_4$Sb$_5$ – A New Aliovalent Half-Heusler Alloy with Intrinsic Low Thermal Conductivity
Blair F. Kennedy; 1 and Jan-Willem Bos$^2$; 1 Heriot-Watt University, United Kingdom;
$^2$University of St Andrews, United Kingdom

Half Heusler (HH) alloys are leading contenders for thermoelectric power generation and cooling. Traditional XYZ HH materials are characterised by large electronic power factors, $S^2n$, and are limited by high lattice thermal conductivity, $\kappa_{lat}$ which limits the achievable figure of merit, $zT$.[1]

Recently a new class of HH materials has emerged that uses mixtures of aliovalent elements. The archetypal example is the TiFe$_2$N$_8$Sb family, which is a mixture of 17 electron TiFeSb and 19 electron TiN$_8$Sb. Hence, an equal mixture of these ternary systems achieves the required average 18 valence electron count required for semiconducting behaviour. In comparison to regular XYZ materials, these complex compositions are characterized by low $\kappa_{lat}$ and modest $S^2n$, leading to $zT$ approaching unity.[2] This approach is general, and can also be applied to the X and Z

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sites, leading to work on X_{0.5}Y_{0.5}Z and XYZ', Z'[0.5] compositions by multiple groups.  
As part of this recent new direction of research, this contribution is focused on the aliovalent Zn_{1-x}Ti_xNiSb system, which links 17 electron ZnNiSb with 19 electron TiNiSb. The x = 0.5 composition has exactly 18 valence electrons. Samples were prepared between 0.40 ≤ x ≤ 0.65; with x ≤ 0.4 not accessible under the used conditions, whilst Ti-rich samples can likely be prepared over the full range (to x = 1). This difference occurs because TiNiSb forms with Ti vacancies and is close to an 18-electron system, hence removing the electronic driving force for insolvency.

In terms of thermoelectric properties, the samples are characterized by very low κ_{lat}=0.40 K/W m^{-1}K^{-1}, comparable for all investigated samples. The electrical response suggests a small bandgap, E_F ≈ 0.4 eV, with evidence for bipolar transport. Varying the composition away from x = 0.5 leads to a transition to p-type (x < 0.5) or n-type (x > 0.5) degenerate semiconducting behaviour. The best observed performance is zT = 0.18 for p-type Zn_{0.5}Ti_{0.5}NiSb and zT = 0.33 for n-type Zn_{0.5}Ti_{0.5}NiSb.

The origin for the low κ_{lat} in these materials is not fully resolved. Typically, mass and strain disorder are the main drivers of phonon scattering. However, for the aliovalent HH materials, atomic mass and size differences are typically small, whilst the velocity of sound is only about 10-20% reduced compared to the XYZ materials. We have used synchrotron X-ray scattering and pair distribution function analysis to probe the local structure of Zn_{1-x}Ti_xNiSb. This confirms that there is not a large source of local lattice strain, e.g. the Ti-Ni and Zn-Ni distances are comparable. Hence, the structure does not substantially deviate from the average unit cell obtained from diffraction. This suggests that differences in bond strength (bond disorder) may play a crucial role in the low κ_{lat} in the aliovalent HH materials.

References:

2:15 PM EN08.02.03 Thermoelectric Compounds TzSb, T = Ti to Ni
Peter F. Rogl1, Raimund Podloucký1, Gerda Rogl1 and Ernst Bauer2; 1Univ Wien, Austria; 2TU Wien, Austria
We present results of a combined experimental and first-principles study on compounds TzSb (T=Ti to Ni). Physical properties i.e. electrical resistivity (4.2 - 800 K), Seebeck coefficient (300 - 800 K), specific heat (2 - 110 K), Vickers hardness and elastic moduli (RT) have been defined for the above mentioned polycrystalline single-phase materials. From X-ray single crystal and Rietveld analyses all these phases, of which ZnSb and Cr_{1-x}Sb are novel representatives, were found to crystallize with the ordered MnaAlGe-type (space group P4/mmm), whereas NiZnSb is a half Heusler phase. The thermal stability has been investigated by differential thermal analysis. For the polycrystalline compounds TzSb (relative densities >90%) the electrical resistivity is gradually changing from typical metallic behaviour (TiZnSb) to semiconductor-like features with resistivities decreasing with rising temperature (T>V, Cr). Specific heat curves C_p vs T and C_p/T vs T^2 of TiZnSb and CrZnSb conform with a simple metal behaviour revealing Sommerfeld coefficients of 6.4 (1) mJ/molK^2 and 12.4 (2) mJ/molK^2 and low-temperature Debye-temperatures of 273(5) K and 245(5) K, respectively.

Rather low Seebeck coefficients (S<30 µV/K), power factors (pf<0.05mW/mK^2) and an estimated thermal conductivity of 3-6 mW/cmK, yield low thermoelectric figures of merit consistent with the rather metallic behavior of the materials. It should be noted that TiZnSb and VZnSb reveal negative Seebeck values with shallow minima at about 500 K, whereas CrZnSb exhibits a positive Seebeck coefficient which gradually tends towards zero at 800 K.

Indentation hardness and elastic moduli of TZnSb were extracted employing the accelerated mechanical property mapping (XPM) mode and were found to be within 5.5±1<HV<6±1 GPa and P<100±1 Gpa for Ti-Ti, V, but somewhat lower E=80±10 GPa for CrZnSb. The Poisson ratio in all cases was v=0.24 (taken from DFT calculations).

A detailed analysis of the structure types TzSb adopted by the 3d transition elements clearly reveals that electropositive elements T=Ti,V,Cr,Mn,Fe crystallize with the tetragonal MnAlGe-type but with rising electronegativity T=Fe,Co,Ni,Fe crystalize with the tetragonal MnaAlGe-type with a cubic half-Heusler superstructure or to a (2a(2a=2a) superstructure of it. The case of Fe with three modifications constitutes the border range.

A variety of physical properties are derived from first principles such as structural and magnetic structural stabilities, charge transfer and atomic size, elastic properties, electronic structure (density of states, band structure), electronic transport properties (Seebeck coefficient and resistivity) within Boltzmann's transport theory. All the results are obtained for fully relaxed structural parameters. Concerning magnetic ordering the in-plane antiferromagnetic ordering of T-magnetic moments in the tetragonal MnaAlGe-type is dominant. The influence of T- vacancies for VZnSb and Cr_{1-x}ZnSb are investigated and the results emphasize the role of such vacancies.

2:30 PM EN08.02.04 Mapping The Configuration Space of Intrinsic Properties and Dopability of Half-Heusler Compounds
Angela Pak1, Kamil Ciesielski2, Eric Toberer3 and Elif Ertekten3; 1University of Illinois at Urbana-Champaign, United States; 2Colorado School of Mines, United States; 3University of Illinois at Urbana-Champaign, United States
In this work, we utilize computational approaches to characterize the half-Heusler phase half-space in order to identify patterns in how properties relevant to thermoelectric (TE) materials vary with chemistry. Identifying novel TE materials is a challenge due to the unique, and typically disparate, set of intrinsic properties required (thermal and electronic conductivity) together with the need to access high p-type or n-type carrier concentrations. Although half-Heuslers have long been known as candidate TE materials, the hundreds of compositions that have been experimentally realized represent a small proportion of the possible chemistries. Of these possible chemistries, we focus on the 1,126 that are expected to be semiconductors based on the “18 valence electron rule”. In addition to fundamental understanding, design rules that link chemistry to indicators of TE performance are critical for this purpose, band edge density of states, band edge degeneracy, and thermal conductivity are useful for accelerated materials discovery. Towards identifying these design rules, we evaluate candidate half-Heusler transport properties using first-principles simulations and transport-empirical models. This approach utilizes a filtering scheme that successively eliminates compounds based on their electronic structure, TE performance, stability, dopability, and transport properties. The analysis yields trends across chemical phase space. For instance, Rh and V-containing chemistries consistently have strong n-type TE performance, Ni and Sb-containing chemistries are consistently strong p-type semiconductor perform, and Ta, or W-containing chemistries are good for both p and n-type performance. Furthermore, good n-type TE is found to arise from chemistries exhibiting high carrier mobility as a result of low band mass, while for p-type performance a high band degeneracy at the valence band edge further enhances performance. Chemistries that exhibit good TE performance for both n and p-type are found to have comparatively low thermal conductivities relative to what is typical for half-Heuslers. This presentation will focus on the key results of the computational analysis and a comparison to the experimental, the features of half-Heusler compounds that make them particularly suitable for TE applications, and ongoing work in stochastic assessment of trends using machine learning.

2:45 PM EN08.02.05 Effect of Magnetic Entropy in The Thermoelectric Properties of Fe-Doped Fe2VAl Full-Heusler
Tarachand Tarachand1, Naohito Tsujii1, Takao Mori1,2, Fabian Garmroudi3 and Ernst Bauer3; 1Institut für Materialwissenschaften, Technische Universität Wien, Austria
Spin entropy is involved in the transport of heat/charge carriers in magnetic materials, and can provide new opportunities to improve the conversion efficiency of thermoelectric materials over that of the conventional case [1-3]. Here, we have explored the effect of magnetic entropy on thermoelectric properties of well-characterized Fe-doped full-Heusler, Fe_{2+y}VAl_{1-x}, with x ≤ 0.1. These samples are prepared by arc melting, spark plasma sintering and annealing, producing high-density crystalline products. The low-temperature magneto-thermoelectric measurement shows exotic results, including a significantly high power factor near 300 K.

The itinerant weak ferromagnetic behavior of studied samples is confirmed from the magnetoization. A systematic increase in magnetic transition temperature (T_C, 40 K to 223 K) and saturation magnetization (M_s, 0.13 to 0.41µB/Fe) with increasing Fe doping (x = 0.0 to 0.1) is observed. Applying a magnetic field causes a clear suppression in the magnitude of thermopower (S) and T/S (entropy term) with a negative magnetoresistance near the T_C for all the samples, demonstrating a clear effect of spin fluctuation [2]. The spin fluctuation leads to an enhancement in S of ~34% than diffusion thermopower and hence a whopping enhancement in thermoelectric power factor of 18% for x=0.1 at the TC. The temperature-dependent behavior of S ruled out the contribution of magnon drag. Interestingly, Fe doping can shift the T_C towards room temperature and lead to a spin fluctuations induced enhancement in the S, but it also increases the overall carrier density and hence deteriorates the magnitude of S. Multiparabolic band model fitting reveals the formation of additional spin states with large effective mass near the Fermi level, which can be eliminated/suppressed by applying the magnetic field. Callaway model fitting of thermal conductivity reveals Fe doping increases the number of point defects, causing a significant reduction in lattice thermal conductivity. This study demonstrates the role of spin fluctuation in enhancing the thermopower/ thermoelectric performance of Fe-doped Fe2VAl and opens a vista for the strategy's applicability for various thermoelectric materials.
Beyond Bismuth Telluride: Magnesium-Based Compounds Redefine Thermoelectric Excellence

An innovative technique has been developed to combine two different layered materials, bismuth antimony telluride (BiSbTe) and tungsten diselenide (WSe2), which are well-known for their validate the existence of WSe2 and Te as heterogeneous phases. The sharp XRD peaks observed indicate strong crystallinity and evidence that the crystals are grown in a highly c-oriented resulting in hetero-nanocomposite thin films. Various characterization techniques are employed to determine thermoelectric properties. Both x-ray diffraction (XRD) and Raman spectroscopy here, to break the trade-off, we develop GeTe/Mg3Sb2-based TEGs with minimal electrical contact resistance and total thermal resistances. Our TEG allows for simultaneous boost in the efficiency and the output power (10.1% and 1.94 W/cm2), demonstrating outstanding room temperature thermoelectric performance. In addition to electrical characteristics, the specimens have a low electronic thermal conductivity, ke. The overall outcome is a significant increase in the power factor which is computed up to 156 cm⁻¹ K⁻² demonstrating outstanding room temperature thermoelectric performance. In addition to electrical characteristics, the specimens have a low electronic thermal conductivity, ke. The calculated room temperature ke values are 0.10 W m⁻¹ K⁻¹ and 0.87 W m⁻¹ K⁻¹ for the samples grown at 573 K and 723 K, respectively. Additionally, a qualitative measurement of lattice thermal conductivity was conducted through Raman spectroscopy for different lattice power conditions, providing enough room for the highly improved figure of merit value. The enhanced thermoelectric transport characteristics of the periodically encapsulated WSe2 in the BiSbTe matrix place it among the best thermoelectric materials with excellent performance for thermoelectric conversion, such as solid-state refrigeration and power generation.

References


Acknowledgments

This work was supported by the Japan Science and Technology Agency (JST), MIRAI program grant (JPMJMI19A1).

SESSION EN08.03: Materials for Thermoelectric Modules
Session Chair: Jeff Snyder
Tuesday Afternoon, April 23, 2024
Room 336, Level 3, Summit

3:30 PM EN08.03.01
Beyond Bismuth Telluride: Magnesium-Based Compounds Redefine Thermoelectric Excellence

Pingjun Ying, Heiko Reith, Cornelius Nielsch and Ran He; Leibniz-Institut für Festkörper- und Werkstoffforschung, Germany

Thermoelectric (TE) technology converts heat directly into electricity, and is a promising source of clean electricity. Commercial TE modules are based on Bi2Te3 compounds because of their unrivalled TE properties at low-grade heat-related temperatures (<550 K). However, the scarcity of elemental Te severely limits the applicability of these modules. Here, we present the performance of TE modules assembled from Te-free compounds, including p-type MgAgSb and n-type Mg3(Sh,Bi,Bo)2, using a simple, versatile and therefore scaleable processing route. We demonstrate module-level conversion efficiencies of 3% and 8.5% for temperature differences of 75 K and 260 K, respectively, as well as maximum cooling of 72 K when used as a cooler. These principles of proof will pave the way for robust, high-performance and sustainable solid-state power generation and cooling to replace the highly rare and toxic Bi2Te3.

4:00 PM EN08.03.02
Simultaneous Enhancement of Efficiency and Output Power in GeTe/Mg3Sb2-Based Thermoelectric Generator
Tsutomu Kanno; Panasonic Holdings Corporation, Japan

Recently, there have emerged many reports on thermoelectric generators (TEGs), claiming record-breaking efficiency values. From a viewpoint of practical applications, a problem is the trade-off between the efficiency and the output power in the presence of electrical contact resistance. Thus, high efficiency does not necessarily lead to high cost-performance (W/S).

Here, to break the trade-off, we develop GeTe/Mg3Sb2-based TEGs with minimal electrical contact resistance and total thermal resistances. Our TEG allows for simultaneous boost in the efficiency and the output power (10.1% and 1.94 W/cm²), owing to excellent material performance and high input heat flow [1]. We also discuss a simple and reliable protocol to avoid errors in efficiency measurement [2].

References


4:30 PM EN08.03.03
Implication of Alloying The Anionic Framework in Mg3Sb2 for p-Type Zintl Thermoelectrics
Nagendra S. Chauhan and Takao Mori; NIMS, Japan, Japan

Solid solutions of n-type Mg3Sb2 has garnered growing attention due to its remarkable thermoelectric potential for harnessing low grade waste heat. However, achieving high performing p-type conduction around room temperature has remained challenging, fundamentally due to greater degeneracy in conduction band relatively to the valence band. As a Zintl compound, β-Mg3Sb2 crystal structure constitutes of an anionic framework of double layer [Mg3Sb2]2⁻ wherein Mg2⁺ cations are located between these layers. In this work, we present the implication of (Bi, Sn, Ge, Te) alloying at the anionic framework of Mg3Sb2 solid solutions to favorably tune the p-type conduction for attaining higher power factors by band engineering. Altering the anionic framework through alloying allowed for the electronic structure to enhance the valley degeneracy at the top of valence bands. Simultaneously, the prospects of enhancing phonon scattering by the distorted lattice, point defects, and nano-precipitates was examined for attaining lower lattice thermal conductivity at near room temperature. The alloyed p-type Mg(3Sb,Bi,Ge,Sn,Te)2 with its tailored properties, shows promising potential as an economical alternative to α-MgAgSb, thereby facilitating the practical realization of Mg3Sb2-based thermoelectric power generators for harnessing low-grade heat.

4:45 PM EN08.03.04
Highly Improved Thermoelectric Performance in Periodically Ablated BiSbTe: WSe2 Nanostructured Films
Karan Giri, Yan-Lin Wang, Ling-Chun Chao, Chuan-Wen Wang, Hung-Shuo Chang, Wen-Chih Hsieh and Chun-Hua Chen; National Yang Ming Chiao Tung University, Taiwan

An innovative technique has been developed to combine two different layered materials, bismuth antimony telluride (BiSbTe) and tungsten diselenide (WSe2), which are well-known for their great efficacy in waste heat recovery and extremely low thermal conductivity, respectively. To enhance the thermoelectric properties even more, WSe2 as a secondary target is encapsulated periodically in the primary target BiSbTe using a pulse laser deposition technique. The WSe2 for the first time, is co-ablated with the BiSbTe at four distinct deposition temperatures, resulting in hetero-nanocomposite thin films. Various characterization techniques are employed to determine thermoelectric properties. Both x-ray diffraction (XRD) and Raman spectroscopy validate the existence of WSe2 and Te as heterogeneous phases. The sharp XRD peaks observed indicate strong crystallinity and evidence that the crystals are grown in a highly c-oriented manner. The electrical transport properties are greatly improved due to the optimized hole concentration, resulting in significantly high electrical conductivity in hundreds to thousands of S cm⁻¹ for the samples grown at 573 K and 723 K, respectively. Furthermore, the room temperature and temperature-dependent Seebeck coefficient measurements exhibit highly optimized values, providing evidence of a satisfactory trade-off between the thermoelectric parameters. The overall outcome is a significant increase in the power factor which is computed up to 156 μW cm⁻¹ K⁻² demonstrating outstanding room temperature thermoelectric performance. In addition to electrical characteristics, the specimens have a low electronic thermal conductivity, ke. The calculated room temperature ke values are 0.10 W m⁻¹ K⁻¹ and 0.87 W m⁻¹ K⁻¹ for the samples grown at 573 K and 723 K, respectively. Additionally, a qualitative measurement of lattice thermal conductivity was conducted through Raman spectroscopy for different lattice power conditions, providing enough room for the highly improved figure of merit value. The enhanced thermoelectric transport characteristics of the periodically encapsulated WSe2 in the BiSbTe matrix place it among the best thermoelectric materials with excellent performance for thermoelectric conversion, such as solid-state refrigeration and power generation.

SESSION EN08.04: Thermal Transport and Phonon Dynamics
Session Chairs: Eleonora Isotta and Lilia Woods
Wednesday Morning, April 24, 2024
Room 336, Level 3, Summit
The effective thermal conductivity (TC) of a material is determined by various microstructural factors. Different phases in a material often have distinct thermal conductivities and their geometrical configurations dictate the thermal path. In addition, the thermal resistance of the crystalline surface disturbs the thermal transport, while it can be enhanced by the crystalline surface coated by a high conductive material. Due to these various and complicated factors, investigations for effective TCs within polycrystalline microstructures have been limited to the controlled microstructures under selected TC regimes. In this study, we use the numerical method to estimate effective TCs within complex multi-phase systems, which are validated using experimental measurements. For simulations, our comprehensive mesoscale model is used to investigate microstructure-aware effective TC variations within porous nanostructured media. Our code includes features beyond the state-of-the-art in Monte Carlo simulations, which allow for drastic computational savings of at least an order of magnitude, making large scale simulations feasible. We have developed a model for the abatement of the utility of the pores of the solid medium, whose interaction with the solid is computed in a self-consistent manner by solving the Poisson equation. This provides the charge exchange and band variations that the solid thermoelectric material experiences. Once this is achieved, the Monte Carlo simulator provides the thermoelectric performance.

We show that it is possible to achieve very high power factor improvements using this solid/liquid hybrid material structure. This happens in two ways: 1) Appropriate choice of an electrolyte can cause favourable band bending in the solid material, resulting in increased carrier density and conductivity, at the levels which optimize the power factor. 2) Rather than relying on intentional doping, we enhance charge density within the material domain by the use of the electrolytes into the pores. This avoids the strong ionized impurity scattering associated with the doping typically required, since now this is achieved electrostatically.

Finally, the simulator we present goes beyond this system, and can be generally used to enable the understanding of transport in highly disordered nanostructured TE materials in a very effective and efficient way.

Acknowledgements:

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 863222 (UncorrelaTEd).

References:


9:15 AM EN08.04.04
Thermal Conduction Pathways within Complex Polycrystalline Microstructures
Younggil Song, Nick C. Du, Dong-Xia Qu and Tae Wook Heo; Lawrence Livermore National Laboratory, United States

The effective thermal conductivity (TC) of a material is determined by various microstructural factors. Different phases in a material often have distinct thermal conductivities and their geometrical configurations dictate the thermal pathway. In addition, the thermal resistance of the crystalline surface disturbs the thermal transport, while it can be enhanced by the crystalline surface coated by a high conductive material. Due to these various and complicated factors, investigations for effective TCs within polycrystalline microstructures have been limited to the controlled microstructures under selected TC regimes. In this study, we use the numerical method to estimate effective TCs within complex multi-phase systems, which are validated using experimental measurements. For simulations, our comprehensive mesoscale model is used to investigate microstructure-aware effective TC variations within porous materials. The model can compute effective TC within realistic digital microstructures with diffuse interfaces using the FTT method, and the simulation results show quantitative agreement with the experiments [1].

In order to characterize the TC behaviors for porous microstructures, we carried out simulations with wide TC ranges of both the gas and the solid phases. The simulations show two different regimes for the TC variations due to (i) the porosity of a microstructure and (ii) the TC difference between the two phases. We suggest the semi-analytical model by introducing structure and intensification factors to capture the effective TC variations [2]. Additionally, we simulated the effective TCs for a ternary system (Fe, Fe3O4, and Air) within porous microstructures, which show reasonable agreement with experiments. Moreover, our simulation method can be extended to evaluate the effective TCs by varying additives and their topological features. We expect our combined experimental, analytical, and numerical approach can shed light on how the effective TC of a complex microstructure can be tailored, allowing for better designing materials microstructures for improved thermal conductivities under the wide range of operation conditions.

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


9:30 AM EN08.04.05
From Rattling to Incipient Ionic Conductivity: Neutron Scattering Studies of Tetrahedrite
Paz Vaquero, Sebastian Long, Shriparna Mukherjee, David Voneshen and Anthony V. Powell; University of Reading, United Kingdom; ISIS Pulsed Neutron and Muon Source, Rutherford Appleton Laboratory, United Kingdom

The thermoelectric performance of tetrahedrites, which are minerals composed predominantly of environmentally-friendly and abundant copper and sulfur, is currently attracting considerable interest. Tetrahedrites, which are p-type materials with low lattice thermal conductivities, crystallise in a collapsed sodalite structure in which corner-sharing CuS4 tetrahedra form cages. Each cage contains an octahedral cluster formed by six trigonal-planar copper cations.

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We have exploited a range of neutron scattering techniques to investigate the origin of low thermal conductivity in tetrahedrite, Cu₁₂Sb₄S₁₃, which has been previously attributed to the rattling vibrations of the trigonal-planar copper ions and has also been linked to a phonon instability arising from a low-temperature phase transition. Analysis of neutron and synchrotron X-ray diffraction data collected on tetrahedrite shows that copper rattling is a direct consequence of a tetragonal-to-cubic phase transition at 90 K, which results in a sharp increase, by approximately 200%, of the atomic displacement parameters of the trigonal-planar copper cations. This phase transition occurs because of the orbital degeneracy of the highest occupied 3d cluster orbitals of the copper clusters found inside the sodalite cages. In the high-temperature cubic phase, the trigonal-planar copper cations form regular octahedral Cu₃⁺ clusters, which are electronically degenerate. Below 90 K, tetrahedrite contains pentameric Cu₅⁺⁺ clusters. The Jahn-Teller electronic instability which leads to the formation of “molecular-like” Cu₇⁺ clusters, suppresses copper rattling vibrations due to the strengthening of direct copper-copper interactions.

At temperatures above 200 K, quasielastic neutron scattering (QENS) measurements on tetrahedrite, Cu₁₂Sb₄S₁₃, and copper-rich tetrahedrite, Cu₁₄Sb₁₃S₁₃, combined with molecular dynamics simulations, reveal that copper ion diffusion occurs. However, although the copper ions are mobile between 200 and 400 K, they are largely trapped inside the sodalite cages. Analysis of inelastic neutron scattering (INS) data reveals the presence of a low-energy optical mode at 3-4 meV, which can be attributed to the intra-cage diffusion of the trigonal-planar copper ions. This low-energy optical mode, which softens on cooling revealing strong anharmonicity, is capable of strongly scattering the heat-carrying acoustic phonons, and hence lowers the lattice thermal conductivity.

Recent advancements in the field of thermoelectric materials have highlighted the substantial benefits of employing 3D interconnected nanowire scaffoldings. These scaffoldings have demonstrated a significant enhancement in thermoelectric efficiency when compared to 1D nanowires and films grown under similar electrodeposition conditions. A key contributing factor to this improvement is the marked reduction in thermal conductivity (κ) observed in Bi₂Te₃ 3D nanowire networks, while concurrently preserving high electrical conductivity.

Employing a comprehensive approach, we have conducted an in-depth analysis of these structures, employing the Gauß and Krumhansl Equation through a Finite Element methodology, coupled with ab initio calculations for the transport parameters from the Kinetic Collective Model (KCM). Our findings have revealed that the laplacian (viscous) term in the Gauß and Krumhansl Equation is chiefly responsible for the observed reduction in heat flux within the interconnections. Specifically, the hydrodynamic nature of heat within these interconnected regions has led to a remarkable decrease in the thermal conductivity, as compared to that of the individual nanowires lacking such interconnectednesss.

Through this investigation, we shed light on the critical influence of hydrodynamic effects on heat transport in intricate nanowire networks, offering valuable insights for the development of more efficient thermoelectric materials.

10:00 AM BREAK

SESSION EN08.05: Computational Guided Materials and Defect Engineering
Session Chairs: Johannes de Boor and Neophytos Neophytou
Wednesday Morning, April 24, 2024
Room 336, Level 3, Summit

Advances and Challenges in Computation-Guided Design and Discovery of Thermoelectric Materials -- from Direct Physical Modeling to Language Models Elif Ertekin; University of Illinois at Urbana-Champaign, United States

My presentation will highlight some of our recent attempts to make the computation-experiment handshake applied to the discovery and optimization of thermoelectric materials. We will describe the importance and state-of-the-art of accurate simulations of both intrinsic material properties and dopability in computation-guided search for new materials, focusing on the design space of diamond like semiconductors, ordered vacancy compounds, binary chalcogenides, and half-heuslers. Finally, we'll discuss where computational approaches have success and what aspects are missing and should be realized to enable true computation-guided design and optimization -- focusing on strategies to optimize doping and carrier concentrations, and alloying strategies. Time-permitting, I will depart from direct physical modeling to show some of our recent work in the use of language-based representations in the search for thermoelectric materials and discuss some observations of the merits and possible shortcomings of data-based methodologies.

Investigating The Potential of III-V Type-I Clathrates as Thermoelectrics: A Computational Perspective
Alexander Squires and David O. Scanlon; University of Birmingham, United Kingdom

The significant impact of III-V semiconductors on the electronic materials landscape is indisputable, demonstrated by their widespread use in high-profile applications such as integrated circuits, LEDs, and advanced photovoltaics. Innovations in materials discovery have ushered in the synthesis of type-I clathrate structures with a III-V host framework, exhibiting remarkable p-type mobilities [1]. Clathrate structures, consisting of nanometre-sized polyhedral cages encapsulating guest atoms or molecules, have stirred interest as prospective battery electrodes, photovoltaics, but most relevantly as thermoelectrics [2]. The highly electronically conductive framework coupled with weakly bound “rattler” guest atoms leads to fast electron transport and poor thermal transport, thus fulfilling the phonon-glass electron crystal concept and paving the way for exceptional thermoelectric materials. Despite this notable potential, there exist significant discrepancies between theoretical predictions and experimental studies of these materials’ properties [1], which our research aims to resolve. In our study, we integrate atomistic simulations with data-driven methodologies to screen and characterize both existing and novel clathrates within the III-V compositional space. Employing the SMACt materials informatics tool [3], we efficiently navigate the vast compositional search space of III-V clathrates using economical heuristic tools, refining the search by evaluating the stability of the proposed clathrates using density functional theory. We further utilized spin-orbit coupling corrected hybrid density functional theory to provide a comprehensive first-principles characterization of these materials' electronic structures. Finding that this alone does not reconcile the experimental-theoretical disparities, we explore the strong influences of disorder and off-stoichiometry on their target properties. Our findings present deeper insights into this exciting class of materials, and offers a range of potential new applications.

1. Owens-Baird et al., Journal of the American Chemical Society, 2020, 142, 4, 2031–2041

11:15 AM EN08.05.03
Advancing Thermoelectric Materials: A CALPHAD Approach to Charged Defects in Semiconductors
Adetoye H Adekoya and Jeff Snyder; Northwestern University, United States

Thermoelectric (TE) devices that offer a route for energy recovery/production often need to be optimized by doping with other elements to improve the thermoelectric figure of merit (zT) which qualifies the efficiency of the device. The solubility of these elements in the bulk system is usually in such dilute concentrations that they can best be described as 0-D defects in an otherwise essentially uniform crystal. However, these defects/dopants are essential to the efficient performance of thermoelectric devices. As a result, an accurate understanding of the solubility limits of these dopants is necessary for the manufacture of high-performing Thermoelectric. Phase diagrams, which are lines of equilibrium or phase boundaries at specific thermodynamic conditions, can be useful for visualizing the solubility limit. To that end, the method called Computer Coupling of Phase Diagram and Thermochromy, or alternately Calculation of Phase Diagrams (CALPHAD) is an established technique for visualizing the phase diagram of material systems.

In our previous work, we showed that CALPHAD is a viable tool to both visualize the effects of the dominant defects on the shapes of the phase diagram as well as provide an estimate of the defect concentration. We further extend those principles into describing charged defects in semiconductors. The CALPHAD technique has been used extensively as a thermodynamic framework to optimize the manufacture of alloys by modeling the Processing, structure, properties, and performance relationship. By developing a formalism for describing these charged defects in a CALPHAD framework, we set the stage for a more complete integration of CALPHAD with thermoelectric materials and semiconductors in general
We demonstrate a computational approach to optimize the dopant profile of a thermoelectric material, accounting for the effect of the dopant on multiple interrelated indicators of performance. While most computational studies of dopants in TE materials primarily focus on optimization of carrier concentrations with the assumption that bulk/intrinsic properties of the material remain unchanged, in cases of high concentrations doping can affect other aspects of performance through modifications to carrier mobilities, thermal conductivity, and density of states. These competing effects often make it challenging to identify optimal doping concentrations. In this work, we use the example of Ga and Sb co-doping as a case study for the multi-objective optimization of n-type achievable TE performance in the group IV-VI binary halogenides with AB stoichiometry. Although recent reports show improved performance in n-type PbS based on co-doping with Ga and Sb, a predictive model that describes doping effects on multiple properties would reveal ultimate performance achievable and the carrier concentrations at which it occurs. We present models to assess how co-doping with Ga and Sb affect carrier mobilities, thermal conductivity, electronic density of states, and carrier concentrations in PbS and PbSe. The density of states under PbSe is higher than PbS, which show increased disordering after Ga, Sb co-doping. The defect properties show the stability of the co-doped system over a single dopant, which shows the stability of co-doped Ga-Sb defect would be stable over single point defect Ga and Sb. Our analysis reveals opportunities for multi-objective optimization of TE properties through understanding the change in effective mass, mobility, thermal conductivity, and optimized carrier concentration.

11:45 AM EN08.05.05

Micro Thermoelectric Devices: From Thermal Management to Powering the Internet of Things
Heiko Reith1, Nithin Pulumat1, Aditya Dutt1 and Konnelius Nielsch1,2,3; 1IFW Dresden, Germany; 2Institute of Applied Physics, TUD, Germany; 3Institute of Materials Science, TUD, Germany

Micro-thermoelectric devices (μTEs) hold significant potential for various applications in the biomedic field, powering internet-of-things devices, and thermal management. To enable their use in such applications, robust packaging is crucial, allowing direct thermal contact between the μTEs and the target heat sink and source. However, conventional packaging techniques designed for larger modules are unsuitable for μTEs due to excessive thermal resistance between the encapsulating material and the device, which hampers performance. In this study, we present the fabrication of μTEs using optimized geometry and contact resistance, coupled with a novel packaging technique that seamlessly integrates with on-chip systems. Our fabrication process involves the creation of micro thermoelectric coolers (μTECs) with vertically free-standing leg pairs, eliminating the need for a top plate. To meet real-world requirements, we embed these free-standing devices to form a flat surface at the top level, ensuring direct thermal contact with the heat sink. This embedding not only enhances mechanical stability but also provides chemical stability. We employ photolithography as the filling material due to its low thermal conductivity and excellent processability. By characterizing the μTECs with and without photolithoset using a thermoreflectance thermal imaging technique, we analyze the devices’ cooling efficiency and the impact of the photolithoset matrix on their performance. The fabrication process of the μTEC involves a combination of photolithographic patterning and electrochemical deposition of Bi2(Te,Si)xTe3 and Te, which serve as the n-type and p-type thermoelectric materials, respectively. Through optimization of the geometry and contact resistance of the μTECs, we achieved a maximum cooling effect of approximately 10.8 K at an applied electrical current of 235 mA. Furthermore, our reliability studies demonstrated a rapid response time of 700 μs and over 100 million cooling cycles without device failure. We also conducted finite element analysis to investigate the impact of geometry and contact resistance on the cooling power density and net cooling temperature. Our study highlights the potential of μTECs in powering applications requiring high cooling performance while maintaining excellent reliability.

References:
[3] Porrungroj, C.; Andrei, V.; Ertekin; University of Illinois at Urbana-Champaign, United States

1:30 PM EN08.06.01

Thermoelectric–Photoelectrochemical Water Splitting under Concentrated Solar Irradiation
Virgil Andrei; University of Cambridge, United Kingdom

Photoelectrochemical (PEC) systems utilize sunlight to directly convert water and carbon dioxide into useful chemicals like hydrogen, synthesis gas, or ethanol. Such devices may lower the costs of sustainable fuel production by integrating light harvesting and catalysis in one compact device. However, light absorption suffers losses from thermalization and the inability to use low-energy photons, which limits the overall solar-to-chemical conversion efficiency. Here, we demonstrate that PEC reactors can utilize this waste heat by integrating thermoelectric modules, which provide additional voltage under concentrated light irradiation. While most single semiconductors require external bias, we already accomplish unassisted water splitting under 2 sun irradiation by using a Bi2Te3 photoanode to a thermoelectric element, whereas the photocurrent of a perovskite-Bi2Te3 tandem system is enhanced 1.7-fold at 5 sun. This strategy is particularly suitable for photoanodes with more positive onset potentials like hematite, with thermoelectric-perovskite-Fe2O3 systems achieving a 29.7× overall photocurrent increase at 5 sun. This approach enables the realization of high-efficiency, low-cost, and compact PEC devices for water splitting under concentrated solar irradiation.

References:

1:45 PM DISCUSSION TIME

SESSION EN08.06: Novel Architecture and Applications
Session Chairs: Saniya LeBlanc and Marisol Martin-González
Wednesday Afternoon, April 24, 2024
Room 336, Level 3, Summit

2:00 PM +EN08.06.03

Thermoelectric Transport with Metamaterials
Lilia Woods; University of South Florida, United States

Thermoelectricity is a basic transport phenomenon encompassing thermodynamically reversible heat-to-electricity conversion. Much of the current research in this area has been focused on the thermodynamic study of materials as a viable route to optimize existing and engineer new compositions for better practical devices. Here I would like to explore a macroscopic perspective that helps us think differently of controlling thermoelectricity. Using thermodynamics, circuit theory, and transformation optics an efficient approach is offered for the design of thermoelectric metamaterials with targeted functionalities. For example, thermoelectric cloaks and rotators can be achieved by enforcing preservation of the invariance of the governing and constitutive thermodynamic equations. Using basic relations for in-parallel and in-series connected components, the independent control of the coupled via Seebach coefficient thermal and heat currents can also be achieved. Our pathways for constructing metamaterials capable of achieving such functions is especially exciting for the construction of actual devices.

[3] Porrungroj, C.; Andrei, V.; Ertekin; University of Illinois at Urbana-Champaign, United States
3:30 PM *EN08.07.01
Process-Structure-Property Relationships for Laser Additive Manufacturing of Thermoelectric Materials for Low and High Temperature Applications
Sania LeLHAnh; The George Washington University, United States

Thermoelectric materials enable direct, solid-state conversion of heat to electricity and vice versa, so they offer functional power generation and heat pumping capabilities. Additive manufacturing offers the potential to structure thermoelectric materials and devices at multiple length scales, thus improving both intrinsic properties, overall system performance, and application integration. We report on experimental and computational investigation of process-structure-property relationships for laser powder bed fusion of thermoelectric materials including bismuth telluride (for applications near 100 °C) and silicon germanium (for applications near 1000 °C). Strategies for non-spherical powders were developed, and the process parameters that lead to conduction mode melting were determined. The process has been demonstrated on multiple tools, both custom setups and commercial tools. The structure of both single melt tracks and bulk parts were characterized at nano-, micro-, and meso-scales for varying process parameters such as laser power, scan speed, and powder layer thickness. Finite element modeling of laser energy deposition and heat diffusion within the powder bed resulted in simulations of spatial and temporal temperature gradients during laser processing of thermoelectric material. These simulations were compared to in-situ, long wavelength infrared sensor data collected during processing experiments. The ratio of temperature gradient and solidification rate was used to predict the transition between equiaxed and columnar grains and compare the prediction to the experimentally observed grain morphology. A kinetic Monte Carlo simulation was used to simulate the formation of grain structure during solidification. Thermoelectric properties (Seebeck coefficient, electrical conductivity, and thermal conductivity) were measured on fabricated bulk samples, and structure and property characterization results indicate a link between the process-dependent nanostructure and the Seebeck coefficient, including a transition between n- and p-type behavior and graded Seebeck coefficient. These results indicate functional grading of thermoelectric properties during the additive manufacturing process may be possible. Finally, the power generation performance impact of unique device shapes (e.g., layered, hourglass, and hollow shapes) enabled by additive manufacturing was modeled for high and low temperature and heat flux boundary conditions, and selected promising shapes were fabricated. This work provides knowledge about how rapid melting and solidification of thermoelectric materials during laser additive manufacturing impacts the material structure and properties. The results show how variations in process parameters can be leveraged to enable functional grading of thermoelectric properties within the material by manipulating the material at the nano and micro-scales. The additive manufacturing technique enables fabrication of unique shapes at the mesoscale that show improvements for system-level performance of thermoelectric devices.

4:00 PM EN08.07.02
3D Ink Printing and Casting of Nb0.8Ti0.2FeSb and Half-Heusler Thermoelectric Couples
Alexander Proschel, Duncan Zavanelli, Jeff Snyder and David C. Dunand; Northwestern University, United States

Current manufacturing processes for inexpensive, mechanically stable, high performing p-type half-Heusler Nb0.8Ti0.2FeSb as ball milling and hot pressing are unsuitable for continuous processing, geometrically limited, and require subsequent slicing and assembly steps to fabricate thermoelectric couples. Additionally, current assembly of half-Heusler couples typically relies on brazing or soldering, both of which are unsustainable for long-term use. Thus, new additive manufacturing synthesis of Nb0.8Ti0.2FeSb and half-Heusler couples is necessary to improve utility and eliminate the costly slicing and assembly steps. This talk will present a new procedure for ink casting of bulk Nb0.8Ti0.2FeSb with subsequent half-Heusler couple assembly as well as direct 3D ink printing of a complete half-Heusler thermoelectric couple. This synthesis approach utilizes polymer-based inks loaded with elemental metallic precursor powders which can be co-printed or cast at ambient temperature to produce thermoelectric legs or complete half-Heusler couples.

4:15 PM EN08.07.03
Flexible, Scalable and Reliable Fully Screen-Printed Thermoelectric Generators
Irene Brunetti1,2, Federico Ferrari1,3, Nathan James Patka1, Sina Abdolhosseinzadeh1,4, Lambert Jan Anton Koster1, Jakob Heier1, Ulrich Lemmer1, Martijn Kemerink1,2, InnovationLab, Germany; 5University of Groningen, Netherlands; 6Instituto Italiano di Tecnologia (IIT), Italy; 7Swiss Federal Laboratories for Materials Science and Technology (Empa), Switzerland; 8Heidelberg University, Germany

Global energy demand is expected to increase by almost 50% in the next 20 years. Currently, traditional energy sources such as oil, gas, and coal have played a significant role in global energy production. However, they are also responsible for the increase in pollution and are harmful to human health. New energy sources are necessary to support this high demand, in a sustainable way. The thermal energy can be converted into electrical energy in a completely eco-friendly way thanks to thermoelectric generators (TEGs). Due to their flexibility, lightness, affordability, and natural abundance, organic thermoelectric materials are the perfect competitors for making flexible TEGs that can readily conform to complex surfaces. However, up to now, the research has primarily focused on making simple proof-of-concept devices not application-oriented, to highlight the thermoelectric performance of the organic materials. Moreover, demonstrator-devices typically show performance that is far below what one would expect based on the figures of merit of the constituent materials. Here, we present a new fabrication method to make vertical, fully printed, large-area, flexible, monolithic TEG with a high-density of thermocouples scalable up to m², compatible with all the screen-printable inks with performance that matched the expectations based on the figures of merit of the constituent materials. The TEGs were made screen printing five layers on top of each other on a 25 μm thick Kapton substrate, recreating the II-shape structure, where device legs are oriented perpendicular to the heat flows. A silver bottom contact necessary for the electrical connection was screen printed, followed by an insulator layer with cavities designed to create a mask for the vertical thermocouples. Successively, the p-type layer and the silver layer were screen-printed to fill alternatively the cavities, thereby creating the vertical thermocouples. Finally, the top silver contact was screen printed to electrically complete the circuit. We demonstrated the proof-of-concept by using as p-type the well-known and commercially available poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) to make vertical TEGs composed of 4 and 8 thermocouples, with a surface area of 0.5 cm² and 1 cm², respectively. The devices exhibited an ideal behaviour perfectly scalable in accordance with numerical simulations. After the validation of the fabrication method, we utilized a recently reported additive-free graphene, not previously assessed for thermoelectric applications, as p-type material to make a vertical TEG composed of 8 thermocouples. The power output at a ΔT = 25°C provided by the additive-free graphene device was over five times higher than that of the PEDOT:PSS TEG. Additionally, the measures were once again in accordance with numerical simulation. The additive-free graphene TEG provides a remarkable, among the organic thermoelectric TEG, power density of 15 mW/cm² at ΔT = 29.5 °C. Scaling this device to a 100 cm² large TEG will result in a power output of 1.5 μW, sufficient to power low-energy electronic devices such as sensors, wearables, and wireless communication systems. The fully screen-printable large-area TEGs presented are also extremely lightweight and flexible. Specifically, the additive-free graphene TEG provides an estimated power output of 1 μW/g, and its internal device resistance remained constant even when the device was rolled into a cylinder with a bending radius of 1 cm. Future work for this technology will involve making larger devices on thinner substrates to considerably increase the power output. Using a 5 μm substrate the power output of a 100 cm² additive-free graphene TEG will increase by an order of magnitude. Furthermore, due to the versatility and reliability of the process, it will also be possible to use inorganic materials as active inks with enhanced thermoelectric performance to further increase the power output.
Moreover, the material structure and chemical composition, and the associated performance, can be precisely tuned by the laser power and scanning speed. For instance the unique microstructure of the laser-printed material imparts remarkable flexibility to the typically brittle Bi2Te3 thick films. Samples can withstand extreme bending with a radius of curvature as small as 0.75 mm while experiencing minimal changes in performance over a 10 mm bending radius. Additionally, we can simultaneously modify the stoichiometry of the material to optimize its power factor. This innovative approach holds promise for the advancement of flexible TEGs and their diverse applications.

4:45 PM EN08.07.05
Flexible Thermoelectric Generators based on Template-Assisted Electrodeposition of Bismuth Telluride inside Commercial Filters Olga Caballero-Calero, Pablo Cerviño Solana, M. Jesús Ramírez Peral, Miguel Ángel Tenaguillo Arrese and Marisol Marín-González; IMN-CNM, Spain

Miniaturized thermoelectric generators utilizing bismuth telluride (n-type) and tellurium (p-type) semiconductors have been fabricated within commercial polyester filters. Employing electrochemistry for fabrication for both the electrical contacts and the active thermoelectric material, we create an intricate network of nanostructured bismuth telluride or tellurium, which is electrically connected to the top and bottom electrodes. The control over the electrochemical process allows us to maintain the flexibility of the commercial filter in the final device. It is mandatory to be flexible in applications such as harvesters of body heat to power wearable devices, where adaptability to human skin is essential.

Electrochemical deposition is a cost-effective and scalable fabrication method, but does not use high vacuum or expensive facilities, but has the advantage of allowing conformal growth of the material when a template is used. Given that the commercial filters have hollow structures in the order of tens to hundreds of nanometers in diameter and microns in length, the obtained material will be nanostructured with those dimensions. Our work demonstrates enhanced thermoelectric performance compared to electrodeposited thin films due to the nanostructure [1]. Also, with the control of the different parameters during the electrochemical deposition (temperature, applied voltage, etc.), the stoichiometry, morphology, and crystallographic orientation can be tailored. Once the samples were grown, scanning electron microscopy images, X-Ray diffraction images, and Raman spectroscopy were used to get complete information on the material and optimize the filling of the template, the material composition (which is crucial in the case of bismuth telluride), and crystal orientation to have the best performing material for applications in the out-of-plane direction, that is, with the temperature gradient applied in the direction of the thickness of the template. Once these first parameters were optimized, and a high filling ratio of nanostructures oriented along the [110] direction with stoichiometric composition was obtained [2], the transport properties were also measured (Seebeck coefficient and electrical conductivity) to fine-tune and optimize the material. For the final thermoelectric generator, which uses the gold electrode evaporated in one of the faces of the filter to perform template-assisted electrochemical deposition as the bottom electrode, a top electrical contact needs to be implemented. This has been made by electrochemically depositing nickel on top of the previously grown bismuth telluride or tellurium nanostructure. In this way, the electrical contact between the different nanostructures of thermoelectric material and the top electrode is granted, and a macroscopic electrode is formed on the top of the filter, which simplifies the use of the generator.

Finally, the optimization of the geometry of the thermoelectric generators was firstly studied by simulations carried out with COMSOL MULTIPHYSICS and then implemented in actual devices. For the moment, thermoelectric generators consisting of 2 or 4 pairs of legs fabricated inside the commercial filter have been implemented.

References

5:00 PM EN08.08.02
An Efficient High-Throughput Approach for Investigating Anharmonic Lattice Dynamics Hrushikesh P. Sahasrabuddhe1,2, Zhuoying Zhu2, Junsoo Park2,3, Alex M. Ganose2,4, Rees Chang2,5, John W. Lawson3 and Anubhav Jain; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States; 3NASA Ames Research Center, United States; 4Imperial College London, United Kingdom; 5University of Illinois at Urbana-Champaign, United States

This work introduces a high-throughput framework specifically designed for anharmonic phonon calculations. The method is based on the efficient fitting of the force constant (FC) matrix implemented in the hiPhive 1 framework and subsequent calculation of harmonic and anharmonic properties. In particular, we determined the set of optimal parameters: FC fitting methods, cutoffs, supercell size for finite displacement DFT calculations, the magnitude of atomic displacements, and the number of perturbed supercells. Our workflow can calculate phonon band structure, phonon DOS, finite temperature free energy, heat capacity, coefficient of thermal expansion (CTE), and lattice thermal conductivity (λ). A temperature-induced anharmonic phonon renormalization (APRn) 2 scheme to tackle dynamical instability is also included in the workflow, which is shown to predict the finite temperature stability of cubic GeTe 3 and ZrO2 4 phases.

Our workflow exhibits an impressive 100 to 1000X speedup compared to conventional approaches when calculating anharmonic vibrational properties. We conduct a rigorous benchmarking process against experimental measurements, encompassing CTEs, and computationally calculated phonon DOS. The CTEs and obtained from the workflow agree well with the experimentally reported values with a Pearson correlation coefficient of 0.94 and 0.99, respectively. The Pearson correlation coefficient of phonon DOS varies from 0.63 in CsTe to 0.96 in BP.

In this workflow, we integrate lattice dynamic packages like hiPhive with the Materials Project (MP) 5 tech stack using Atomate2. We aim to use this workflow to curate a high-quality dataset of materials with finite temperature phase diagrams and anharmonic vibrational properties in a high-throughput way. This dataset will be used to identify novel thermoelectric materials, solid-state ionic conductors for solid-state batteries, photovoltaic absorber materials, and solar cells. It will also aid in the predictive synthesis of solid-state reactions.


5:00 PM EN08.04.04
Controlling Defects in Epitaxial Thin Film Growth of Mg2Sn1-xGex by Modulating Mg Flux Rate in MBE Kenneth M. Senado1,2, Takashi Aizawa2, Isao Ohkubo2, Takahiro Baba1,2, Akira Uedono1, Takeaki Sakurai1 and Takao Mori1,2; 1University of Tsukuba, Japan; 2National Institute for Materials Science, Japan

Defects manipulation in thermoelectric materials is emerging as a key in optimizing their performance. However, because thin film processes differ from bulk synthesis methods, the manipulation of defects in thin films vary significantly from their bulk counterparts. We explore in this study how Mg flux rate modulation in molecular beam epitaxy (MBE) growth affects the defects formation of Mg2Sn1-xGex (x = 0.05 and 0.12) epitaxial films. Mg flux rates were varied in the range of Mg:Sn(Ge) = 3.9-9.1, while Sn and Ge flux rates were fixed at 1.65 atoms×s-1nm-2. Although the relative Mg supply rate largely exceeded 2, the obtained films consisted of Mg2Sn phase as a main component, because the excess Mg can easily evaporate at the growth temperature of 380°C. However, the Mg flux rate can impact the film growth dynamics. On the other hand, at the high Mg rate, the presence of Mg interstitials (IMg) is hinted within the Moiré patterns. The formation of Moiré patterns can be associated with strain relaxation, and their occurrence increases at higher Mg flux rates could be attributed to the role of Mg in altering strain distributions and controlling the defects. Structural analysis through XRD pole figures also unveiled the presence of stacking faults in the films. The total thermal conductivity measured at room temperature of the thin films tends to decrease with an increasing Mg flux rate. These
findings suggest a delicate balance between improved overall crystal structure and the presence of localized structural variations that may contribute to the decrease in thermal conductivity and total improvement of the thermoelectric properties of Mg-based thin films.

5:00 PM EN08.08.06
Impact of Excess Cu on Phase Separation and Thermoelectric Properties of Arc Melted Ti<sub>0.5</sub>Zr<sub>0.5</sub>NiCu<sub>y</sub>Sn Blair F. Kennedy<sup>1</sup> and Jan-Willem Bos<sup>2</sup>; <sup>1</sup>Heriot-Watt University, United Kingdom; <sup>2</sup>University of St Andrews, United Kingdom

Alloys based on XNiSn (X = Ti, Zr or Hf) are leading n-type half-Heusler thermoelectrics. They have large power factors <sup>ST</sup>, but are limited by an inherently high lattice thermal conductivity, <sup>3</sup>κ<sub>lat</sub>. Alloying Ti, Zr and Hf on the X-site in the crystal structure affords significant reductions of <sup>3</sup>κ<sub>lat</sub> however. Ti and Zr/Hf mix poorly during materials synthesis, typically resulting in the presence of multiple HH phases in the final product. The presence of multiple HH phases has been attributed to phase segregation, and has been linked to low <sup>3</sup>κ<sub>lat</sub>, below values expected from alloying.

In this contribution, the impact of excess Cu on the HH phase distribution of Ti<sub>0.5</sub>Zr<sub>0.5</sub>NiCu<sub>y</sub>Sn (y = 0.025, 0.1) is discussed. Structural characterisation of samples treated at varying temperatures reveals minimal impact on the phase distribution for y = 0.025, compared to not having Cu. By contrast, samples with y = 0.1 show improved homogeneity and can be made single phase at high temperature. The homogenous y = 0.1 sample has the lowest <sup>3</sup>κ<sub>lat</sub> of all samples, confirming that alloying is the dominant phonon scattering effect. A highest <sup>4</sup>zT = 0.7 is found for multiphase Ti<sub>0.5</sub>Zr<sub>0.5</sub>NiCu<sub>0.025</sub>Sn, with a lower <sup>4</sup>zT = 0.5 observed for single phase Ti<sub>0.5</sub>Zr<sub>0.5</sub>NiCu<sub>0.1</sub>Sn. This lower value is due to over-doping and a compromised <sup>3</sup>ST.

This work demonstrates that (1) the poor mixing of Ti and Zr/Hf in XNiSn alloys is predominantly a kinetic effect and not driven by thermodynamic phase segregation. (2) That there is no evidence that multiphase behaviour leads to significant reductions of <sup>3</sup>κ<sub>lat</sub> in our samples.

References

5:00 PM EN08.08.07
Alloying-Induced Structural Transition in The Promising Thermoelectric Compound CaAgSb A K M Ashiquzzaman Shawon<sup>1</sup>, Weeann Guert<sup>1</sup>, Kamil Ciesielcki<sup>2</sup>, Rachel Orenstein<sup>2</sup>, Jiaying Qu<sup>2</sup>, Elif Erturk<sup>3</sup> and Alexandra Zevalkink<sup>1</sup>; <sup>1</sup>Michigan State University, United States; <sup>2</sup>Colorado School of Mines, United States; <sup>3</sup>University of Illinois at Urbana-Champaign, United States

AMX Zintl compounds, crystallizing in several closely related layered structures, have recently garnered attention due to their exciting thermoelectric properties. In this study, we show that the orthorhombic CaAgSb can be alloyed with hexagonal CaAgBi to achieve a solid solution with a structural transformation at a = 0.8. This transition can be seen as a switch from 3D to 2D covalent bonding, in which the interlayer M-X bond distances expand while the in-plane M-X distances contract. Measurements of the elastic moduli reveal that CaAgSb-<sub>Bi</sub> becomes softer with increasing Bi content, with the exception of a step-like 10% stiffening observed at the 3D-to-2D phase transition. Thermoelectric transport measurements reveal promising Hall mobility and a peak <sup>11</sup>zT of 0.47 at 620 K for the intrinsic CaAgSb, which is higher than previous reports for unmodified CaAgSb. However, alloying with Bi was found to increase the hole concentration beyond the optimal value, effectively lowering the <sup>11</sup>zT. Interestingly, analysis of the thermal conductivity and electrical conductivity suggests that the Bi-rich alloys are low Lorenz-number (<sup>L</sup>) materials, with estimated values of <sup>L</sup> well below the non-degenerate limit of <sup>L</sup> = 1.5 x 10<sup>6</sup> W·Ω·K<sup>-2</sup>, in spite of the metallic-like transport properties. A low Lorenz number decouples electrical and electronic thermal conductivity, providing greater flexibility for enhancing thermoelectric properties.

5:00 PM EN08.08.13
Oxide Thermoelectric Materials for Green Energy Generation Kriti Tyagi, Rohit Yadav and S. R. Dhakate; CSIR-National Physical Laboratory, India

BiCuSeO<sub>2</sub> oxy-chalcogenides are considered promising thermoelectric materials due to high Seebeck coefficient values combined with intrinsically low thermal conductivity. BiCuSeO<sub>2</sub> showcases properties of a semiconductor and possess low electrical conductivity values. The two essential step must be taken in sequence to create test materials for use in thermoelectric modules are the calcination of the mixed precursors (BiCuSeO<sub>2</sub>) and subsequent consolidation into precisely dense pellets by spark plasma sintering (SPS) technique. By tracking the evolution of structural and morphological measurements, the current work optimizes the processing times for ball milling and calcination on the phase formation of polycrystalline BiCuSeO powder. The work also focus on designing different synthesis routes and their comparison to find out the most suitable route for synthesizing pristine BiCuSeO.

5:00 PM EN08.08.14
Computational Design of SiGeSn Alloys for Thermoelectric Applications Li-Wen Lin and Szu-Chia Chien; National Central University, Taiwan

Owing to the increasing demand for sustainable energy, significant effort has been made towards the development of energy-related materials. Among various candidates, thermoelectric materials have drawn considerable attention. Si-Ge alloys have a long history as effective thermoelectric materials for waste heat recovery. More importantly, recent studies have shown that Si-Ge alloys with the Ge content of 20% possess excellent materials properties as thermoelectric materials. By introducing Sn into Si-Ge alloys, the thermal conductivity can be reduced with a small impact on electrical conductivity, thus making SiGeSn alloys promising thermoelectric candidates. However, challenges in precise composition control and complex synthesis methods in experiments may limit their studies and applications. To this end, this work seeks to employ computational methods to help search for the optimal composition ratios of SiGeSn alloys with the aim of facilitating the development of SiGeSn thermoelectric materials.

In this work, the Alloy Theoretic Automated Toolkit (ATAT), utilizing special quasi-random structure (SQS) modeling, is employed to create random Si<sub>x</sub>Ge<sub>y</sub>Sn<sub>z</sub> alloys with various Si, Ge and Sn content. The electronic structure characteristics are calculated using density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP) whereas their thermoelectric properties are assessed by BoltzTraP software, which applies the Boltzmann Transport Equation (BTE) for obtaining key thermoelectric parameters such as the Seebeck coefficient, electronic conductivity, electronic thermal conductivity, and power factor. Our result shows that with the composition of Si<sub>x</sub>Ge<sub>y</sub>Sn<sub>z</sub>, the highest figure of merit of around 0.8 can be achieved. By integrating these computational tools, this work offers comprehensive insights into the intricate correlation between composition ratios and the thermoelectric properties in SiGeSn alloys. It is anticipated that the findings from this work can offer insights into the design of high-performance thermoelectric materials.

References

5:00 PM EN08.08.16
Drastic Lowering of Lattice Thermal Conductivity induced by Alloyovariant Substitution of TiCoSb-Based Half-Heusler Compound Dipanwita Bhattacharjee<sup>1</sup>, Nagendra S. Chauhan<sup>2</sup>, Tamnoy Maiti<sup>3</sup>, Yury V. Kolen'ko<sup>4</sup>, Yuzuru Miyazaki<sup>2</sup> and Amrita Bhattacharya<sup>1</sup>; <sup>1</sup>Indian Institute of Technology Bombay, India; <sup>2</sup>National Institute for Materials Science, Japan; <sup>3</sup>Indian Institute of Technology Kanpur, India; <sup>4</sup>International Iberian Nanotechnology Laboratory, Portugal; <sup>5</sup>Tokyo University, Japan

The performance of the state-of-the-art ternary half-Heusler (HH) compounds is limited by their intrinsically high lattice thermal conductivity (<sup>L</sup>κ). In this study, we present a stable n-type biphasic-quaternary (Ti,V)CoSb HH alloy that is equivalent to previously reported nanostructured HH alloys in terms of lattice thermal conductivity (<sup>L</sup>κ~ 2 W/mK) within a temperature range of 300-800 K. Alloyovariant substitution of TiCoSb, resulting in an effective 18.5% valence electron count (Ti<sub>0.5</sub>V<sub>0.5</sub>CoSb), results in a significant reduction in <sup>L</sup>κ and synergistic enhancement of the power factor with a peak <sup>4</sup>zT of 0.4 (~ 0.05) at 873 K. The lowering of <sup>L</sup>κ in Ti<sub>0.5</sub>V<sub>0.5</sub>CoSb HH alloy is attributed to an enhancement in phonon scattering driven by spinodal decomposition upon annealing. First-principles DFT calculations are performed to investigate the structure, stability, electronic structure, and transport properties of the synthesised alloy, which accredits the
decrease in lattice thermal conductivity to the alloy's increased anharmonicity. The changing electronic band-structure upon substitution and an increase in carrier concentration have a great correlation with the observed electrical characteristics. Hence, new prospects for discovering biphase-quaternary HH compositions with intrinsically lower $\kappa$ for potential thermoelectric applications are supported by this study.

### 5:00 PM EN08.08.17

**Defect Engineering in Bi$_2$SeO$_2$ by Tuning Synthesis Conditions - A Combined Experimental and Theoretical Study**

Michael Toriyama$^1$, Andrei Novitskii$^2$, Ilia Serhiienko$^{2,3}$, Takao Mori$^{2,3}$, Jeff Snyder$^1$ and Prashun Gorai$^4$; $^1$Northwestern University, United States; $^2$National Institute for Materials Science, Japan; $^3$University of Tsukuba, Japan; $^4$Colorado School of Mines, United States

Recently, Bi$_2$SeO$_2$ has emerged as a promising $n$-type counterpart to $p$-type BiCuSeO in thermoelectric (TE) devices. However, there are significant variations in the reported charge carrier concentration of Bi$_2$SeO$_2$ spanning several orders of magnitude, resulting in diverging reports of TE properties. These predominantly arise from the disparate synthesis routes used, which in turn affect the defect thermodynamics in the system. In this study, we employ a combined experimental and theoretical approach to demonstrate how defect engineering controlled by synthesis conditions can be used to tailor the transport properties of $n$-type Bi$_2$SeO$_2$. Through first-principles calculations, we identify the dominant native defect in Bi$_2$SeO$_2$ as the donor-like selenium vacancy ($V_{Se}$). We predict that increasing the synthesis temperature ($T_{SSR}$) of nominally undoped Bi$_2$SeO$_2$ will lead to an increase in $V_{Se}$ and, consequently, electron concentration. We observe a rise in carrier concentration by nearly two orders of magnitude between samples synthesized at $T_{SSR} = 773$ K and $T_{SSR} = 1173$ K. This results in the enhancement in both the quality factor and the TE performance with a remarkable $zT$ value of 0.25 at 773 K achieved for self-doped Bi$_2$SeO$_2$. Our findings underscore a noteworthy relationship between processing conditions and the transport properties of Bi$_2$SeO$_2$ rooted in defect engineering.

### 5:00 PM EN08.08.18

**Side-Chain Engineered $p$ or $n$-Type Nonaqueous Polymeric Ionic Gels for Sustainable Ionic Thermoelectrics**

Sungyong Kim, Seyeong Lim and Taiho Park; Pohang University of Science and Technology, Korea (the Republic of)

Although ionic hydrogels have been developed recently for innovative wearable electronics, they necessitate high humidity to diffuse ions in water and fast self-healing, which negatively impacts their performance and stability in ambient conditions (e.g., dry environments). In this study, we compare the performance and stability of these materials. This contribution will summarise our current understanding of the impact of interstitial Cu in the XNiSn Heuslers, which goes beyond carrier doping and affects underlying electronic properties development.

### 5:00 PM EN08.08.21

**Enhanced Density of States Mass in Cu Containing XNiSn Half-Heusler Alloys – A New Route Towards High Thermoelectric Performance**

Robert Quinn$^1$, Sonia Barczak$^1$ and Jan-Willem Bos$^2$; $^1$Heriot-Watt University, United Kingdom; $^2$University of St. Andrews, United Kingdom

Half-Heusler alloys are leading contenders for application in commercial thermoelectric generators. They combine strong performance with good engineering properties and thermal stability. There has been great progress in $p$-type half-Heusler alloys in the past decade, with $zT = 1.5$ achieved in NbFeSb and ZrCoBi. There have been fewer developments in $n$-type Heusler alloys with the best performance in compositions based on ZnNiSn, with peak $zT = 1.2-1.3$.

We have investigated the use of interstitial Cu in the XNiSn half-Heusler alloys. This cheap base metal is an alternative to the usual $n$-type dopant Sb. In addition to being an efficient $n$-type donor, its use leads to a suppression of thermal conductivity and a more homogeneous microstructure. Our latest work reveals an enhanced density of states effective mass ($m_{DoS}^* = 4.1$ me$_f$) for Cu-doped XNiSn half-Heusler samples rich in $X =$ Ti. This enhancement over typical values of 3 me$_f$ occurs without substantial drop in electron mobility. This enables improved power factors and peak $zT = 1$ at 773 K in TiNiSn-based samples with interstitial Cu used as a mineraliser, dopant and to suppress thermal transport. Bandstructure calculations show the emergence of a second band at the conduction band minimum. This brings the performance of TiNiSn-based compositions close to the leading $n$-types based on Sb-doped ZnNiSn and is a significant development.

This contribution will summarise our current understanding of the impact of interstitial Cu in the XNiSn Heuslers, which goes beyond carrier doping and affects underlying electronic properties and microstructure of these materials.

### References


### 5:00 PM EN08.08.23

**A Computational Investigation of Bi$_2$MO$_4$Cl (M = Y, La and Bi) as Thermoelectric Materials**

Shipeng Bi$^3$ and David O. Scanlon$^2$; $^1$University College London, United Kingdom; $^2$University of Birmingham, United Kingdom

In the process of primary energy consumption, a large amount of waste heat is generated. Thermoelectric materials (TEs) can convert waste heat energy into electric energy, which is crucial to solving the current energy crisis and mitigating global warming. In general, the performance of TEs can be determined by the dimensionless figure of merit, $ZT$, that is evaluated from its electronic and thermal properties. However, it is difficult to maximise $ZT$ due to the interaction between different parameters.

In recent years, mixed anionic oxides have shown great potential in the field of TEs. Recently, the mixed anionic oxides Bi$_2$MO$_4$Cl (M = Y, La and Bi) was shown to exhibit excellent stability in photocatalytic water oxidation reactions, but their thermoelectric properties have not been explored. We postulated that this quaternary structure with heavy elements will lead to a low lattice thermal conductivity, and they can be synthesised at a relatively high temperature, thus can maintain stability at high temperatures, so we performed density functional theory (DFT) calculations to study the thermoelectric performance of Bi$_2$MO$_4$Cl (M = Y, La and Bi). Our results showed that Bi$_2$MO$_4$Cl (M = Y, La and Bi) belongs to p-type TEs and exhibits an average $ZT$ of about 1 at 1000 K.

### References


### 5:00 PM EN08.08.24

**Thermoelectric Enhancement of Thin Si Films by means of Block Copolymer Driven Nanostructuration**

Alex Rodriguez-Iglesias$^1$, Iñigo Martín-Fernández$^1$, Francesc Pérez-Murano$^1$, Sungyong Kim$^1$, Seyeong Lim$^1$, Taiho Park$^1$; Pohang University of Science and Technology, Korea (the Republic of)

In this work, we demonstrate a novel strategy to enhance the thermoelectric performance of thin Si films by means of block copolymer driven nanostructuration. The block copolymers are used as templates to create nanoscopic heterostructures in the Si films, which are then used to fabricate thermoelectric devices. The results show a significant enhancement in the figure of merit ($ZT$) of the Si films, with values up to 2 at room temperature.

### References

Thermoelectricity explains the conversion of heat into electricity and vice versa, and a plethora of applications are available nowadays for thermoelectric systems in the fields of cooling, power generation and sensing. Traditionally, the most used thermoelectric materials have been based on chalcogenides, as the main reason that has driven the material choice has been the maximization of the thermoelectric figure of merit (ZT). This figure of merit indicates the performance capabilities of a material as a thermoelectric, and depends on its Seebeck coefficient and its electrical and thermal conductivities. Nevertheless, these widely used materials are based on alloys of scarce, expensive, and toxic elements (Bi, Te, etc.) that are difficult to integrate within the semiconductor industry. On the contrary, silicon (Si) is a poor thermoelectric material when in its bulk form but it has been shown to improve around 100 times its thermoelectric performance when it is nanostructured in two- or one-dimensional structures, becoming a competitive alternative [1]. This improvement is mainly justified by the effective reduction of the phononic thermal conductance in the nanostructured material.

In this contribution, we present the study of suspended Si ultra-thin films as thermoelectric material, which are much easier to integrate into semiconductor technologies. Although the enhancement in thermoelectric performance of thin films is modest when compared to one-dimensional structures, this is compensated and enhanced by introducing surface nanostructuring with the aim to reach thermoelectric figures of merit similar to the best reported values in the literature for Si structures. These structures are based on rough surface Si nanowires (NWs), whose large-scale fabrication remains unsolved as the synthesis of high density and uniform Si NW arrays with homogeneous nanoscopic surface morphology is a challenging process. Here, we present a cost-effective and scalable approach for the fabrication of the membranes by block copolymer (BCP) nano patterning. BCP based technologies present manufacturing advantages, as it is a technology easy to scale up for high-volume manufacturing, very cost-effective and capable of achieving sub-10 nm resolution [2].

Nanostructured Si membranes are fabricated on the device layer of a Silicon on Insulator (SOI) wafer with ultrathin device layer (30 – 50 nm). A thin film BCP is self-assembled perpendicularly oriented to the Si surface. The BCP used for surface nanostructuration is polystyrene-block-polymethylmethacrylate (PS-b-PMMA) with cylindrical or lamellar morphology and a period between 28 and 80 nm. After self-assembly, the PMMA block is selectively removed, and PS features are transferred into the Si underneath by reactive ion etching (RIE). As a result, we obtain a nanostructured surface with a hexagonal distribution of holes when a BCP with cylindrical morphology is used as a mask, and a fingerprint-type nanostructuration when a lamellar BCP is used as a mask. The period of such structures is controlled by properly blending BCPS of different molecular weights and the depth and the shape of the walls are tuned by the RIE conditions.

The final structures are doped by spin-on dopant to achieve an optimal doping concentration, 10^19-10^20 cm^-3, for thermoelectric applications. This method has been chosen because it’s a low cost, wafer scale compatible and non-destructive process, and the characterization of the doping values obtained has been done with the 4-probe method on the thin films. We will study the effect of surface nanostructuration on the thermoelectric performance. The thermal conductivity of the membranes will be evaluated using the Seebeck approach on an appropriate test structure, in order to find the most optimal nanostructuration conditions for thermoelectricity.

conductivity, and thermal conductivity. The precise manipulation of the electronic band alignment at the micro/nanoscale can serve to disentangle these TE properties by selectively filtering out detrimental spectral fractions of the charge carriers. Among the diverse array of TE materials, magnesium silicide-based materials are the preferred choice for this purpose due to their spontaneous formation of nanostructured composites comprising distinct phases with varying band gaps dependent on the Si:Sn ratio, driven by a miscibility gap in the solid solution series. Furthermore, these materials are emerging as compelling candidates due to their potential to serve as cost-effective and environmentally friendly components, showcasing exceptional TE properties within the mid-temperature range of 500-800 K. However, the conventional bulk property measurements often lack the sensitivity required to detect the subtle effects of charge carrier filtering, necessitating micro/nano-scale characterizations of TE properties (Seebeck coefficient and thermal conductivity) of multi-phase materials. In our research, we have integrated several locally resolved experimental techniques with electronic transport modeling. The transient Seebeck microprobe, with its micron-scale resolution, allows us to map the distribution of the Seebeck coefficient. Combining the Seebeck coefficient map and the compositional map, obtained by establishing a simple correlation between the grey value in backscattered electron (BSE) images and the chemical composition from EDX point analysis, enables a local correlation between the Seebeck coefficient and the phase composition in multiphase materials. Moreover, employing transport modeling offers insights into the local distribution of the reduced Fermi level and the alignment of valence and conduction bands, enabling the generation of a micro-scale carrier concentration map. Furthermore, utilizing Kelvin probe force microscopy with nano-scale spatial resolution can provide the value of the Fermi level position with respect to the vacuum level, enabling generation of the same carrier concentration map at the nano-scale. Our work also demonstrates the potential of selective doping, using Bi as a dopant, to precisely modify the band positions of individual phases, a prerequisite for material enhancement by energy filtering. This localized characterization technique also aids our understanding of the inter- and diffusion of Mg, Sn, and Sb from one phase to another, resulting in distinct changes in the thermoelectric properties of each phase. This knowledge is vital for optimizing the thermoelectric properties, as it can either amplify or attenuate the effects of selective doping. Hence, this integrated approach represents a crucial step towards optimizing composite materials through effective energy filtering.

9:30 AM BREAK

10:00 AM EN08.09.04
New Members of The Ca4AlSi3 binary Structure Type: Structure and Thermoelectric Properties
Susan M. Kauzlarich; University of California, Davis, United States

Compounds of the Ca4AlSi3 structure type show some of the highest ZTs at high temperatures for p-type compounds. We have shown that preparing these phases with binary precursors of the appropriate composition provides a high-fidelity route to phase pure powders. This allows for broad exploration of this structure type and the resulting thermoelectric properties. We have initiated an investigation of the Eu- and As-containing compounds. In principle, for Eu42MAs11, the following compounds should be possible with M = Mn, Zn, Cd, Mg, Fe. I will present the synthesis of these phases, and the thermoelectric properties and compare them with other compounds of this structure type.

10:30 AM EN08.09.05
Cu5Si6S as a Self-Doped Thermoelectric
Adair Nicolson1 and David O. Scanlon2; 1University College London, United Kingdom; 2University of Birmingham, United Kingdom

Thermoelectric materials can convert thermal energy into electrical energy, taking advantage of the waste heat generated during many industrial processes. Currently, some of the best performing materials are chalcogenides containing toxic elements such as PbSe and PbTe.[1] Therefore, there is a need for research into new thermoelectric materials, which contain earth-abundant and non-toxic elements. Kesterites, for example Cu2ZnSnS (CZTS), have been shown to have lattice thermal conductivity lower than PbTe, and equivalent to PbSe, showing that a low lattice thermal conductivity can be achieved without the inclusion of heavy atoms by increasing the structural complexity of the material.[2] However, generating sufficient charge carriers through doping is a challenge, due to the complex quantum defect chemistry. Taking inspiration from the kesterites, we have computationally investigated the ternary Cu2SiSe3 as a potential thermoelectric, as it has been previously shown to be intrinsically p-type due to the high concentrations of copper vacancies.[3] There is also a large dopability window to increase the concentration of charge carriers further.

In this work we use the AMSET[4] code to calculate the electronic transport properties using the momentum relaxation time approximation and which when combined with lattice thermal conductivities calculated using Phonopy[5], with force-constants fitted using the hiphive package[6], enabling the calculation of the thermoelectric figure of merit, ZT. A ZT of 0.91 is predicted in a self-doped crystal at 800 K, increasing to > 1.5 at higher carrier concentrations.


10:45 AM EN08.09.06
Changes in Physical Properties for HPT-Processed p-Type Skutterudite DD8-xFeCoSb12
Gerd Roegl1, Vilma Bursikova2, Kunio Yubuta3 and Peter F. Regl1; 1University of Vienna, Austria; 2Masaryk University, Czechia; 3Kyushu University, Japan

To build thermoelectric generators, which can directly convert heat into electricity, materials with a high figure of merit, ZT, are essential. Severe plastic deformation (SPD) via high-pressure torsion (HPT) was successfully applied to produce in a fast and energy saving way bulk nanostructured skutterudites directly from powders. SPD introduces many defects into the sample and in parallel the crystallite size is significantly reduced. HPT-processed DD8-xFeCoSb12 is a high-quality thermoelectric material with 1.12 < ZT < 1.35 at 750 K. During measurement-induced heating these defects anneal partially out, and the grains grow. It was observed that while heating HPT processed material from room temperature to about 850 K, changes of the temperature-dependent physical properties, most of all the electrical resistivity, the density, and the thermal expansion occur more or less simultaneously around 600 K. For the first time we have combined in situ TEM observations as well as measurements of the elastic modulus and hardness in order to get a deeper insight into the microstructural behavior of a p-type skutterudite, DD8-xFeCoSb12 (DD = didymium) during increasing temperature from 300 K to 823 K.

11:00 AM EN08.09.07
BaCu2-xTpxP2 (T = Al, Ga, In, Si, or (Si+Zn)): A New Group Semiconductor 'Golden Goose' in The ThCr2Si2 Family with Ultra-Low Thermal Conductivity and High Seebeck Coefficient
Arkaja Sarkar1,2, Gayatri Viswanathan1,2, Stasia Harycki1, Andrew P. Porter1, Alexander Gundlach-Graham1, Aaron Rossini1 and Kirill Kovnir1,2; 1Iowa State University, United States; 2Ames Laboratory, United States

ThCr2Si2-type layered materials are a large family of compounds with applications ranging from thermoelectricity to magnetism, with most of them showing metallic behavior. In this study, we synthesized a variety of new ThCr2Si2-type materials with the general formula BaCu2-xTpxP2 (T = Al, Ga, In, Si, or (Si+Zn)), most being charge balanced semiconductors, a rarity in this family. They all crystallize in the ThCr2Si2-type tetragonal I/mmm space group, with CuT jointly occupying the same 4d crystallographic site. In the case of BaCuAlP2 and BaCu1.3Si0.7P2, Ba atom occupies a single crystallographic site. However, the introduction of Zn in the BaCu1.3Si0.7P2 system results in the expansion of the unit cell by 4%, splitting the Ba atom along the crystallographic c-direction. Similar structural distortions are observed for BaCuGaP2 and BaCuInP2 as well. Such structural disorder of the Ba atoms leads to the occurrence of clathrate-like rattling behavior along the c-direction, as observed from heat capacity measurements. This in turn leads to ultra-low thermal conductivity (as low as ~0.4 W/m-K at 550 °C) at high temperatures. All BaCu2-xTpxP2 materials show semiconducting behavior, making them potential solar absorbers. The composition with the lowest Zn-content, BaCu1.3Zn0.7Si0.5P2, exhibits a clear semiconductor-to-metal transition upon heating above 155 K. The materials show high Seebeck coefficients, such as ~300 μV/K at 550 °C for BaCuAlP2, making them promising candidates for thermoelectric applications. Band structure and density-of-states calculations on ordered hypothetical structures reveal clear semiconductor nature for the trial-based materials and semi-metallic nature for the Si-based ones.

11:15 AM EN08.09.08
Exploration of The Effects of Yb41Sn90 and Yb41MnSn90 Secondary Phases on The High Performing Zintl Thermoelectric Material Yb41MnSn90
Leah E. Borgsmiller and Jeff Snyder; Northwestern University, United States
The high performing Zintl thermoelectric material Yb$_2$MnSb$_2$ has been of interest to the thermoelectrics community for years. However, a major challenge with this material is that it exists in a very busy region of phase space, making it susceptible to having considerable amounts of secondary phases. In particular, the Yb$_2$Sb$_2$ phase has been repeatedly reported as a negative secondary phase, but there have been discrepancies in the literature regarding the effect of this phase as a secondary phase in 11-1. Since the Yb$_2$Sb$_2$ material is a poor metal, it would be expected to hinder thermoelectric performance, and yet there have been studies where large amounts of this metallic phase have relatively no effect on transport, and even one case where it seemed like the Yb$_2$Sb$_2$ phase contributed to an improvement in the thermoelectric performance. Recently, a related phase, Yb$_2$MnSb$_2$, has been reported and has been shown to have a high Seebeck coefficient and ultralow thermal conductivity making it a decent p-type thermoelectric material. Despite having very different properties, Yb$_2$Sb$_2$ and Yb$_2$MnSb$_2$ have extensive crystallographic and stoichiometric similarities, which makes distinguishing between these two phases difficult, especially if they are only present in small amounts as a secondary phase. In this work, we consider the properties of these two possible secondary phases and explore the consequences of these materials as secondary phases in the high performing Yb$_2$MnSb$_2$ material.

11:30 AM EN08.09.10
Enhanced Thermoelectric Performance in Hybrid Inorganic-Organic Conducting Polymer Systems
Iris Nandhakumar, Pawan Kumar, Syed Zafirulin Hussain Shah, and Kedar Hippalgaonkar
1University of Southampton, United Kingdom; 2IMRE, Singapore; 3NTU, Singapore

We carefully considered the properties of these two possible secondary phases and explore the consequences of these materials as secondary phases in the high performing Yb$_2$MnSb$_2$ material.
thermoelectric modules designed to operate at temperatures up to 350°C in a recently funded EU Horizon project.\(^2\)

RGs has developed significant expertise in various areas, including COMSOL simulations, thermo-mechanical engineering, interface engineering, device aging, and testing, positioning the company to offer TEG solutions for both single-stage and cascaded device architectures tailored to a range of source temperatures and heat flux densities.


2. https://www.start-heproject.com/

2:30 PM EN08.10.04
Optimal Transient Operation in Thermoelectric Cooling and its Relation to Thermoelectric Properties
Jaden Lucas, Udit Halder, Lakshmi Amulya Nimmagadda, Prashant Mehta and Sanjeev Sinha; University of Illinois at Urbana-Champaign, United States

It has been well known for many decades that there exists an optimal Peltier current to achieve the best performance in steady-state Peltier cooling. At this constant current, there is a minimum steady-state cold-end temperature that can be achieved across a thermoelectric cooler. However, in a transient operation over a short time window, the temperature drop can be improved with an transient current pulse where the minimum transient temperature depends on the shape of the current pulse [1]. Here, we apply optimal control theory to find for the first time, a temperature minimizing transient current pulse. We consider a thermoelectric cooler with a heat load at the cold end, and model it as a discrete control system and use gradient descent to find a cost-minimizing current [2]. The optimal current diminishes the temperature rise due to the low frequency components of the heat loads, and this performance improvement depends strongly on thermal conductivity [3]. We also consider transient cooling of a thermoelectric below the minimum steady-state temperature. We observe that an optimal current pulse holds the temperature below its steady-state value for longer than a comparable constant current pulse. This work provides new insights into the upper limit of the transient performance of thermoelectric coolers.


2:45 PM EN08.10.05
Boron-Mediated Interface Engineering for Enhancing The Thermoelectric Performance of Bi$_2$Te$_2.7$Se$_0.3$ Films
Yen-Line Wang, Karan Giri, Chuan-Wen Wang, Ling-Chun Chao, Hung-Shuo Chen, Wen-Chih Hsieh and Chun-Hua Chen; National Yang Ming Chiao Tung University, Taiwan

Nanostructuring has become one of the most practically proven and effective strategies in enhancing the thermoelectric figure of merit, which significantly propels thermoelectric materials to the forefront of progress in fundamental research and advanced applications. Accompanied by nanostructuring, heterogenization, which frequently shows excellent synergistic effects with nanostructures, has appeared as an applicable and feasible solution for a further breakthrough. Hexagonal boron nitride (h-BN), exhibiting remarkable thermal and chemical stability, is a potential candidate as the heterogeneous additive since the thermal conductivity of a single h-BN is much lower than that of graphene. In this work, to improve the thermoelectric properties of Bi$_2$Te$_2.7$Se$_0.3$ (BTS) thin films, BTS and h-BN were co-deposited on a SiO$_2$/Si substrate by a dual-beam laser system. The BN addition is expected to synergistically optimize the thermoelectric properties and stability of the BTS films. According to the x-ray diffraction, the crystal structure of the formed BTS:BN hetero-nanostructured films deposited at a temperature higher than 400 °C shows a preferred orientation of (000), which significantly improves the carrier mobility (~105 cm$^2$/V·s$^{-1}$). The optimized Seebeck coefficient is ~197 μV/K$^{-1}$ and the corresponding power factor is 29 μW/(cm·K)$^{-2}$. Raman spectroscopy was performed to analyze the thermal transporting of the formed BTS:BN films. A non-local thermal equilibrium phenomenon of Raman signal collapse at lower laser energy was found, indicating that introducing h-BN additive can effectively reduce the thermal conduction of the BTS films and, thus, can effectively improve the thermoelectric performance.

3:00 PM BREAK

3:30 PM EN08.10.06
Recent Progress on Thermoelectric Materials and Modules
Zhifeng Ren and Kornelius Nielsch; University of Houston, United States

Thermoelectric modules based on thermoelectric materials can either generate cooling/heating using electrical power or electrical power from heat. Thermoelectric property improvement of materials is only the first step for thermoelectric modules for a variety of applications. How to make efficient modules is equally important as the materials improvement. The thermoelectric properties of the traditional materials are not good enough to make efficient modules to compete with the traditional coolers using compressor or steam engines. However, in the past fifteen years, we have been able to not only achieve some good progress on improving the thermoelectric properties of the traditional materials but also discover new materials with better properties and lower cost. At the same time, thermoelectric modules have also been improved for record-breaking cooling and power generation performances due to the advance in module fabrication. In this talk, I will present some of the advances in both the materials and devices.

4:00 PM EN08.10.07
A Path to Sustainable and Scalable Production of High-Performance Thermoelectric Materials
Maria Ibáñez\(^1\), Tobias Kleinmanns\(^2\), Francesco Milillo\(^3\), Mariano Calcabrini\(^1\), Christine Fiedler\(^4\), Sharona Horta\(^5\) and Daniel Balazs\(^6\); 1ISTA, Austria; 2UNIBA, Italy

Over the past few years, there has been a significant surge in interest surrounding solution-based techniques due to their cost-effectiveness and scalability in the production of high-performance thermoelectric materials. This approach involves the synthesis of particles in a solution, followed by their purification and thermal processing to yield the desired dense polycrystalline material. In contrast to traditional methods, solution-based syntheses offer the ability to manipulate particle characteristics, including size, shape, crystal structure, composition, and surface chemistry, to an unprecedented degree. This fine-tuned control over powder properties opens up distinct opportunities for crafting thermoelectric materials with meticulously controlled microstructural attributes.

In this presentation, our primary focus will be on Ag$_2$Se, an important thermoelectric material for harnessing thermoelectricity at or near room temperature, an area where the selection of high-performance materials is currently limited. While Ag$_2$Se shows great promise, the main problems are the large discrepancy in the reported thermoelectric properties and difficulties in replicating its exceptional performance. These discrepancies often stem from defects within the material, such as vacancies, interstitial atoms, dislocations, grain boundaries, and precipitates.

We will show that our solution-based synthesis method enables precise defect control, especially avoiding fluctuations in stoichiometry. Additionally, we will illustrate how we can fine-tune microstructural defects, including strain, dislocations, and grain boundary density, leveraging the characteristic phase transition of Ag$_2$Se during the sintering process. Our results will highlight that besides stoichiometry, the microstructure is crucial for tuning Ag$_2$Se transport properties and how this control can be provided by our novel synthetic route. Furthermore, we will highlight the sustainability and scalability of our approach, where solvents can be recycled and energy consumption minimized, contributing to a more environmentally friendly production process.

4:15 PM EN08.10.08
Optimization of Sb$_2$Te$_3$ and Bi$_2$Te$_3$ Thermoelectric Films for Infrared Detection and Energy Harvesting
Rugman Zahir\(^1\), Robert E. Peale\(^1,2\), Javier Gonzalez\(^2\), Darian Smalley\(^1\), Masahiro Ishigami\(^1\), Akash Hari Bharath\(^1\), Kalpathy Sundaram\(^1\) and Edgar Nino\(^1\); 1University of Central Florida, United States; 2Truventic LLC, United States

We are developing antenna-coupled thermoelectric junctions for infrared detection and energy harvesting. COMSOL Multiphysics simulations identify Sb$_2$Te$_3$ and Bi$_2$Te$_3$ thermoelectric materials as ideal for the thermocouple junction at the antenna feed. Joule heating at the antenna feed from currents induced by antenna-collected radiation generates thermoelectric voltage and current for detection and energy conversion. In this work, we optimized the properties of RF sputtered telluride films for these applications. We performed a two-level full factorial optimization experiment with three factors: Argon gas pressure, substrate temperature, and RF power. Their low and high values were 7 and 8 mTorr, 175 and 225 deg C, and 15 and 25 W, respectively. The resulting eight depositions were performed using glass substrates in randomized order. A mid-point deposition at 7.5 mTorr, 200 deg C, and 20 W RF power was performed to reveal curvature in the main effects. We found for Sb$_2$Te$_3$ a maximum Seebeck coefficient of 149 μV/K, minimum resistivity 88 μΩ·m, and a maximum power factor (squared Seebeck coefficient over thermal conductivity).
Cu$_2$ZnSiTe$_4$: A Potential Thermoelectric Material with Promising Electronic Transport

Sanghyeon Lee; Yonsei University, Korea (the Republic of)

In this presentation, we report a new high-performance n-type PbSe thermoelectric system embedded with a very low concentration nanoscale, semiconducting alloys. Through atomic-resolved experiments, we found that the heavy chalcogen 'Te' atom, contributes to the comparatively low bandgap of 0.58 eV. This results in a promising power factor of 3.95 (n-type) and 3.06 (p-type) nWm$^{-1}$K$^{-2}$ at 900 K, together with a favourable electronic band topology. Additionally, 'Te' atoms are responsible for the mixing of the optical and acoustic phonon branches, which act as a high temperature results in low lattice thermal conductivity (about 0.7 mWm$^{-1}$K$^{-1}$). The compound yields a promising TE figure of merit (ZT) of 2.67 (n-type) and 2.11 (p-type) at 900 K. We predict Cu$_2$ZnSiTe$_4$ as a viable option for TE applications. We believe our study will motivate experimentalists to explore this compound for future investigation for TE applications.

5:00 PM EN08.11.09

Cu$_2$ZnSiTe$_4$: A Potential Thermoelectric Material with Promising Electronic Transport

Himanshu Sharma, Bhawna Sahni, Tanusri Saha-Dasgupta and Aftab Alam; Indian Institute of Technology, Mumbai, India; 2University of Warwick, United Kingdom; 3S. N. Bose National Centre for Basic Sciences, Kolkata, India

Transition metal-based quaternary chalcogenides have attracted a lot of interest for a variety of renewable energy applications, especially thermoelectrics (TE). Although this class of compounds have low symmetry and complex structure which contribute to low lattice thermal conductivity, achieving a high figure of merit (ZT), is still a challenge for this class of materials. Here, we present a new high-performance n-type PbSe-based thermoelectric material, Cu$_2$ZnSiTe$_4$, with a high figure of merit (ZT). The compound yields a promising TE figure of merit (ZT) of 2.67 (n-type) and 2.11 (p-type) at 900 K. We predict Cu$_2$ZnSiTe$_4$ as a viable option for TE applications. We believe our study will motivate experimentalists to explore this compound for future investigation for TE applications.

5:00 PM EN08.11.11

High Thermoelectric Performance in n-Type PbSe via Embedding Coherent Nanostructure

Hyunsook Lee and In Chung; Seoul National University, Korea (the Republic of)

PbSe has been regarded as a potential candidate for replacing state-of-the-art thermoelectric (TE) PbTe-based materials, owing to the scarcity of Te. In contrast to the progress in a p-type counterpart, effective strategies to enhance TE performance of n-type PbSe have been rare until recently. For example, band convergence to decouple Seebeck coefficients and electrical conductivity for higher power factor has not been possible because of a large energy gap between first and second conduction bands. In the case of its p-type version, PbSe has been regarded as a potential candidate for replacing state-of-the-art PbTe-based materials. In contrast, effective strategies to enhance TE performance of n-type PbSe have been rare until recently. For example, band convergence to decouple Seebeck coefficients and electrical conductivity for higher power factor has not been possible because of a large energy gap between first and second conduction bands. In this presentation, we report a new high-performance n-type PbSe thermoelectric system embedded with a very low concentration nanoscale, semiconducting alloys. Through atomic-resolution TEM, we observed the formation of coherent interfaces between the surrounding matrix and endotaxial nanostructures. The coherent nanostructure provides additional phonon scattering mechanisms induced by mass fluctuation across the interface, remarkably suppressing a lattice thermal conductivity down to ~0.32 W m$^{-1}$ K$^{-1}$. Concurrently, incorporating alloys effectively manipulate the electronic band structure, consequently increasing the conduction band effective mass maximum and a magnitude of Seebeck coefficient. Both effects synergistically improve the TE performance, showing a record-high TE figure of merit, ZT, of ~2.0 at 823 K, for all n-type PbSe and PbTe-based materials to date. This result shows that the strategy of designing coherent endotaxial nanostructures could be an effective means of controlling electrical and thermal transport properties independently.

SESSION EN08.12: Topological Materials

Session Chairs: Ernst Bauer and Kornelius Nielsh

Friday Morning, April 26, 2024
Room 336, Level 3, Summit
Thermoelectric materials attract great interest due to their promising application to power generation and Peltier cooling devices. Semiconductor thermoelectric has been mainstream thus far, since the existence of a bandgap makes a large thermopower ($S$) and thermal conductivity high ($\kappa$). Semiconductor physics predicts that the carrier concentration of around $10^{19}$ cm$^{-3}$ is appropriate to achieve high $S \approx 200 \mu$V/K, and high conductivity ($\sigma$) $\times 10^3 \Omega^{-1}$ cm$^{-1}$. Bi$_2$Te$_3$, the most representative thermoelectric material thus far, well exemplifies the prediction and shows the best thermoelectricity around 300 K. On the other hand, semimetals, in which electrons and holes necessarily coexist, have been out of range of the searching field for the thermoelectric materials, since the compensation between electrons and holes degrades the net $S$.

We have recently discovered that a transition-metal chalcogenide Ta$_2$PdSe$_6$ exhibits an extraordinary thermoelectric property despite its semimetal character [1][2]. Ta$_2$PdSe$_6$ crystallizes in a layered structure, each layer of which consists of quasi-one-dimensional chains formed by prismatic TaSe$_6$ and square-planer PdSe$_6$. The thermoelectric property measured along this direction is highly exotic; an ultra-high $S$ above $10^4 \Omega^{-1}$ cm$^{-1}$ is compatible with a substantial $\kappa$ of $40 \mu$W/K cm at 20K. As a result, the Peltier conductivity $P(\approx S\sigma)$ is the highest among the thermoelectric materials thus far. The value of 100 Acm$^{-1}$K$^{-1}$ means that a 1cc sample can generate a current of 100 A when it is put across a temperature difference of 1 K. Furthermore, we have found that thermoelectric property of Ta$_2$PdSe$_6$ is relatively small (100 Wm$^{-1}$K$^{-1}$) for such good electrical conductor associated with significant violation of the Wiedemann-Franz law. As a result, the thermoelectric figure of merit $z(=S^2\sigma/\kappa)$ of Ta$_2$PdSe$_6$ at 13 K becomes as high as 0.04, which is comparable to the value of Bi$_2$Te$_3$ at 300 K. Roughly speaking, 60 times larger thermal conductivity is cancelled by 60 times larger power factor ($=S^2\sigma$) in Ta$_2$PdSe$_6$ as compared Bi$_2$Te$_3$. The comparable $z$ from distinct transport parameters strongly indicates a new design rule of high-performance thermoelectric semimetals. In the presentation, we will discuss the origin of the anomalous transport properties of Ta$_2$PdSe$_6$ from the viewpoint of the carrier dynamics.

Some of the best thermoelectric (TE) materials to date are also topological insulators (TIs). While many studies have investigated the effects of topologically-protected surface states on TE properties, it is still unclear how the bulk band structure of a TI can benefit the TE performance. Here, we perform high-throughput transport calculations using density functional theory (DFT) to reveal that TIs, when properly optimized, tend to outperform normal insulators as TEs. Models based on Boltzmann transport theory show that warping driven by band inversion, a key characteristic of TIs, is beneficial for TE performance because of reduced transport mass and effectively higher valley degeneracy. The model also reveals that the band inversion strength is a critical material property dictating the TE performance, where TIs with strongly inverted bands exhibit higher $z$. We suggest potential avenues for tuning the band inversion strength and, as a result, enhancing the TE performance in TIs, such as alloying and strain engineering. Our study marks TI as a serious candidate for TE applications owing to band inversion-driven warping.

Thermoelectric materials which undergo dynamic phase conversion through Cu$_2$Se alloying. The addition of Cu$_2$Se enhances electrical transport properties while reducing lattice thermal conductivity. At elevated temperatures, the material undergoes dynamic changes in its phase compositions, achieving a promising $zT$ for n-type systems of ~1.63 at 823 K for intermediate-temperature applications. Transitioning to p-type lead chalcogenides, these materials exhibit superior thermoelectric performance due to valence band conversion. Improvements on n-type materials are more difficult because of the absence of easy electronic band conversion. However, introducing GaSb doping into their n-type counterparts has led to significant improvements as well. This intervention causes conduction band conversion and increases the average power factor, culminating in a high $zT$ of across a wide temperature range. Building on our previous results, we have also explored the fascinating domain of entropy-enhanced materials, using the PbGeSnCdxTe3(1-x) family as a case study. The high-entropy effect from alloying not only stabilizes the material's cubic phase but also significantly improves thermoelectric properties to a maximum $zT$ of 1.63 at 875 K. PbS-based compounds are less well-developed by can become key players in this arena. By alloying PbS with GeS, we achieved a multi-tiered optimization of its electrical and thermal transport properties, involving Ge$^2+$ substitution, the formation of a secondary phase of PbS+GeS12, and enhanced electron mobility. The resultant 14% GeS-alloyed samples yield a $zT$ of 1.32 at 923 K, outperforming standard PbS-based PbS by approximately 55% and setting a new benchmark for n-type PbS-based thermoelectric systems. This presentation aims to provide new insights and spark interdisciplinary discussions on optimizing thermoelectric materials for a sustainable energy future.

References
Alternative thermoelectric materials can substitute the commercially dominant bismuth telluride technology that are highly desirable for heat conversion and thermal management applications. Magnesium silicide based solid solutions Mg2X (X = Si, Ge, Sn) are among the most promising thermoelectric (TE) materials due to their high thermoelectric efficiency.

However, stable thermoelectric properties are of utmost importance for successful large-scale application. Intrinsic defects like Mg interstitials and Mg vacancies affect the properties of Mg2X significantly, therefore Mg diffusion is a potential concern here. Annealing experiments and in-situ measurements at high temperature show that degradation of Mg2X is a two-step process, where in the first step loosely bound excess Mg sublatures from the surface, reducing the charge carrier concentration, and only in the second step, after the solubility limit of Mg vacancies has been reached, Mg2X decomposes into other phases. Variation of the annealing temperature allows us to develop a kinetic model which can be used to predict material stability at different application temperatures, we also find indications that this process can be decelerated by sealing of the surfaces.

In this work, we image the thermal conductivity of individual grain boundaries via spatially resolved frequency-domain thermoreflectance. Measurements with microscale resolution reveal a crucial perspective to enable grain-boundary engineering for the next generation of high-performance thermoelectrics.

Grain boundaries have a central importance in materials science. They can critically control thermal and electronic transport, determining the performance of energy and electronic materials. In thermoelectric materials, grain boundaries can be leveraged to suppress the thermal conductivity, but can also detrimentally suppress the carrier mobility. Grain boundaries are not all equal: all grain boundaries behave the same: misorientation angle, symmetry, and morphology are found to strongly correlate with the effective thermal boundary resistance. Extracting transport properties from microscale imaging can provide comprehensive understanding of how microstructure works. This development can improve our understanding of carrier-defect interactions, advancing the engineering of materials for thermoelectrics.

### 2:00 PM EN08.14.02

**Optimization Study of \( (T_{\text{hH}})_{\text{Fe}} \) Half-Heusler Thin Films Using CombinatorialSynthesis, High-Throughput Power Factor Mapping and Thermorelectroconductance**

**Thermal Conductivity Property Measurements**

Dylan J. Kirsch, 1,2; Joshua Martin, 1; Nathan Johnson, 1; Chasimitha Sarker, 1; Rohit Pant, 1; Ronald Warzoha, 1; Apurva Mehta, 1 and Ichiro Takeuchi, 1; 1Northwestern University, United States; 2Michigan State University, United States

The Seebeck coefficient and electrical resistivity were measured using our custom-built high-throughput scanning probe. Thermal conductivity and heat capacity were measured on our discrete combinatorial hH thin films using a custom-built, automated Frequency Domain Thermoreflectance (FDTR) instrument. Maximum TE figure-of-merit \( zT \) values at room temperature are calculated to be \( >0.08 \) for compositions \((Nb_{0.41}Ta_{0.33}Ti_{0.26})_{28.5}Fe_{40.3}Sb_{31.2}\) and \((Nb_{0.42}Ta_{0.33}Ti_{0.25})_{35.0}Fe_{31.7}Sb_{33.3}\) having thermal conductivity values \( <2.25 \pm 0.27 \) W m\(^{-1}\) K\(^{-1}\). Our custom suite of high-throughput combinatorial instruments can now measure all of the properties needed to calculate the \( zT \) of any promising and unoptimized TE material system.

### 2:15 PM EN08.14.03

**Microscale Imaging of Thermal Conductivity Compression at Grain Boundaries**

Eleonora Isotta, 1, Shizhou Jiang, 1, Alexandra Zevalkink, 2, Jeff Snyder, 3 and Oluwaseyi Balogun, 1

Grain boundaries have a central importance in materials science. They can critically control thermal and electrical transport, determining the performance of energy and electronic materials. In thermoelectric materials, grain boundaries can be leveraged to suppress the thermal conductivity, but can also detrimentally suppress the carrier mobility. Grain boundaries are not all equal: they are associated to several degrees of freedom, and can come in multiple orientations, symmetries, and chemistries. Recent evidence suggests that some types of grain boundaries could be more beneficial than others for the thermoelectric performance. Despite the importance, we lack a clear understanding of how grain boundaries modify the microscale transport owing to the scarcity of local investigations. Usually the role of grain boundaries is inferred from bulk, effective measurements. However, understanding how grain boundaries impact transport locally is a crucial perspective to enable grain-boundary engineering for the next generation of high-performance thermoelectrics.

In this work, we image the thermal conductivity of individual grain boundaries via spatially-resolved frequency-domain thermoreflectance. Measurements with microscale resolution reveal a suppression in thermal conductivity at grain boundaries both in thermoelectric SnTe and multicrystalline silicon. In contrast to conventional thermal modeling, which assumes that all boundaries are perfect scatterers and lead to uniformly suppressed thermal conductivity, we observe a non-uniform suppression localized within a few microns of a boundary. Furthermore, not all grain boundaries behave the same: misorientation angle, symmetry, and morphology are found to strongly correlate with the effective thermal boundary resistance. Extracting transport properties from microscale imaging can provide comprehensive understanding of how microstructure works. This development can improve our understanding of carrier-defect interactions, advancing the engineering of materials for thermoelectrics.

### 2:30 PM EN08.14.04

**Using Bulk Thermoelectric Measurements to Identify Grain Boundary Transitions in NbFeSb**

Duncan Zavaneli, 1, Ruben Bueno Villoro, 2; Ran He, 1 and Jeff Snyder, 1; 1Northwestern University, United States; 2Max-Planck-Institut für Eisenforschung GmbH, Germany

Grain boundaries have seen much recent interest for improving the performance of thermoelectrics, with their capacity to reduce thermal conductivity. Thermally activated charge carrier scattering from grain boundaries is detrimental to performance, far outweighing the benefits to thermal conductivity in many materials. If charge scattering of grain boundaries could be reduced or eliminated, then reducing grain size could be used to improve the thermal properties of many thermoelectrics. In half-Heusler materials, experimental observations have shown that compositional changes at the grain boundary from dopant segregation are correlated to a reduction in the detrimental scattering from boundaries. However, there is currently no good method to identify this behavior based on bulk thermoelectric measurements. In this presentation, we propose a method to model the behavior of grain boundaries such that transitions in grain boundary properties can be identified. This enables the identification of changes in chemistry or structure of grain boundaries prior to in depth characterization of individual grain boundaries in the material.
Heusler intermetallic compounds present a wide variety of compositions that fulfill the requirement of avoiding toxic or scarce elements. The Fe2VAl family of Heusler alloys shows a large potential and versatility for thermoelectric thin films with tunable properties via doping with additional elements such as Ti, Ta, Si, and others [1-3]. The doping allows the fabrication of p- and n-type alloys in the same family, which simplifies future thermoelectric device fabrication. While the undoped alloy Fe2VAl is a p-type material, the introduction of W, Si, or Ta results in a n-type one. P-type alloys are obtained with Ti and Zr, both with an increase in Seebeck values compared to the undoped case. The addition of these materials can also be performed in an off-stoichiometric manner [4,5].

Sputter deposition is a well-established, inexpensive, and very versatile technique for the fabrication of a wide variety of material systems. The chemical composition can be highly controlled by the simultaneous use of several magnetrons with different elements (codeposition) to achieve the desired film content or doping concentration, which is needed to optimize the thermoelectric properties [6]. From a fundamental point of view, the possibility to explore the influence of crystal orientation on thermoelectric performance is very appealing, offering a perfect scope for experiment versus theory comparison. In this sense, physical vapor deposition techniques are excellent tools for obtaining thin films with desired orientations through the use of adequate substrates in terms of crystal symmetry and lattice match. In this contribution, we present results on Fe2VAl thin films fabricated by magnetron dc sputtering. Two different sample series have been prepared with varying deposition temperatures (RT-950°C) and with two different substrates and, consequently, two crystalline orientations owing to the different epitaxial relations. Films grown on MgO (100) are (100)-oriented, while Al2O3 (11-20) substrates induce a (110) orientation. In both cases, the (111) diffraction peak Fe2VAl corresponding to the L21 fully ordered phase can be observed in asymmetric configuration diffraction measurements.

The results of the characterization of the thin films with X-Ray Diffraction and SEM imaging are shown, proving epitaxial growth for both series. The electric conductivity, Seebeck parameter, and power factor are reported. We observe a large difference in the thermoelectric performance depending on the growth orientation of the films. With these results, we prove the large potential of sputtering to produce high-quality Fe2VAl films ready for further desired compositional variation and tuned doping via codeposition.

References


Acknowledgments

Financial support by the Ministerio de Ciencia e Innovación with the ThermHeus (TED2021-131746B-I00) project and the ERC Advanced Grant POWERbyU (ERC-2021-ADG-101052603) is acknowledged. We acknowledge the service from the MiNa Laboratory at IMN, and funding from CM (project S2018/NMT-4291 TEC2SPACE), MINECO (project CSIC13-4E-1794) and EU (FEDER, FSE).

3:00 PM BREAK

SESSION EN08.15: Sustainable and Flexible Modules
Session Chairs: Jan-Willem Bos and Tsutomu Kanno
Friday Afternoon, April 26, 2024
Room 336, Level 3, Summit

3:30 PM EN08.15.01
Heat Conduction in a Printed Thermoelectric Film Koji Miyazaki: Kyushu University, Japan

We have developed printed thermoelectric thin films using inorganic materials such as Bismuth Telluride. The process involved crushing the material into fine powders and mixing it with polymeric acid in an organic solvent. The resulting viscous solution was screen-printed onto a substrate and annealed in an Argon atmosphere. The heated polymeric acid transformed into polyanide at 400°C, acting as an adhesive between the thermoelectric powders. However, we found that the electrical conductivity of the resulting film was very low due to the low packing density. To address this issue, we decided to create a composite material by incorporating printable materials. We chose the lead-free halide perovskite, CsSnI3, which displayed relatively good thermoelectric properties as a printable material. We mixed the Halide perovskite into the Bismuth Telluride solutions and printed them onto the substrate. After heating the film on a hotplate, the halide perovskite precipitated in the pores, resulting in a composite film of Bi2Te3/CsSnI3. This composite film displayed improved electrical conductivity and low thermal conductivity, while the Seebeck coefficient slightly decreased. We also found that the thermal conductivities of both Bismuth telluride and Halide perovskite were low, and the high interfacial thermal resistance between them was measured to be in the order of 10^3K/(m2W). This high interfacial thermal resistance explained the low thermal conductivity of the composite film, following a conventional model with interfacial thermal resistance. Ab initio calculations helped us understand the mechanisms behind the high interfacial thermal resistance. We believe that our printing process can be applied to other thermoelectric materials, allowing us to create film-shaped thermoelectric generators. Then, we applied the present printing technique to Cobalt antimonide Skutterudite. The Cobalt antimonide shows a high power factor at room temperature although thermal conductivity is also high. The effective thermal conductivity of the printed film is low, as well as keeping a relatively high power factor at room temperature. The packing density should be increased to improve the electrical conductivity of the printed Cobalt antimonide Skutterudite. This method can be applied to make thermoelectric energy harvester for room temperature use.

4:00 PM EN08.15.02
An Organic Thermoelectric Generator by Local Doping of Highly-Aligned Polymer Films Nathan James Pataki1,2, Shubhradip Guchait3, Martin Brinkmann3 and Mario Caironi1; 1Istituto Italiano di Tecnologia, Italy; 2Politecnico di Milano, Italy; 3Centre National de la Recherche Scientifique (CNRS), France

The growing number of distributed microelectronics in the Internet of Things (IoT) requires versatile, scalable and affordable power sources. Heat-harvesting organic thermoelectric generators (TEGs) are regarded as a potential key component of the future energy landscape. Research surrounding the structure-property relationships in organic thermoelectric materials has led to extraordinary advances in the power factors of preferentially aligned polymer films [1-2], yet there has been little effort to actually leverage these advances and transfer aligned polymer films into a functional TEG. In this work, we previously reported shear-force method is used to induce in-plane orientation of regioregular poly[(3-hexylthiophene) (P3HT)] and poly[6,6-bis[3-phenyl-2-yl]thieno[3,2-b][1,4] thiophene (PBTBT)] films which are then floated onto ultrathin parylene substrates. A scalable inkjet printing method along with an ink formulation of the p-type dopant tris(4-bromophenyl)ammonium hexachlororanionitromine), known as magic blue (MB), enabled high-precision local doping of the oriented polymer films to pattern a conductive TEG architecture. This novel fabrication method was used to scale the oriented TEGs up to 10 thermoelectric couples resulting in a maximum power output of 1.1 mW and an open circuit voltage of 0.6 mV at ΔT=50K. This work represents the first example of an oriented TEG and demonstrates the value of local doping as a precise and scalable fabrication method for future TEGs.


4:15 PM EN08.15.03
2D/3D-Printed Bismuth Telluride-Based Flexible Thermoelectrics for Low-Scale Energy Harvesting Francisco Molina-Lopez: KU Leuven, Belgium
The swift development of the Internet of Things (IoT) and wearable electronics is urgently demanding innovative power solutions. Batteries alone can barely satisfy this demand for two main reasons: Firstly, battery replacement limits the implementation of some scenarios of IoT in which nodes might be highly distributed in difficult access locations; Secondly, batteries are often too bulky and rigid to be seamlessly integrated on thin and soft wearable electronics, or small IoT nodes. Thermoelectric generators (TEGs) refer to renewable power sources able to assist or even replace batteries by generating electricity from the abundant waste heat in the environment. Conveniently, it has been suggested that for low-power applications, TEs can surpass other thermal engines in terms of efficiency. [1] Furthermore, TEs are also capable of on-demand cooling and heating. However, to meet the form factor required by the IoT and wearables (namely repeated bendability/stretchability, conformability to curved surfaces, and large areas), important advancements must be made on traditional TEGs, which are rigid, and hard to scale up to large-area devices.[2]

My group is working towards the development of high-performance thermoelectric materials that can be directly 2D- or 3D-printed on flexible substrates. In particular, I will describe our progress in the formulation of bismuth telluride powder as a printable paste/ink, and the process of selective laser sintering and the direct ink writing (DIW) to form in-plane and through-plane TEGs, respectively. Printing techniques can potentially reduce the material waste and cost of TEGs. Moreover, in combination with a flexible substrate, printing enables innovative device architectures, such as large-area and flexible devices that can be easily integrated on the skin/smart textiles to power wearables using the heat emitted by the human body, as well as adapt to hot curved surfaces, like hot pipes or engines, to power IoT nodes. Because we target energy harvesting around room temperature, bismuth telluride is used as a benchmark material to showcase our processes and device architectures. However, our technology is likewise compatible with emerging polymeric materials, which will also be presented for comparison. If successful, this line of research will holistically tackle the main bottlenecks of TEGs, paving the way to their broad implementation in wearables and other low-power energy harvesting applications.

Acknowledgments
This work was supported by the European Research Council (ERC) un-der the European Union’s Horizon 2020 research and innovation pro-gramme: Grant Agreement No. 948922 – 3DALIGN; the Research Foundation - Flanders (project number 11E2621N); and the Internal Funds KU Leuven, C1 project C14/21/078.


4:45 PM EN08.15.04
Electrodeposited Silver Selenide Films: From Pourbaix Diagram to a Flexible Thermoelectric Module
Cristina V. Manzano, Cristina Llorente del Olmo, Olga Caballero-Calero and Marisol Martin-Gonzalez; Institute of Micro and Nanotechnology, Spain

In the last few years, the exploration of new thermoelectric materials with low-toxicity, earth-abundance, and high-efficiency has become essential. Following this trend, sustainable, easily scalable, and cost-effective fabrication methods, such as electrochemical deposition, are also desirable. In this work, the Pourbaix diagram of silver–selenium–water was developed to find an adequate pH and reduction potential for the electrodeposition of stable silver selenide. Based on this diagram, a solution without the incorporation of additives was developed. Silver selenide films were electrodeposited at different reduction potentials, and after the deposition, compositional, morphological, and structural characterizations of the silver selenide thin films were analysed. The thermoelectric properties of the electrodeposited silver selenide films were measured at room temperature. The maximum power factor was found for the films grown at 0.071 V with a value of 3421 ± 705 mW/mK² and a thermal conductivity of 0.56 ± 0.06 W/mK. Even better, when it can be done by employing a technique that is easily scalable to an industrial level analysing. The thermoelectric properties of the electrodeposited silver selenide films were measured at room temperature. The maximum power factor was found for the films grown at 0.071 V with a value of 3421 ± 705 mW/mK² and a thermal conductivity of 0.56 ± 0.06 W/mK. Even better, when it can be done by employing a technique that is easily scalable to an industrial level.

SYMPOSIUM EN09
Nanostructured Electrocatalysts for Energy Applications
April 23 - May 8, 2024

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* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
Phase Engineering of Nanomaterials (PEN) Hua Zhang,1,2; 1City University of Hong Kong, China; 2City University of Hong Kong Shenzhen Research Institute, China

In this talk, I will summarize the recent research on phase engineering of nanomaterials (PEN) in my group, particularly focusing on the rational design and synthesis of novel nanomaterials with unconventional phases for various promising applications. For example, by using wet-chemical methods, we have successfully prepared novel Au nanostuctures (e.g., the hexagonal-close-packed (hcp) 2H-Au nanosheets, 4H-Au nanoribbons, and crystal-phase heterostructured 4H/fcc/2H/crystalline heterophase Au nanorods), epitaxially grown metal nanostuctures on the aforementioned unconventional Au nanostructures and 2H-Pd nanoparticles, and amorphous/crystalline heterophase Pd, PdCu, Rh and Rh alloy nanosheets. In addition, by using gas-solid reactions, metastable 1T-phase group VI transition metal dichalcogenides (TMDs), e.g., WS2, WSe2, MoS2, MoSe2, W8S8Se2, and MoS2, have been prepared. Moreover, the salt-assisted 2H-to-1T phase transformation of TMDs have been achieved, and the phase transformation of TMDs during our developed electrochemical Li-intercalation process has been observed. Impressively, the lithiation-induced amorphization of Pd3P2S8 has been achieved. Currently, my group focuses on the investigation of phase-dependent physicochemical properties and applications in catalysis, (opto-)electronic devices, clean energy, chemical and biosensors, surface enhanced Raman scattering, photothermal therapy, etc., which we believe is qualitatively quite and very important not only in fundamental studies, but also in future practical applications. Importantly, the concepts of phase engineering of nanomaterials (PEN), crystal-phase heterostructures, and heterophase nanomaterials are proposed.
1:30 PM EN09.02.01
Ordered Metal Nanowire Networks for High Performance Catalytic Electrodes Adam Squires; University of Bath, United Kingdom

We present a new method for the production of ordered 3D metal-nanowire network films using a coating of lipid inverse cubic phase as the template for electrodeposition. We have produced platinum films which show a previously unreported "single diamond" nanochannel architecture with tunable nm-scale pore and wire diameters, and lattice parameters down to below 10 nm. The nanochannel architecture gives high electrocatalytic performance and stability towards fuel cell oxidation reactions; and the production and removal of the template is facile, using mild conditions and green solvents (water, ethanol) in simple half-hour steps, representing an attractive route to high performance nanomaterials.

1:45 PM EN09.02.02
Fast and Facile Microwave Synthesis of Cubic CuFe2O4 Nanoparticles for Electrochemical CO2 Reduction Judith Zander and Roland Marschall; University of Bayreuth, Germany

Electrochemical CO2 reduction is a promising strategy for the sustainable synthesis of carbon-based chemicals or fuels such as CO, or CH3[1] Copper-based materials are of special interest due to their broad substrate scope. While copper itself is the first known metal catalyst able to directly yield CH4, CO, methanol, or C2-, products such as ethanol can also be obtained, e.g. from oxide derived catalysts.[2][3] Another interesting copper oxide is the spinel CuFe2O4, due to its versatile electronic and magnetic properties. Those can be tuned via variations in the cation distribution between octahedral and tetrahedral sites.[4] Changes in the cation distribution, or degree of inversion, can additionally lead to a structural transformation between the cubic and tetragonal form, due to the strong Jahn-Teller effect of Cu2+. Both degree of inversion and structure are strongly dependent on the synthesis conditions.[4] In this contribution we introduce a fast microwave-assisted solvothermal synthesis of cubic CuFe2O4. Very short synthesis times of 1 min and low temperatures of 120 °C in ethylene-glycol/water mixtures could be realised, without a loss of phase-purity and no necessity for subsequent thermal treatment.[5] The degree of inversion was found to decrease with increasing synthesis time, whereas the particle size and crystallinity was almost independent of the synthesis conditions. The influence of the synthesis conditions – and thus material properties – on the activity in electrochemical CO2 reduction to CO in 0.1 M KHCO3 was investigated. The best activity was obtained for CuFe2O4 with an intermediate degree of inversion of approx. 0.75, together with a large crystallite size and micro-strain. Since hydrogen was produced as the only site-product, CuFe2O4 can be an interesting candidate for the production of syngas.

References:
The water oxidation to extract electrons from water molecules for the oxygen evolution reaction (OER) is essential for the development of a sustainable system to synthesize valuable chemicals such as hydrogen and organic compounds from H2O and CO2. The catalysts consisting of earth-abundant elements are required for the system integration with minimized cost and total CO2 emission in its lifecycle.

We have developed a 10 nm-sized highly crystalline red rust catalyst for OER composed of pure β-phase FeOOH(Cl) hyperfine nanorods (an average diameter of 3 nm and a length of 14 nm) synthesized by a facile one-pot process at room temperature and ambient pressure. [1] This one-pot process yields β-FeOOH(Cl) nanorods sizes more than 10 times smaller than those by conventional methods. The process also enables doping with Ni ions in the crystal lattice (β-FeOOH(Cl)/Ni) and simultaneous surface-coating with amorphous a-Ni(OH)2 (a Ni to Fe ratio up to 22 at%), which forms a core/shell structure. [2] The overpotential for electrochemical OER over anodes stacked with the core-shell β-FeOOH:Ni/a-Ni(OH)2 was 170 mV, and an OER current of 10 mA/cm2 was obtained at an overpotential of 430 mV in a 0.1 M KOH solution. The high current density at low potential compared with many Fe-rich oxide and (oxy)hydroxide electrodes reported previously.

X-ray absorption fine structure analysis (XAS), Mössbauer spectroscopy, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and impedance spectroscopy suggested that surface coating with the a-Ni(OH)2 lowered the OER overpotential of β-FeOOH(Cl), resulting in reduced total impedance in the electrode. Mössbauer spectroscopy suggested interaction between Fe and Ni species [2], and operando X-ray absorption spectroscopy (XAS) under biased conditions in the aqueous solution revealed a characteristic behavior that does not occur in Fe-Ni mixed oxide systems. [3] The nearest neighbor structure and valence of Fe3+ ions did not change under the OER conditions. In contrast, Ni ions showed second nearest neighbor ordering which was assignable to β-Ni(OH)2, and a fraction of Ni2+ ions was partially oxidized to Ni3+ at the bias for OER. This is presumably the change at the interface of the β-FeOOH:Ni nanorods and the surface a-Ni(OH)2. This Ni valence change was reversible, following the sweep of the electrical bias. These findings show an essential role of Fe-Ni interactions in the core/shell β-FeOOH:Ni/a-Ni(OH)2 accompanied by Ni species' structural and partial valence change under the electrical bias.

Further, after treatment in an alkaline solution of the β-FeOOH:Ni/a-Ni(OH)2, accompanied by Ni species' structural and partial valence change under the electrical bias.

Efficient and long-lasting electrocatalysts with superior performance are essential for the efficient and sustainable production of green hydrogen, ensuring high yield and minimal energy consumption. Electrocatalysts based on transition metal oxides have a significant advantage due to their abundant natural resources, adjustable physical properties, and their compatibility with various solutions. Among the various oxide catalyst materials, ferroelectrics have received attention for their semiconducting properties and switchable spontaneous polarization, particularly as promising photoredox catalysts in solar water splitting. However, their potential as electrocatalysts has been largely overlooked until now. Here we present an effective electrocatalytic electrode composed of a BiFeO3/nickel foam heterostructure. This heterostructure exhibits a lower overpotential and higher current density compared to a bare nickel foam electrode. Additionally, when in contact with an alkaline solution, the interaction between hydroxyls and the BiFeO3 surface induces a significant area of upward self-polarization. This phenomenon reduces the adsorption energy of subsequent adsorbates and enhances the efficiency of the oxygen and hydrogen evolution reactions. Our work illustrates a unique approach, utilizing functional semiconductor materials for the development of highly efficient electrocatalytic electrodes.
Photocatalysts often have limited light absorption capabilities and suffer from rapid electron hole recombination [1]. This issue can potentially be addressed through suitable band edge line-up of two or more semiconductors, particularly z-scheme systems, which have superior charge separation and light harvesting properties [2]. The present study explores a z-scheme system with CBO (Copper bismuth oxide) and MoS2 (molybdenum sulfide), which have good light harvesting abilities and efficient charge separation. CBO has a narrow bandgap, good light harvesting capability, and high negative conduction band potential [3]. However, pristine CBO has high charge recombination and unfavourable band edge line-up with the water oxidation reaction. MoS2, a 2D material is recognized as an excellent co-catalyst for advanced oxidative processes with improved light harvesting, efficient interface charge transfer, and separation [4]. CBO@MoS2 is synthesized using two step hydrothermal method. The synthesized catalyst is characterized using several techniques, including XRD, Raman, PL, UV-Vis, and TEM. The catalyst has shown a significantly higher H2O2 production rate of 1457 µM h⁻¹ and a current density of -1.6 mA cm⁻² at 0.2 V, both of which are an order of magnitude higher than the pure components. The improved photocatalytic activity of CBO@MoS2 is mainly attributed to the efficient separation of the electron-holes pair due to staggered band alignment and the z-scheme heterojunction that retains the strong redox ability of both CBO and MoS2. Mechanistic insight in H2O2 production is also provided using mott–schottky analysis, scavenger study and kinetic modelling.

References

5:00 PM EN09.04.06
Schiff Bases Complexes prepared from Polyethylene Terephthalate and Amine for Alkaline Water Electrolysis

Tu Huan Chiang and Si-Rong Xu; National United University, Taiwan

Alkaline water electrolysis is considered a viable technology for large-scale hydrogen production due to its use of non-precious metal catalysts. This process involves two half-slow-rate electrochemical reactions, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). In contrast to non-precious metal electrocatalysts, typically employed for acid-media reactions where slow electrochemical activities, precious metals like Ir/Ru compounds for OER and Pt for HER are used. However, relying on such relatively scarce and precious metals is unviable for this technology. In this context, molybdenum (Mo)-based electrocatalysts materials are very promising and are currently attracting a growing interest in the energy field. Transition metal carbides and nitrides demonstrate very interesting electrocatalytic properties, close to those of noble metals, allowing term performances in non-precious metal technologies.

This study investigates metal Schiff base complexes derived from polyethylene terephthalate (PET) and various amines. PET materials have been used for packaging since the 1960s, with interesting alternative to make this technology economically viable. Indeed, transition metal carbides and nitrides demonstrate very interesting electrocatalytic properties, close to those of noble metals. In this context, molybdenum (Mo)-based electrocatalysts materials are very promising and are currently attracting a growing interest in the energy field. Transition metal carbides and nitrides demonstrate very interesting electrocatalytic properties, close to those of noble metals.

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References

5:00 PM EN09.06.05
Laser-Synthesis of Nanostructured Carbides Molybdenum Catalysts for HER/OER Reactions

Guillaume Dubois1, Fabien Grassier2, Corinne Lagrost3, Tetsuo Takahashi4, Yusaku F. Nishimura5, Yoriko Matsuo6 and Takeshi Morikawa7; Toyota Central R&D Labs., Inc., Japan

Molybdenum carbides are recognized as excellent co-catalysts for advanced oxidative processes with improved light harvesting, efficient interface charge transfer, and separation [4]. CBO@MoS2 is synthesized using two step hydrothermal method. The synthesized catalyst is characterized using several techniques, including XRD, Raman, PL, UV-Vis, and TEM. The catalyst has shown a significantly higher H2O2 production rate of 1457 µM h⁻¹ and a current density of -1.6 mA cm⁻² at 0.2 V, both of which are an order of magnitude higher than the pure components. The improved photocatalytic activity of CBO@MoS2 is mainly attributed to the efficient separation of the electron-holes pair due to staggered band alignment and the z-scheme heterojunction that retains the strong redox ability of both CBO and MoS2. Mechanistic insight in H2O2 production is also provided using mott–schottky analysis, scavenger study and kinetic modelling.

References
Sulfur-Doped Activated Carbon derived from Discarded Surgical Masks for High-Performance Supercapacitors Hsiu-Ying Chung and Zhi-Bin Huang; National Sun Yat-sen University, Taiwan

Consumption and discarded face masks are urgently driven by the spread of COVID-19 and the flu epidemic and general medical operations. To reduce the severe environmental pollution, the discarded surgical masks were recycled and subsequently prepared as high-added value supercapacitor electrode materials for energy storage. This study synthesized sulfur-doped activated carbon from the discarded face masks. Additionally, nanoscale manganese oxide was incorporated into sulfur-doped activated carbon to improve the electrochemical properties of supercapacitors. The resulting porous materials were analyzed using SEM, BET and XPS. Due to the synergistic effect of activated carbon and nanomanganese oxide, the capacitance of the hybrid electrode increased by more than 20%, and the capacitance retention rate was approximately 80% after 500 cycles.

5:00 PM EN09.04.07
Mechanistic Insight into Dual-Atom Catalysts for The Oxygen Reduction Reaction Courtney Brea1 and Guoxiang (Emma) Hu2; 1Queens College (City University of New York), United States; 2Georgia Institute of Technology, United States

Incorporating a second transition metal to iron-nitrogen-carbon single-atom catalysts (Fe-N-C SACs) to design dual-atom catalysts (DACs) was demonstrated to offer a promising opportunity to enhance the oxygen reduction reaction (ORR). However, it has been challenging to clearly elucidate the structure–property relationship at the atomic level. Here we apply a computational workflow integrating configuration generations, phase diagram constructions, and reaction free energy calculations to provide an insightful understanding of the active site structures and catalytic mechanisms of ORR on DACs. Using Fe-Cu as an example, we generated all possible configurations by tiling the hexagonal lattice and investigate their atomic structures under incorporation of a second transition metal to iron-nitrogen-carbon SACs. Further analysis reveals a linear correlation between the limiting potential and the magnetic moment on Fe. These mechanistic insights pave the way for the rational design of efficient platinum group metal-free (PGM-free) catalysts for ORR.

5:00 PM EN09.04.08
Electrochemical CO2 Reduction over Nanoparticles derived from an Oxidized Cu–Ni Intermetallic Alloy Tomiko M. Suzuki, Toshitaka Ishizaki, Satoru Kosaka, Naoko Takahashi, Noritake Isomura, Juntaro Seki, Yoriko Matsuoka, Keiichiro Oh-ishi, Ayako Oshima, Kosuke Kitazumi, Keita Sekizawa and Takeshi Morikawa; Toyota Central R&D Labs., Inc., Japan

Research and development on the electrocatalytic CO2 reduction reaction (CO2RR) to valuable hydrocarbons and alcohols has attracted great interest because of the potential to produce sustainable fuels. To date, copper (Cu) and Cu-based compounds are the most studied metal electrocatalysts that have demonstrated the ability to convert CO2 and CO into large amounts of C2 and C3 molecules [1]. Furthermore, studies of Cu particle catalysts have reported that their particle size, crystalline phase, and morphology are highly correlated with C2 selectivity [2]. As one approach to control C2 selectivity on Cu catalysts, the use of Cu-based bimetallic alloys has been reported [3], especially the combination of Cu with CO-producing metal species such as Ag, Au, Zn, and Pd. On the other hand, combinations of Cu with hydrogen-producing elements such as Fe, Ni, and Pt have been reported to improve the activity and selectivity of hydrogen production compared to pure Cu electrodes, making it difficult to improve C2 and C3 activity with these combinations.

In this study, we demonstrate that Ni species have a positive effect on the formation of C2 compounds in the CO2RR of Cu-based catalysts. To avoid size-dependent selectivity of copper catalysts, Cu–Ni interatomic alloy NPs (0-83 at% Ni, NiCu) were tested in fuel cells with diameters around 10 nm were synthesized by one-pot and two-step synthesis using copper(II) acetylacetonate and nickel(II) chloride [4]. Since these Cu-Ni NPs were easily spontaneously oxidized in air at room temperature, these partially oxidized NPs were loaded onto carbon paper supports and used as electrocatalyst.

The electrochemical CO2 reduction reaction was evaluated using a three-electrode system in a closed batch single-compartment reactor filled with 0.05 M KHCO3 aqueous solution bubbled with CO2. Electrolysis was performed at −1.2 V (vs. RHE) using a cathodic electrolyte as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. The CuNi-NP was driven as a catalyst for hydrogen production in the early stages of the electrolysis, but activated into an excellent CO2 reduction catalyst in the subsequent electrolysis. The dependence of the C2 selectivity on the Ni content was investigated using various activated Cu–Ni NPs electrodes. Activated Cu–Ni (3–2 at% Ni) alloy nanoparticles enhance selectivity for ethylene and ethanol formation over oxide-derived Cu nanoparticles by electrocatalytic CO2RR in aqueous solution. The Cu–Ni (19 at%) NPs exhibited 35% efficiency for C2 and the suppression of H2 formation down to 9%. These results demonstrate that the addition of Ni to the Cu NPs facilitates C2 bond formation. The activated catalyst consists of metallic Cu, Cu–O, Ni, and Ni–O species, as confirmed by X-ray absorption spectroscopy measurements [5].

The present research suggests that further investigation is worthwhile to broaden the possibility of an unprecedented oxide-derived Cu–Ni and other CO2RR catalysts.

References

5:00 PM EN09.04.11
Metal Nanoparticles Supported on Hexagonal Boron Nitride Nanosheets as an Efficient Catalysts for Oxygen Evolution Reaction Congoong Ou, George Bepe, Zhuohao Yu, David Sanchez and Mauricio Terrones; The Pennsylvania State University, United States

The oxygen evolution reaction (OER) is a crucial step in the electrochemical water-splitting process that can be used as a competitive and sustainable method for clean energy production, energy storage, and electrochemical sensing applications. However, due to the commonly sluggish kinetics of the OER steps, newer catalytic materials that can lower the reaction overpotential are vital to enhance the overall OER efficiency. In this work, ultrathin hexagonal boron nitride (hBN) nanosheets fabricated by a molten metal assisted intercalation method is used as the supporting structure for metal nanoparticle deposition, then employed as efficient catalyst material for OER in alkaline environments. Different metals and metal combinations including Pt, Pd, Ru, Fe, Ni, NiFe, PtAg, and PdAg are tested in this system as dopant materials. Aligning with the goal of using non-precious metal-based catalysts as the alternative to the current benchmarks of Ir and Ru based OER catalysts, our hBN supported Fe nanoparticle sample exhibited competitive electrochemical performance and low overpotential. Additionally, annealing of the hBN supported Fe sample in Ar at 800°C showed further improvements of such catalytic activity and an increased current density. High-resolution transmission electron microscopy (HRTEM) was done to reveal the structural and crystallinity characteristics of the metallic nanoclusters and/or atomically dispersed metal atoms confined on the hBN framework. X-ray photoelectron spectroscopy (XPS) is carried out to characterize the changes of chemical valence state of the dopant metals before and after annealing to offer more insights into the OER reaction mechanism. Electrochemical cycling testing was conducted to evaluate the stability of the metal-supported hBN catalysts that could be applied to hydrogen fuel cells and/or metal-air batteries.

5:00 PM EN09.04.12
Synthesized Transition Metal-Based Nanosheet Electrocatalysts for Alkaline Water Electrolyzers Seemohan Lee1, In Tae Kim2, Yoo Sei Park2 and Yangdo Kim1; 1Pusan National University, Korea (the republic of); 2Chungbuk National University, Korea (the republic of)

Hydrogen is a completely carbon-free energy source with high energy density and conversion efficiency, and it has become a promising alternative to fossil fuels. The best way to produce green hydrogen without carbon emissions is through water electrolysis. Water electrolysis involves two reactions: the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). Although HER is produce hydrogen, production efficiency is more directly associated with OER. The two most famous water electrolysis technologies are alkaline water electrolyzers (AWEs) and proton exchange membrane water electrolyzers (PEMWEs). The recently developed AEM electrolyzer exhibit both the advantage of AWE, PEM electrolyzers mentioned above. This electrolyzer can greatly reduce the ohmic loss using solid ionomer membrane and is operated in alkaline condition, allowing the use of non-precious metals as electrocatalysts. The performance of AEM water electrolysis is still lower than that of PEM electrolyzers due to the sluggish electrocatalyst kinetics for oxygen evolution reaction (OER). To overcome this obstacle, it is strongly necessary to develop high-performance and cost-effective OER electrocatalysts.

In this study, we developed CuOH2 nanosheets onto ZIF67 for OER electrocatalyst. The obtained material, labeled as CuOH2@ZIF67, improves its conductivity and intrinsic activity. In addition, the AEM electrolyzer equipped with CuOH2@ZIF-100 shows better performance at high current densities than that of RuO2 by reducing the mass transport of the AEM electrolyzer. Our approach is applicable for large-scale hydrogen production as an OER catalyst since it does not require precious metals and enables cost-effective, high-efficiency catalyst production through simple synthesis.

5:00 PM EN09.04.14
Templated Multiwall Polycrystalline MoS2 Nanotubes with Tunable S-Vacancies for High-Performance H2 Evolution Reaction Yang Tian; University of Arkansas, United States

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
As the demand for clean energy intensifies, hydrogen (H₂) is leading a candidate for next-generation energy solutions. Currently, the catalysis for the hydrogen evolution reaction (HER) predominantly relies on noble metals like platinum, which are scarce and economically unsustainable for large-scale applications. Consequently, there's an urgent need for cost-effective, abundant, and efficient catalysts. MoS₂, a low-cost material, has been identified as a potential substitute due to its ability to significantly reduce overpotential in H₂ production. While 2D MoS₂ has demonstrated promising HER results, its synthesis via chemical vapor deposition (CVD) is costly and complex, hindering large-scale production. In this study, we present a novel approach to synthesize templated multiwall polycrystalline MoS₂ nanotubes using hydrothermal methods. Comprehensive characterization using XRD, EDX, and XPS confirmed the successful coating of MoS₂ on Titanate nanofiber supports. By controlling sulfur vacancies on the MoS₂ surface, we can modulate the HER performance. Our optimal conditions yielded an overpotential of approximately 280 mV at 10 mA cm⁻² with a MoS₂ coating ratio of 1 wt% when treated at 240°C for 5 days.

5:00 PM EN09.04.16
Synthesis of MFI and BEA Type Zeolite Membrane Reactor
Abduljelil W. Sahir and Pyung Soo Lee; Chung Ang University, Korea (the Republic of)

Zeolite membranes were found to be an appealing material for separation and catalytic chemical reactions considering suitable pore diameter, catalytic characteristic together with their thermal and chemical stability. This study presents fabrication of MFI type and BEA type single layer and MFI/BEA bilayer membranes. First both zeolite type crystals were prepared by hydrothermal reaction in a self-pressured autoclave reactor. Primary growth was conducted by seeding the zeolite crystals on porous alumina support. Thereafter, secondary growth solution was made accompanied by hydrothermal treatment for secondary growth. The manipulation of synthesis time and temperature was conducted in order to achieve a continuous and defect-free membrane, while also maintaining the desired optimal thickness range of 5μm-7μm. Membrane morphology and thickness was characterized via FE-SEM. Furthermore, the performance of the membranes evaluated in pervaporation-assisted catalytic esterification of alcohol and carboxylic acid.

5:00 PM EN09.04.17
Interfacial Polymerization of Covalent Organic Frameworks For The Application of Ammonia Production
Chi-Chen Chen¹, Ming-Chung Wu² and Tz-Feng Lin¹;¹Feng Chia University, Taiwan; ²Chang Chung University, Taiwan; ³Chang Gung University, Taiwan

Novel supramolecular structural column, covalent organic frameworks (COFs), was determined by various exact chemical structures such as benzo[1,3,5]triazalen, benzene-1,3,5-tricarboxaldehyde, benzene-1,4-diamine, or 2,4,6-Formaldehyde etc. derivatives. The one-pot synthesis of COFs was achieved from the precursors which was dissolved in the unmixed Bronsted acid and Bronsted base under the Schiff-base reaction system. NMR, TGA, DSC, SEM, PLM, FTIR, contact angle and X-ray scattering (SAXS/WAXS) were used to detect the relationship of effective ammonia production and intermolecular exchange reaction, in order to control the processing conditions. An overall understanding of the physical mechanism of COFs nafion film would be investigated according to the influence of the structural changes on the crystallinity as well as crystal phase morphology. Therefore, our work demonstrates a practical potential for COFs as an ammonia production platform.

5:00 PM EN09.04.18
On The Interplay of Quantum Capacitance and Pseudocapacitance in rGO with Regulated C/O Ratios
Archna Sharma and Alok Shukla; Indian Institute of Technology Bombay, India

Superconductors have evolved as material energy storage devices, utilizing graphene as electrodes to store charge electrostatically. During the process, electric double layers are formed at electrode/electrolyte interface, offering electric double layer capacitance (EDLC). Although large surface area and high conductivity of graphene are favorable for enhanced EDLC, intrinsically low quantum capacitance of graphene limits the overall performance. Utilization of graphene as electrodes reduces graphene oxide (rGO) has been increasingly gaining favor as an alternative material based on graphene owing to its cost-effective means of production. Experimental characterizations have identified abundant epoxy and hydroxyl functional groups on its basal plane, while hosting relatively fewer carbonyl and carboxyl groups at its edges. Interestingly, these oxygen-containing species on the surface of rGO serve as electrochemically active sites for enhanced pseudocapacitance in aqueous EDLCs. While rGO electrodes have demonstrated superior performance compared to graphene electrodes, the reported capacitances have shown inconsistent responses to different C/O ratio. This highlights the necessity to comprehend the impact of the degree of reduction on the total capacitance and theoretical simulations can offer valuable insights to decode the contributions to the total capacitance. Therefore, in this work, density functional theory (DFT) calculations have been employed for studying the capacitive behavior of rGO functionalized with epoxy and hydroxyl functional groups with different coverages on their basal planes. We have considered the cases for low-level, medium-level and high-level oxygen functionalization depending upon the C/O ratio. Under low-level oxygen functionalized graphene (LOFG), rGO with C/O ratios of 8, 6.4 and 5.33 are considered, while for medium-level oxygen functionalized graphene (MOFG) and high-level oxygen functionalized graphene (HOFG), rGO with 4.57, 3.35 and 3.29 C/O ratios are considered, respectively. We have computed EDLC of rGO subjected to different degrees of reduction using implicit solvent model. The computation of EDLC from this method is validated by first calculating EDLC of graphene (116.52 Fg⁻¹) and compared with the experimental value (125-135 Fg⁻¹). Our calculations show that dispersed coverage of rGO with more of epoxy groups offer relatively higher EDLC than that with more of hydroxyl groups. However, in both the cases, EDLC decreases monotonically for decreasing C/O ratio. Quantum capacitances (Cq) of LOFG, MOFG and HOFG are directly related to the changes in density of states (DOS) near the Fermi level. LOFG with more epoxy groups have zero bandgap, possessing higher Cq while MOFG & HOFG with more hydroxyl groups have lower bandgap opening, possessing higher Cq. As bandgap gets wider, maximum Cq is obtained at higher voltages. OH-induced enhancement in quantum capacitance Cq shows much better performance of graphene with zero bandgap opening; Pseudocapacitance (Cpseud) too exhibits the similar pattern, depicting decreased capacitance with decreasing C/O ratio. Such a behavior is explained by studying the variation in dipole moment and work function change. Maximum total capacitance is offered by GO at C/O ratio of 5.33, well in accordance with an experimental study. Suppression of EDLC is mitigated by the enhancement in both Cq and Cpseud, and Cq for LOFG while only increased Cq compensates for MOFG. This study motivates future investigations into control and careful optimization of the oxygen content to balance the quantum induced influences on electrical capacitance and quantum capacitance.

5:00 PM EN09.04.20
Development of Vanadium Oxide/Manganese Selenide Nanocomposite as Robust Bilunarylan Electrocatalyst for Oxygen Evolution Reaction and Hydrogen Evolution Reaction
Samiyalun Maow, Sadiya Akram Khan, Shahid Ali and Muhammad Mansha; Interdisciplinary Research Center for Hydrogen and Energy Storage, King Fahd University of Petroleum, Saudi Arabia

For the expansion of alternative energy structure, it is crucial to develop a bifunctional electrocatalyst for the water splitting process. In this study, we present a novel nanocomposite of Vanadium Oxide and manganese Selenide ((V₂O₅/MSnSe) directly grown on copper foam (CF) using straightforward hydrothermal method, and then characterized via different analytical characteristics. After that the fabricated nanocomposite demonstrates the exceptional electrocatalytic activity for both the hydrogen evolution process (HER) and the oxygen evolution reaction (OER) in a 1.0 M KOH solution. At a current density of 10 mAcm⁻², V₂O₅/MSnSe has exceptionally low overpotentials of 130 mV for HER and 217 mV for OER. Due to the protective properties of the V₂O₅ layers, the catalyst demonstrates precise stability of 50 h in alkaline environments. Furthermore, the fabricated nanocomposite V₂O₅/MSnSe also shows the tafel slope of 44, and 69 mVdec for OER and HER, respectively. Hence, the increased catalyst efficacy is a result of the synergistic interaction between the V₂O₅ and MoSe. On the other hand, the presence of MnSe nanoparticles dispersed precisely and inhibit the aggregation process effectively, maximizing active site exposure. In addition, the presence of V₂O₅ shields these exposed metal particles while increasing the material's electrical conductivity. This study reveals a feasible process for the production of bifunctional electrocatalysts with superior performance and stability. These findings introduce novel concepts for advancing the field of water splitting to produce green energy, which will contribute to the ongoing development of electrocatalytic technology.

5:00 PM EN09.04.21
Electrocatalytic Properties of Pulsed Laser-Deposited Titanium Dioxide—Titania Nanotube and Titania Oxynitride Thin Films Grown on Photo-Adsorbing Single Crystal Substrates with Different Orientations
Sheilah Cherono¹, Ikenna Chris-Okoro¹, Swapnil Nalawade¹, Soyoung Kim², Jacob Som³, Dhananjay Kumar³ and Tanja Cuk⁵;¹University of Colorado at Boulder, United States; ²Joint School of Nanoscience and Engineering, United States; ³Lawrence Berkeley National Laboratory, United States; ⁴Cornell University, United States; ⁵University of Colorado at Boulder, United States

This research focuses on the development of photo/catalytically active titania (TiO₂) and Titania oxynitride (TiON) thin films epitaxially grown on single crystal substrates at different orientations. The films are used as catalysts to examine the electrochemical reactions during water-splitting with the aim of producing hydrogen. The films were grown using pulsed laser deposition (PLD), which has many advantages, including fast response time, energetic evaporants, and congruent evaporation. These advantages were used to determine the optimal growth conditions, which, when combined with careful substrate selection, led to oxide and oxynitride films with well-defined strain and well-controlled vacancies.
A new research trend is exploring highly efficient and prolonged catalysts for oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). Even though, it remains a considerable challenge to understand electrochemical performance enhancement in this field. Herein, we synthesized an interlayered architecture of Cu2WS4@NG nanocomposite and are reported as efficient cathode materials for flexible Zinc-Air batteries. Hierarchical porous interlayers create more active sites due to the unique interlayer architecture. As a result of the synergistic interaction between 2WS4@NG intercalation, the rate of charge transfer is facilitated, the number of active sites is increased, and OER/ORR kinetics is positively influenced in an alkaline environment. Theoretical studies indicate that the interlayered architecture tuning of the electronic structure of Cu2WS4@NG nanocomposite, which is significantly increases the electrical conductivity and catalytic activity. The prepared catalyst will be deliver an excellent half-wave potential for ORR and a low overpotential for OER. Furthermore, the quasi-solid state flexible ZACs will be fabricated and testing for commercial purpose.

Acknowledgement
This work was supported by the Technology development Program (RS-2023-00218880) funded by the Ministry of SMEs and Startups (MSS, Korea), Technology development Program (Project No.: S29607) funded by the Ministry of SMEs and Startups (MSS, Korea). By the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (MEST) [grant numbers: 2021R1A2C1006010], and by the development and technology program (RS-2023-00218880) funded by the Ministry of SMEs and Startups (MSS, Korea).

5:00 PM EN09.04.24
The Effective 2D Interlayer Architecture of Cu2WS4@N-Doped Graphene Nanocomposite for Oxygen Reduction Reaction and Rechargeable Zn-Air Battery Ranjith Balu,1,2, Debabrata Chanda1,2, Mikiyas Mekete Meshesha1,2, Sekh Gwon Jang1,2 and Bee Lyong Yang1,2;1 Kumoh National Institute of Technology, Korea (the Republic of); 2BHs (Green HZ System) Co., Ltd., Korea (the Republic of)

5:00 PM EN09.04.25
More than a Matrix: Tailoring Catalytic Sites in Graphitic Carbon Nitride Joel R. Pennings, Mustafa Yavuz and Michael Pope; University of Waterloo, Canada

Graphitic carbon nitride (g-C3N4) is a promising multifunctional 2D material, especially popular as an eco-friendly and accessible catalyst in oxygen reduction reactions (ORR), hydrogen evolution reactions (HER), and fuel cells [1]. However, the application of g-C3N4 is restricted by a native high e-/h+ recombination rate, poor conductivity, and low surface area, resulting in somewhat sluggish and limited catalytic performance. Research towards ameliorating these limitations has shown that coordinating metals in the lattice gallery space and non-metal substitutional doping are incredibly effective tools for tailoring selective and high-performing catalytic materials [2]. Critically, these tools are often studied in isolation or with sub-optimally prepared g-C3N4, which fails to address the various challenges holistically [3-5]. Our work demonstrates strong improvements in the baseline performance of g-C3N4 due to pre-polymerization supramolecular assembly coupled with extensive exfoliation. We also show that this g-C3N4 synthesis method is highly compatible for both metals coordinated to the nitrogen lone pairs and substitution covalently bonded dopants. These results show uniquely tailored, catalytically active sites in the material, specifically improving the ORR and HER performance. Specifically, we fabricated exfoliated g-C3N4 nanosheets with transition metals (Fe/Na/Co/Mg/Pt) covalently bonded to the active sites, which had been secondarily engineered via covalently bonded interstitial dopants (P/S). These materials were subjected to ORR and HER electrochemical assessments and traditional characterization techniques to preliminarily grasp the advantages and limitations of our material preparation procedures. These material variations offer a wide range of selectivity towards catalytic systems and applications while holistically improving the catalytic performance and preserving the stability, and sustainability of the g-C3N4 system.

Related group papers:

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5:00 PM EN09.04.26
Microwave-Assisted Molten Salt Synthesis of Chevrel Phase Chalcogenides Ankita Kumari, Johnathan D. Rivera and Jessica C. Ortiz-Rodriguez; University of California, Davis, United States

The increase in energy demand has brought about the development of efficient energy-conversion technologies. Currently, natural gas reforming is the most common method to generate hydrogen fuel, but this process is energy-consuming and also releases greenhouse gases into the atmosphere. Renewable hydrogen production has long been considered a clean energy carrier and a highly promising alternative to transition away from fossil fuels. Alternatively, electrochemical proton reduction is a sustainable and green method for producing hydrogen gas – a process that leaves virtually no carbon footprint when coupled to renewable sources of electricity. Chevrel phase (CP; MxMo6S8; M=alkali, alkaline earth, transition, and post-transition metal), a class of molybdenum chalcogenides are especially attractive due to their tunable composition and lower coordination on their molybdenum moieties which has led to previously observed catalytic activity for oxygen evolution, hydrogen evolution, and CO2 reduction reactions. Theoretical studies using various reaction conditions agree that proton adsorption interactions in the chevrel phase occur through the coordinated cation-molybdenum bridging site. Hence, reducing the size of the CP particles will increase the surface-volume ratio exposing a more underscored Mo-S bridging site for proton adsorption.

Traditionally CPs were synthesized by high-temperature solid-state reactions which can take several days and require extremely high-energy input. Although some approaches have been used to reduce the preparation time of CPs, the methods either suffer from uncontrollable particle size, high level of agglomeration, presence of Mo2S imurities, or high energy input. This work presents an efficient route to synthesize size-controlled ternary Chevrel phase chalcogenides (Cu0.5M05S0.5; M=alkali, alkaline earth, transition, and post-transition metal) by microwave-assisted molten salt approach. This methodology has significantly reduced the reaction times from days to minutes resulting in significant time and energy savings yielding highly crystalline, faceted morphology of CPs. The phase, morphology and surface chemistry of the resultant materials were characterized by X-diffraction (XRD), scanning electron microscopy (SEM), Energy dispersive X-ray Spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS). The electrochemical reactions were done in a three-electrode cell with Ag/AgCl as the reference electrode, graphite as the counter electrode, and catalyst ink on Toray paper as the working electrode.

5:00 PM EN09.04.27
Dispersion and Stability Mechanism of Heterogeneous Catalysts Sang-Wook Han1, Eun-Suk Jeong1 and In-Hui Hwang2; 1Jeonbuk National University, Korea (the Republic of); 2Argonne National Laboratory, United States

The dispersion and stability of noble-metal catalysts on transition-metal-oxide supports are considerably important for practical applications of the catalysts. Pt nanoparticles are uniformly and highly dispersed on transition-metal oxides when hydrogen peroxide (H2O2) is applied before calcination at 500 °C. The dispersion and stability of noble-metal catalysts on transition-metal-oxide supports are considerably important for practical applications of the catalysts. Pt nanoparticles are uniformly and highly dispersed on transition-metal oxides when hydrogen peroxide (H2O2) is applied before calcination at 500 °C.
The electrochemical carbon dioxide reduction reaction (CO2RR) is a promising route to reducing excess atmospheric CO2 emissions and producing valuable commodity chemicals. While there is still a need to increase selectivity and activity for electrocatalysts for CO2RR, in order to accomplish these goals, there has been increasing interest in optimizing the microenvironment to boost the activity and selectivity of electrocatalytic sites for CO2 conversion. However, the functional understanding of how to tune the microenvironment is still under development.

This presentation discusses several strategies that are being pursued in my research group to illustrate design principles to optimize the microenvironment for CO2 conversion, which include:

1. Nanostructured model systems to illustrate control of diffusion via engineering electrode structure at micro- and nano-length scales

2. Nanostructured model systems to harness localization of tandem catalysts.

This talk will also share perspectives about harnessing nanoscale materials to control and enhance the microenvironment in order to enhance CO2 conversion.

8:45 AM EN09.05.02
Transition Metal-Doped Electrospun Fibers as Freestanding Electrodes for Carbon Dioxide Electroreduction

Hattie Chisnall, Michael W. Thielke and Ana Jorge Sobrido; Queen Mary University of London, United Kingdom

The electrochemical carbon dioxide reduction reaction (CO2RR) is a promising route to reducing excess atmospheric CO2 emissions and producing valuable commodity chemicals. While there are upwards of 16 products accessible via the multi-electron, multi-step reduction, each pathway is required to proceed via an initial electron transfer from CO2 to the anion radical, CO2-. This first electron transfer step, being the most energetically demanding, proves difficult in the absence of a catalyst due to the high overpotential (-1.9V vs SHE) required to reduce the thermodynamically stable, linear CO2 molecule. The success of CO2RR is therefore guided by efficient electrocatalysts which circumnavigate such high activation energies and promote favourable kinetics. The design of selective electrocatalysts which offer high faradaic efficiencies, reduced overpotentials, and provide high current densities has thus inspired an extensive area of research.

Transition metals have been consistently established as highly efficient electrocatalysts within this field. Within this reach, we have investigated two promising morphologies of active site: molecular-based catalysts with well defined active sites which demonstrate high selectivity for the 2-electron reduction of CO2 into CO and in situ formed copper nanoparticles, which facilitate CO2 conversion into C2+ products. The former has involved investigating the electrocatalytic behaviour of phthalocyanine complexes: aromatic, macrocyclic molecules consisting of four H2O2-Pt/Ti-FS support form into a distorted-anatase TiO2. DFT calculations showed that Pt atoms bond more stably to oxidized-TiO2 surfaces than they do to bare- and reduced-TiO2 surfaces. XAFS measurements and DFT calculations clarified that the presence of extra oxygen atoms due to the H2O2 treatment plays a critical role in the strong bonding of Pt atoms to TiO2 surfaces.

With a need to reduce global emissions and scale up alternative energy sources to fossil fuels, RCC integrates CO2 capture and conversion into a singular electrochemical, thermal, or biological process as a feedstock for value added chemicals. Despite significant progress in CO2 electrocatalyst design to improve efficiency, reproducibility, and selectivity in aqueous media, achieving...
Regulating Spillover Effect in Cu-Ag via Zeolite Frameworks for Efficient CO2 Electroreduction

Dohun Kim, Joon Y. Kim, Woosuck Kwon, Taemin Lee, Uk Sim and Dae-Hyun Nam

Electrochemical CO2 reduction reaction (CO2RR) has been regarded as a promising green technology for lowering atmospheric CO2 level and producing value-added products. For multi-carbon (C2+) chemical production, Cu-based electrocatalysts have been developed by various strategies, such as defect engineering, alloying with other metals, and morphological engineering. Among these various strategies, the spillover effect between Cu and Ag has been considered as an effective avenue for modulating CO2RR selectivity and activities. However, previous works on spillover effect have focused on controlling the Cu/Ag ratio rather than regulating the interface reaction between Cu and Ag.

Herein, we propose a novel strategy to optimize the spillover effect on the Cu surface by modulating anion species in zeolite framework-augmented gas diffusion electrode (GDE). In CO2RR, anions such as Cl, Br, and I can modulate the Cu surface oxidation states and create Cu (0)–Cu (I) mixed sites which facilitate C-C coupling by restricting *CO binding. However, these anions can easily migrate to the anodic side by crossover in anion exchange membrane under high current density conditions. Thus, we augmented AgX (X = Cl, Br, and I)-incorporated zeolite A (AgX-Zeolite A) on Cu electrocatalysts to modulate spillover effect by restricting anion migration. They showed lower hydrogen production and more efficient CO2RR compared to bare Cu electrocatalysts in 1 M KOH electrolyte solutions. Especially, AgCl-, AgBr-, and AgI-Zeolite A on Cu electrocatalysts exhibited 586.3, 495.8, and 456.4 mA/cm2 as maximum partial current densities for C2+, products. This trend is in inverse relationship with the electronegative force of anion species. With increasing electronegative force, the Cu (I) sites become more dominant rather than Cu (0)–Cu (I) mixed sites. However, AgCl-, AgBr-, and AgI-Zeolite A on Cu electrocatalysts showed the 0.89, 1.17, and 1.14 as Faradaic efficiency (FE) ratio of ethanol (CH3CH2OH)/ethylene (C2H4), respectively. These results verified that anion species stabilized by zeolite framework not only accelerate C2+ production but also steer the CO2RR pathway to specific products via spillover effect. Our work provides an insight of zeolite-framework-augmented GDEs for high rate and selective C2+, chemical production in CO2RR.

9:30 AM EN09.05.05

Cation Exchange Ionomer-Based Microenvironment Control of Gas Diffusion Electrode for Efficient CO2 Electroreduction

Yujin Lee, Daewon Bae, Woosuck Kwon, Hansol Choi, Hyungja Ahn, Chang Hyuck Choi, Chanyeon Kim and Dae-Hyun Nam

Electrochemical CO2 reduction reaction (CO2RR) where CO2 is converted into a high-value-added compound can be a great strategy for carbon neutrality. Gas diffusion electrode (GDE) which allows the formation of triple phase boundary (TPB) of catalyst, electrolyte, and CO2 gas has been widely applied for CO2RR. It results in overcoming the CO2 solubility limitation in double phase boundary (DPB) of electrolyte and catalyst, and thus increases the CO2 availability. However, the volume of TPB where the reaction occurs is much smaller than the volume of DPB. Therefore, it is important to increase the volume of TPB for CO2RR activity. Cation exchange ionomer enables us to control the volume of TPB. The hydrophobic chains of ionomer that play a role as gas channel and hydrophilic ionic groups that form a water matrix increase the volume of TPB in GDE-based systems. Here, we verify the effect of ionomer on CO2RR performance in 1 M KOH electrolyte by controlling CO2/H2O ratio and CO2 availability near GDE-based Cu catalyst surface. To distinguish the effect of each part of ionomer, we control the variables of ionomer; (1) Controlling the length of side chain with the application of Nafion as long side chain (LSC) ionomer and Aquivion as short side chain (SSC) ionomer, (2) Fixation of equivalent weight (EW). Compared to the maximum H2 partial current density (JH2) of 71.3 mA/cm2 at bare Cu, Nafion decreases the maximum JH2 to 11.5 mA/cm2 while Aquivion increases it to 26.4 mA/cm2. On the other hand, the maximum CO partial current density (JCO) is 75.1 mA/cm2 at Nafion whereas it is 24.1 mA/cm2 at Aquivion. Nafion and Aquivion also improve the maximum C2H4 partial current density (JC2H4) to 169.5 and 173.3 mA/cm2, respectively. Based on the characterization of ionomers in GDE, we found that LSC ionomer can increase the highest CO2/H2O ratio than SSC ionomer and increase CO2 availability near the active site. Also, we assume that it affects the CO2RR selectivity by tuning the local OH concentration. Improved OH formation by high current density CO2RR at ionomer-augmented catalysts affects the surface charge density that can enhance CO2RR selectivity. Therefore, the key factor of ionomer effect on CO2RR performance enhancement is regulation of the water concentration near the catalyst surface which impacts the CO2 availability and ion conductivity through this water matrix. We expect that this work will suggest a more accurate understanding of the mechanism of ionomer effect on CO2RR and strategy for optimizing the microenvironment of catalyst for efficient CO2RR.

9:45 AM EN09.05.06

Cationic Cu Species Tracked via Operando X-Ray Microscopy during CO2 Electrocatalysis and Their Role in Boosting C-C Coupling Activity

Jongwoo Lim, Juwon Kim, Si Young Lee, Se-Jun Kim, Bonho Koo, Namdong Kim, Matthew Markus, David Shapiro, Shu-Chih Haw, Daan Hein Alese, Norman Salmon, Hyungjun Kim and Yun Jeong Hwang

The solid-liquid interface reactions play a crucial role in controlling the performance and stability of electrocatalysts. In situ vibrational spectroscopy techniques such as Raman and surface-enhanced infrared absorption spectroscopy (SEIRAS) are powerful tools for examining the surface-adsorbed intermediates on the solid-liquid interfaces. In this talk, we report on our use of in situ SEIRAS, Raman, and X-ray absorption spectroscopy to investigate the electrochemical CO2 reduction mechanism over the Cu-based electrocatalysts. The Cu-based electrodes with different oxidation states result in the formation of various CO intermediates such as CO NOP and CO BRIDGE. The co-existence of CO NOP and CO BRIDGE corresponds to the selectivity of CO2-to-C H reaction. Also, the bimetallic electrocatalysts are developed for efficient CO -to-HCOOH and CO -to-CO conversion processes. We found that the surface-adsorbed COO species with
different binding structures play crucial role in the reduction process. The electronic structures of Cu-based electrocatalysts are associated with the formation of surface-adsorbed intermediates and electrocatalytic properties. The formation of surface-adsorbed intermediates and reaction mechanism associated with CO$_2$-to-HCOOH and CO$_2$-to-CO reactions over the bimetallic electrocatalysts will be discussed in detail.

References


11:00 AM EN09.05.08
Role of Reservoir and Diffusion for Electrocatalytic CO$_2$ Reduction to Ethylene on Cu

Sydney H. Hemenway$^{1,2}$, Chansol Kim$^{1,3}$, Nitish Govindarajan$^{4}$, Junho Park$^{1,2}$, Anya Zoraster$^{1,2}$, Calton J. Kong$^{1,2}$, Rajiv R. Prabhakar$^{1}$, Joel Varley$^{1}$, Hee-Tae Jung$^{3}$, Christopher Hahns$^{4}$ and Joel W. Ager$^{1,2,4}$

$^{1}$Lawrence Berkeley National Laboratory, United States; $^{2}$University of California, Berkeley, United States; $^{3}$Korea Advanced Institute of Science and Technology, Korea (the Republic of); $^{4}$Lawrence Livermore National Laboratory, United States

Electrochemical CO$_2$ reduction (EC-CO$_2$R) on Cu is a promising approach to produce value-added chemicals using renewable feedstocks. The ability of Cu to produce multi-carbon products during electrochemical CO$_2$ reduction is conventionally understood in terms of the binding energy of the crucial CO intermediate and the existence of active sites which facilitate C-C coupling. Yet, the vast differences in activity and selectivity towards single and multi-carbon products produced by various Cu preparations suggest that this picture is incomplete. In this work, we find that the effective catalytic activity towards ethylene improves with a larger fraction of less active sites acting as reservoirs of *CO on the Cu surface. This surprising finding can be explained by the rapid supply of *CO from reservoir to active sites which increases the effective activity of active sites. Experimental evidence is provided by real-time measurements of mass flow exiting a gas diffusion electrode cell held at a fixed potential and subjected to different precursor feeds. When the precursor feed is switched from inert Ar to CO, CO reduction to C$_2$+ products begins promptly, as expected. However, when the precursor feed is switched from CO to Ar, CO reduction continues for several seconds (delay time) before transitioning to hydrogen evolution. Control experiments establish that some Cu preparations, most notably oxide-derived Cu, can maintain COR activity in the absence of the gas phase precursor due to reservoir sites on the Cu surface that bind CO but do not convert it. We introduce a microkinetic model which shows that the delay time originates from a less active *CO reservoir that exhibits fast diffusion to active sites on the surface of OD-Cu. Experiments find that delay time and *CO reservoir sizes are affected by the catalyst preparation, applied potential, and microenvironment. Notably, we associate large *CO reservoir surface coverages (maximally 86±5% at -1.52 V vs SHE) with increased ethylene production. We also estimate that *CO can travel long distances (up to 10s of nm) prior to reaction. We propose a broader scope for EC-CO$_2$R catalyst design: in order to design high C$_2$+ activity, in addition to active sites, the role of less active *CO reservoirs in controlling the COR activity must be considered.

11:15 AM EN09.05.09
Copper Silicophosphides: New Ternary Nanocrystals as Electrocatalysts for Carbon Monoxide Reduction

Anissa Ghoridi$^{1,2}$, Ngo-Huan Tran$^{1,2}$, Carlos V. Mendonca Inocencio$^{1,2}$, Amandine Sene$^{1,2}$, Marzenna Barou$^{1,2}$, Emile Defoy$^{1,2}$, Daniel Janisch$^{1,2}$, Fernando Igoa Saldana$^{1,2}$, Edouard De Rolland Dalon$^{1,2}$, Antoine Miche$^{1,2}$, Christel Gervais$^{1,2}$, Cristina Coello-Diogo$^{1,2}$, Sandra Casale$^{1,2}$, Pierre-Olivier Attran$^{1,2}$, Andrea Zito$^{1,2}$, Isabelle Genous$^{1,2}$, Mare Fontecave$^{1,2}$, and David Portehault$^{1,2}$, CNRS, France; 3Sorbonne Université, France; 4Collège de France, France; 5European Synchrotron Radiation Facility, France; 6Synchrotron SOLEIL, France

Incorporating p-block elements into transition metal oxides offers a mean to fine-tune their electrocatalytic properties through localized structural distortion, charge transfer, and hybridization [1]. Beyond simply doping, the design of compounds with specific compositions and crystal structures can significantly expand the range of accessible properties. Notably, copper phosphides and silicides have been explored for their efficiency as catalysts or pre-catalysts in electrochemical water splitting [2,3] and as anodes in Li-ion batteries [4-9]. However, the properties of ternary copper silicophosphides, which possess unique structures distinct from binary phases, have been little investigated. Currently, only three ternary copper phases are known (Cu$_2$Si$_2$P$_3$, Cu$_2$Si$_4$P$_3$, Cu$_4$SiP$_8$) [5-8], and have remained at the status of scientific oddities.

To boost catalytic activity and selectivity for the generation of high-value added products containing C-C bonds in the electrocatalysis of the CO$_2$ reduction reaction (CORR) and of the CO reduction reaction (COR), one approach is to create single metal active sites, which can deeply modify catalytic cycles compared to metal clusters or nanoparticles [7,8]. However, maintaining these single atom sites in an isolated state during electrocatalysis poses a significant challenge. Our strategy focuses on stabilizing these sites within crystallographic structures by seeking additional stabilization through the promotion of covalent bonding to rigid a crystalline structure. It is imperative to design nanostructures with a high surface-volume ratio, thereby amplifying catalytic activity. Copper silicophosphides present an ideal candidate for this purpose.

Here, we present the first synthesis of copper silicophosphide (Cu$_2$Si$_x$P$_y$) nanocrystals using molten salts as reaction media, promoting the nucleation of nanoparticles while limiting their growth [9]. In situ X-ray diffraction measurements conducted at the ESRF ID11 synchrotron beamline during the synthesis reveal the crystallization mechanism from the initial metal salts to the ternary phases. Following a comprehensive characterization of the nanomaterials, including their structure, composition, and morphology (TEM, HRTEM, STEM-EDX, EDS mapping, XPS), we will delve into the promising electrocatalytic properties of Cu$_2$Si$_x$P$_y$ for CORR studied via in situ X-ray absorption spectroscopy at the SOLEIL SAMBA synchrotron beamline.


11:30 AM EN09.05.10
Bimetallic Interface Control of Cu$_2$O Nanocrystals for Efficient CO$_2$-to-C$_2$ Chemical Conversion

Seolah Lim, Woosuk Kwon and Dae-Hyun Nam; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

Electrochemical carbon dioxide reduction reaction (CO$_2$RR) is promising in the pursuit of carbon neutrality, as it converts CO$_2$, the primary contributor to global warming, into valuable high-end fuels and chemical feedstocks. Copper (Cu) is the only metal that has an appropriate *CO binding energy for C-C coupling. Cu-based CO$_2$RR electrocatalysts can produce multi-carbon (C$_2$+) chemicals such as ethylene, ethanol, and acetic acid. Nonetheless, they suffer from low selectivity for producing specific products. Particularly, bimetallic systems including Cu with secondary metals such as Ag and Au for their weak *CO bonds, emerge as a promising strategy to enhance the production of C$_2$+ chemicals. However, the focus of Cu-based bimetallic catalysts has primarily been optimizing the ratio of secondary metals, overlooking the significance of interface control for efficient CO$_2$RR.

In this study, we fabricated the facet-controlled Cu$_2$O nanocrystals (NCs) and studied the effect of bimetallic interface design on the CO$_2$RR. Cu$_2$O NCs includes cube with (100) facets, cuboctahedron (cubo) with (100) and (111) facets, and octahedron (octa) with (111) facets. We introduced Ag and Au as secondary metals to control Cu$_2$O NCs through galvanic replacement. Shape and size distributions of the secondary metals were binary nature which significantly improved selectivity by reaching 57% FE for C$_2$+ and suppressing H$_2$ with a FE of 15% at -0.78 V (vs RHE). In contrast, the Au-augmented Cu$_2$O cube promoted H$_2$ with 25% FE and C$_2$+, with 33% FE at -0.99 V (vs RHE), resulting in reduced performance. To gain deeper insights into the intermediate...
In this work, we developed an automated electron tomography workflow performed in scanning transmission electron microscopy (STEM) mode and utilizing SerialEM 3 for data acquisition.

We demonstrate that Cu surfaces prepared by PE-ALD can reduce CO2, forming value-added products such as carbon monoxide, methane, and ethylene. Parasitic hydrogen evolution was island-growth mode of the metal catalyst. The metal layer was confirmed by grazing incidence X-ray diffraction. The catalyst surface morphology was probed by scanning electron microscopy and atomic force microscopy, highlighting the island-growth mode of the metal catalyst.

We applied a super-voxel model-based iterative reconstruction with adaptive regularization (MBIR-ARAR) for artifact reduction and performed segmentation of the nanoparticles and carbon pores. Simultaneously, there is evidence of an expanding size distribution of closed pores after the AST, possibly stemming from carbon corrosion. These observed degradation mechanisms challenge the assumption that Pt dissolving primarily on the carbon support interior and re-depositing on the surface is a major contributor to ECSA decline, suggesting that factors such as carbon corrosion, dissolution of exterior nanoparticles, and/or particle coalescence also contribute to ECSA loss. This shows the importance of automating the electron tomography workflow, e.g., acquisition, reconstruction, and visualization, for increasing sampling and determining statistical parameters for the measurements. The outlook for utilizing low-dose cryo-tomography for characterization of catalyst degradation mechanisms.

References:
In this work, we utilize X-ray Photoelectron Spectroscopy to quantify the presence of Mn(III) defect states within the TiO2 band gap which are energetically aligned to peroxide generating processes that are only feasible for large-scale chemical plants. During operation, the energy levels of CB and VB of TiO2 are fixed, or "pinned", at $-0.05$ and $3.29$ VRHE, respectively, yet the empty states of the Mn defect states can precisely align with the energetics of H2O2 producing intermediates. Under a higher applied potential, i.e., $+2.3$ V, there would exist a moderate overpotential for the 2e water oxidation, but such a potential also enables the other pathways including 1e water oxidation to produce radicals, leading to an overall reduction in H2O2 production rates due to the reduced selectivity. Thus, this strategy of defect state tuning is best suited to low overpotentials, 90% at $<150$ mV overpotentials was achieved for H2O2 production, accumulating 2.97 mM H2O2 after 8 hours.

Conclusion:
In this talk, we will briefly discuss each of these techniques and give the advantages and inconvenience of each of them. Examples on the utilization of X-ray, synchrotron and neutron diffraction for the development and fundamental understanding of metal hydrids will be given.

3:30 PM *EN09.07.01
Use of X-Ray, Synchrotron and Neutron Diffraction for The Development of Metal Hydrides Jacques Haug; UQTR, Canada

Metal hydrides are attractive solutions for hydrogen storage in a wide range of applications going from fuel cell submarine down to smart phones. In metal hydrides hydrogen is chemically bonded to other elements to form an alloy. Therefore, knowledge of the crystal structure of the metal hydride in its hydride and dehydrided state is essential. Conventional X-ray diffraction gives important information such as crystal structure, crystallite size, microstrains, etc. However, in-situ investigation of fast kinetics is basically impossible with this technique. Synchrotron radiation provides a large flux of photons that enable the recording of phase change of very fast hydrogenation/dehydrogenation kinetics. Unfortunately, X-ray diffraction is not suitable to locate the hydrogen atom in the crystal lattice. Neutron diffraction is practically the only technique that could give the localization of the hydrogen in a metal hydride. However, another synchrotron technique, the Extended X-Ray Absorption Fine Structure (EXAFS) could probe the local environment of each type of atoms. In this talk, we will briefly discuss each of these advantages and give the differentiation for the development and fundamental understanding of metal hydrids will be given.

4:00 PM EN09.07.02
Selective Water Oxidation to H2O2 on TiO2 Surfaces with Sub-Surface Redox-Active Allosteric Sites Devan Solanki and Shu Hu; Yale, United States

Hydrogen peroxide H2O2 is a versatile chemical with applications ranging from industrial to household use such as pulp bleaching, wastewater treatment, and sterilization. In addition to these established uses, H2O2 is emerging as a green energy carrier which can release 96 kJ *mol-1 of energy via exothermic chemical decomposition with only water and oxygen as by-products. Currently, more than 95% of H2O2 produced globally originates from amnethoquine autoxidation. This process requires precious metal catalysts and expensive liquid-liquid extraction processes that are only feasible for large-scale chemical plants.

Electrochemical and photochemical syntheses are promising alternatives for distributed H2O2 production. H2O2 can be produced by 2e- processes both via oxidatively, via water oxidation reaction (WOR) or reductively via oxygen reduction reaction (ORR). These approaches take advantage of abundant energy sources, i.e., renewable electrical or solar energy, and enables the storage of intermittent energy as the free energy of chemical bonds for distributed energy storage. In this work we focus on the water oxidation pathway.

Electrochemical Charge Transfer:
H2O2 can be (photo-)electrochemically synthesized via a two-electron (2e-) water oxidation pathway, as shown in equation 1.

$$H_2O_2 \rightarrow H_2O + 2H^+ + 2e^-; E = +1.77 \text{ V}$$

However, existing catalysts often exhibit low faradaic efficiency (FE) due to the competitive four-electron (4e-) pathway of O2 evolution reaction (OER) equation 2.

$$H_2O_2 \rightarrow O_2 + 4H^+ + 4e^-; E = +1.23 \text{ V}$$

The thermodynamic driving force for OER is always at least $+0.54 \text{ V}$ greater than that of the 2e H2O2 pathway which can allow the undesired O2 evolution pathway to overcome any kinetic barriers and dominate. In addition, the produced H2O2 can be over-oxidized to O2 at an excess potential of at least $+1.09 \text{ V}$ (equation 3).

$$H_2O_2 \rightarrow 2H^+ + 2e^-; E = +0.68 \text{ V}$$

Thus, the partial oxidation of water to hydrogen peroxide presents a model system of a common challenge in catalysis where the desired product is kinetically feasible but thermodynamically unfavorable.

Conclusion:
In this work, we used X-ray Photoelectron Spectroscopy to study the presence of Mn(III) defect states within the TiO2 band gap which are energetically aligned to peroxide generating reactive intermediates. During operation, the energy levels of CB and VB of TiO2 are fixed, or "pinned", at $-0.05$ and $3.29$ VRHE, respectively, yet the empty states of the Mn defect states can precisely align with the energetics of H2O2 producing intermediates. Under a higher applied potential, i.e., $+2.3$ V, there would exist a moderate overpotential for the 2e water oxidation, but such a potential also enables the other pathways including 1e water oxidation to produce radicals, leading to an overall reduction in H2O2 production rates due to the reduced selectivity. Thus, this strategy of defect state tuning is best suited to low overpotentials, 90% at $<150$ mV overpotentials was achieved for H2O2 production, accumulating 2.97 mM H2O2 after 8 hours.

Nano-scale mixing of MnOx and TiOx resulted in a partially filled, highly conductive Mn intermediate band (IB) within the TiO2 mid-gap to transport charge across the TiMnOx coating. This IB energetically matched that of H2O- producing surface intermediates, turning a wide bandgap oxide into a selective electrocatalytic material that can operate in the dark.

4:15 PM EN09.07.03
Kinetic Mechanisms of M-N-C Electrocataltics Saerom Yu, Zachary Levell and Yuanyue Liu; The University of Texas at Austin, United States

Single metal atoms embedded in nitrogen doped graphene (M-N-C) has attracted wide interest as electrocatalysts for various reactions. Although there have been many studies on the thermodynamic mechanisms (mostly based on computational hydrogen electrode model or its variants/derivations), the kinetic mechanisms are less understood partly due to the complexity of
Simulating reaction kinetics at electrochemistry interface. Using an advanced model developed recently in my group, I will show its application to elucidate the mechanisms of M-N-C for CO2 reduction and oxygen reduction.

4:30 PM EN09.07.04

**Synchrotron Radiation Characterization to Understand The Nature of Catalysts during Operation**

Yan-Gu Lin; National Synchrotron Radiation Research Center, Taiwan

Catalysis has been tightly associated to X-ray spectroscopy from the very beginning, and this happy wedding is still holding and faithful. Catalysts studied at beamlines are quite a mirror of the needs of our society, reflecting current issues on global warming, oil shortage and economic struggles. In the recent years, the transition of dynamic atomic/electronic structure has been demonstrated to be induced by some external stimuli during catalysis, which enable one to potentially manipulate the unpaired electrons at the metal centers, thus directly influencing their dynamic structure as well as resulting nature. In this respect, the recent research trends have increasingly transferred from optimizing catalysts to making clear the real active species of the catalysts, especially understanding the underlying mechanisms behind catalytic reactions. Abundant synchrotron-based X-ray spectroscopy methods, including in-situ/operando measurement have been developed and applied, offering nonnegligible characterization assistance to researchers in the field of catalysis, material and chemistry. Regarding the advanced in situ/operando approaches, ongoing characterization efforts employing X-ray absorption spectroscopy (XAS) particularly have successfully unveiled the potential-induced or photo-driven changes in local geometry of the active sites. In this talk, I will illustrate a part of the activities of the NSRRC beamlines through examples to show the establishment of the correlation between atomic/electronic structure and the catalytic properties. The experimental results demonstrate that the operando X-ray characterization provides the unique information for understanding the real reaction mechanism.

**References**


**5:00 PM EN09.08.01**

**Enhancing Energy Efficiency in Bicarbonate Electrolysis through the Development of an Au-NiO-CNT Catalyst for Glycerol Oxidation**

Dohee Kim; Hyeonok Choi; Hojung Lee; Yoonyoung Kim; Eunui An; Youngkook Kwon; and Jihan Oh; 1Korea Advanced Institute of Science and Technology, Korea (the Republic of); 2Ulsan National Institute of Science and Technology, Korea (the Republic of); 3Korea Institute of Energy Research, Korea (the Republic of)

Reducing emitted CO2 through direct air capture is crucial to mitigate climate change. Bicarbonate electrolysis is a method that facilitates CO2 reduction by utilizing bicarbonate generated from aqueous CO2, ultimately yielding syngas or CO as a product. However, the overall energy efficiency of bicarbonate electrolysis is impeded by the high theoretical voltage associated with the oxygen evolution reaction (OER) occurring at the anode to bring energy efficiency and bolster the economic viability of this process. In this work, we developed a novel cell architecture that combines biomass upgrading, glycerol oxidation (GEOR) for glycolic acid (GCA) production with bicarbonate electrolysis. GCA serves as a monomer for bio-plastics; Polyactic-co-glycolic acid (PLGA), but its current production relies on fossil fuels. In this work, we developed an advanced model to achieve sustainable GCA production via GEOR, introducing an Au catalyst design that incorporates NiO support and multi-walled carbon nanotubes (MWCNTs) to enhance the selectivity of GCA production through a synergy effect. We then successfully demonstrated the addition of 4 wt% MWCNTs on Au-NiO catalyst leads to a remarkable achievement of 36% GCA selectivity and 28% glycerol conversion at 0.9 V (V vs. RHE) and 2 h in 0.1 M glycerol and 1 M KOH for GEOR. This showed that a 4.6-fold increase in glycerol conversion and a twofold increase in GCA production compared to the conventional Au-CB catalyst. Additionally, by controlling MWCNT ratio of Au-NiO catalyst, we showed that the amount of Au-NiO catalyst required to achieve 10% glycerol conversion at 0.9 V (V vs. RHE) was reduced by 20 wt%. We conducted operando raman analysis to gain mechanistic insights. Our findings suggested that during GEOR, the NiO support undergoes a transformation into Ni(OH)2, and introduction of MWCNTs on NiO promotes formation of Ni(OH)2. Additionally, our electrochemical impedance spectroscopy (EIS) indicated that MWCNTs improve the electrical conductivity of NiO, which could facilitate Ni(OH)2 formation. Therefore, we demonstrated that the reaction between adsorbed glycerol on Au and Ni-OH transformed on the NiO support, resulting in enhanced conversion of glycerol to GCA. Finally, by combining bicarbonate electrolysis, we achieved an H2/CO ratio of about 2.34 through bicarbonate electrolysis and a GCA selectivity of 26% through GEOR at 200 mA/cm2. This accomplishment confirms the successful development of an efficient system, proficiently yielding valuable compounds at both electrodes.

**5:00 PM EN09.08.02**

**Zirconium Phosphate Layered Nanomaterials as Supports for Earth-Abundant Electrocatalysts for The Oxygen-Evolution Reaction**

Jorge L. Colón; Yannelly A. Serrano-Rosario, Sebastián Muñoz-Torres, Daniela M. Gibson-Colón, Biao Liu, Gabriela A. García-Machado, Antonio Torres-López, Louise M. Defebve and Christopher J. Pollock; 1University of Puerto Rico at Rio Piedras, United States; 2Cornell University, United States

We are studying new applications of layered zirconium phosphate (ZrP) inorganic nanomaterials [1]. The θ phase of ZrP can be directly ion-exchanged with metal complexes and catalysts, producing intercalated phases useful for artificial photosynthesis schemes for water splitting, amperometric biosensors, and drug delivery applications. Recently, we have demonstrated improved electrocatalytic activity of ZrP nanomaterials loaded with metal ions suitable for the oxygen evolution reaction of water splitting. Electrocatalysts have been incorporated as intercalated species, surface bound, on exfoliated layers, and on nanoparticles of different morphologies (hexagonal platelets, cubes, rods, and spheres). Single and bimetallic electrocatalysts based on earth-abundant materials have been studied. Reduction in overpotentials and increases in mass activity have been achieved. Mixed metal NiFe-intercalated ZrP electrocatalysts at 90% Fe metal content proved to have superior OER electrocatalytic performance (decreased overpotentials, increased mass activities, reduced Tafel slopes) compared to adsorbed counterparts. We have recently prepared CoFe electrocatalysts systems and again the intercalated bimetallic system is more active than the surface-adsorbed one. We are starting to work also with Mn electrocatalysts. We are exploring OER activities of other mixed-metal catalysts on ZrP, bifunctional catalysts, and operando synchrotron X-ray absorption spectroscopy studies to elucidate the nature of the active species. We are also exploring efficient solar H2 production using these supports.

**Reference**


**5:00 PM EN09.08.04**

**Superior CO2 Electroreduction Performance on Co-Ni-Nitrogen Bimetallic Sites**

Jianping Chen and Weining Wang; Virginia Commonwealth University, United States

The electrochemical reduction of carbon dioxide (CO2, CECR) plays a crucial role in transitioning towards a sustainable energy and chemical industry. This process has the potential to not only address the rising CO2 levels but also utilize it as a resource to produce valuable fuels and chemicals. Electro catalysts are essential in CO2, CECR, as their ability to selectively and efficiently convert CO2 offers significant environmental and economic benefits. Our research, focusing on nanostructured electro catalysts for energy applications, introduces an innovative nanostructured catalyst that represents a significant advancement in CO2, CECR technology for energy generation and conversion.
Regarding CO₂ ECR, a wide range of catalysts including metals, alloys, metal oxides, functionalized carbons, and metal complexes have been studied for their effectiveness. Despite their remarkable CO₂ conversion capacity, challenges such as sub-optimal energy efficiency, varying activity levels, and undesired hydrogen evolution reactions (HER) present significant obstacles. Addressing these challenges, our study introduces a novel electrocatalyst featuring diatomic metal-nitrogen sites (Co-Ni-N-C). This catalyst is synthesized through a unique process involving ion exchange using a zeolitic imidazolate framework (ZIF) as a precursor, followed by pyrolysis. This method results in nitrogen-doped graphitic carbon, effectively anchoring the Co-Ni bimetallic active sites. This work highlights the potential of nanostructured single-atom catalysts (SACs) and dual-active site catalysts (DASCs) in CO₂ ECR. Transition metal SACs, such as Ni-SAC on nitrogen-doped graphene, have previously shown promising results in CO₂ conversion efficiency. However, our Co-Ni-N-C catalyst takes a step forward by demonstrating a CO yield rate of 53.36 mA mg cat.⁻¹ and a CO Faradaic efficiency of 94.1% at an overpotential of -0.27 V. This performance showcases that Co-Ni-N₆ moiety plays a crucial synergistic role in promoting and sustaining these exceptional ECR activities.

Spectroscopic, microscopic, and density functional theory analyses collectively reveal the synergistic role played by the Co-Ni-N₆ moiety in enhancing catalytic activity. This synergy is crucial in promoting and sustaining exceptional ECR activities. The findings not only emphasize the effectiveness of nanostructuring in electrocatalyst design but also shed light on the pathways for developing various advanced catalysts for sustainable energy conversion. Therefore, our study offers a novel perspective in the field of CO₂ ECR, opening new avenues for the development of efficient, nanostructured catalysts for energy applications.

5:00 PM EN09.08.06
Engineering Efficient Electrocatalysts: Non-Precious Bimetallic ZIF-Based Hybrid Nanocomposites for Oxygen Reduction Reaction Mahshid Mokhtarnejad, Erick Ribeiro, Dibyendu Mukherjee and Bamin Khomami; The University of Tennessee, United States

Synthesis of metal oxides/metal-organic frameworks (MOFs) into hybrid nanocomposites (HNCs), wherein transition metals combined with carbon (C) matrices, due to the excellent conductivity and high porosity present an attractive and cost-effective alternative for engineering electrocatalysts used for oxygen reduction reaction (ORR) in anion exchange membrane fuel cells (AEMFCs). To that end, improving the performance of these materials by adjusting their composition, structure, size, and morphology through an efficient synthesis process is of great technological importance. In this context, the Laser Ablation Synthesis in Solution in Tandem with Galvanic Replacement Reaction (LASiS-GRR) technique is employed as a fast, facile, and green approach for the synthesis, and precise control of complex hierarchical bimetallic Zeolitic Imidazolate Framework (ZIF) structures. Specifically, this novel one-pot, two-step LASiS-GRR process allows for the optimization and of the composition, structure, size, and morphology of Co-based MOFs encapsulated within Zn-based porous MOF crystals “dubbed” ZIF-67@Zn/ZIF-8. The pyrolytic post-processing of these crystals leads to the development of HNCs exhibiting superior ORR electrocatalytic performance in AEMFCs. Overall, this research not only sheds light on the impact of two distinct salt precursors on particle size and morphology during LASiS but also showcases the exceptional performance and stability of post-pyrolytic (Zn@OZIF@C) HNCs in AEMFC applications as non-precious ORR electrocatalysts when compared to state of art Pt- and platinum-group metals (PGM)-based electrocatalysts.

5:00 PM EN09.08.07
Biaxial Strained MoS₂ Nanoshells with Controllable Layers Boost Alkaline Hydrogen Evolution Tao Zhang; Nanyang Technological University, Singapore

Strain in layered transition-metal dichalcogenides (TMDs) is a type of effective approach to enhance the catalytic performance by activating their inert basal plane. However, compared with the traditional uniaxial strain, the influence of biaxial strain and TMDs layer number on local electronic configuration remains unexplored. Herein, via a new in situ self-vulcanization strategy, we realize biaxial strained MoS₂ nanoshells in the form of single-crystalline Ni₃S₂@MoS₂ core-shell heterostructure, where the MoS₂ layer is precisely controlled between 1 to 5 layers. In particular, the electrode with bilayer MoS₂ nanoshells shows a remarkable hydrogen evolution reaction evolution activity with a small overpotential of 78.1 mV at 10 mA cm⁻², and negligible activity degradation after durability test. Density Functional Theory calculations reveal the contribution of optimized biaxial strain together with the induced sulfur vacancies, and identify the origin of superior catalytic sites in these layer-resolved MoS₂ nanoshells. This work highlights the importance of the atomic-scale layer number and multilayer strain in unlocking the potential of two-dimensional TMDs electrocatalysts.

5:00 PM EN09.08.08
Unleashing the Full Potential of Heterostructured Nickel–Cobalt Phosphate for Optically Active High-Performance Asymmetric Quasi-Solid-State Supercapacitor Devices Naegeh K. Allam; American University in Cairo, Egypt

The design of hybrid systems that combine capacitor and battery merits is crucial to enable the fabrication of high-energy and power-density devices. However, the development of such systems remains a significant barrier to overcome. Herein, we report the design of a Ni-Co phosphate (Ni₃₋ₓCoₓ(PO₄)ₓ2H₂O) nanoplatelet-based system via a facile coprecipitation method at ambient conditions. The nanoplatelets exhibit multicrystalline synergy, exceptional charge storage capabilities, rich redox active sites (ameliorating the redox reaction activity), and high ionic diffusion rate/electron transfer kinetics. The designed Ni₃₋ₓCoₓ(PO₄)ₓ2H₂O offered a respectable gravimetric specific capacity and marvelous capability (966 and 595 C g⁻¹ at 1 and 15 A g⁻¹) over the Ni₃(PO₄)₂.8H₂O (327.3 C g⁻¹) and Co₃(PO₄)₂.8H₂O (68 C g⁻¹) counterparts. Additionally, the nanoplatelets showed enhanced photocatalytic storage performance with a 9.7% increase in the recorded photocurrent density. Upon integration of Ni₃₋ₓCoₓ(PO₄)ₓ2H₂O as a positive pole and commercial activated carbon as a negative pole, the constructed hybrid supercapacitor device with PVA@KOH quasi-gel electrolyte exhibits great energy and power densities of 77.7 Wh kg⁻¹ and 15998.54 W kg⁻¹ with remarkable cycling stability of 600 charging/discharging cycles and prominent Coulombic efficiency of 100%. Interestingly, two assembled devices are capable of glowing a red LED bulb for nearly 180 s. This research paves the way to design and fabricate electroactive devices via a facile approach for boosting the design of a plethora of supercapattery devices.

5:00 PM EN09.08.10
Fe-Single-Atom Catalysts on Nitrogen-Doped Carbon Nanosheets for Electrochemical Conversion of Nitrogen to Ammonia Naegeh K. Allam; American University in Cairo, Egypt

Electrochemical nitrogen reduction reaction (NRR) has been established as a promising and sustainable alternative to the Haber–Bosch process, which requires intensive energy to produce ammonia. Unfortunately, NRR is constrained by the high adsorption/activation of the N₂ energy barrier and the competing hydrogen evolution reaction, resulting in low faradic efficiency. Herein, a well-dispersed iron single-atom catalyst was successfully immobilized on nitrogen-doped carbon nanosheets (Fe-SAC-N-C) synthesized from pre-hydrothermally derived Fe-doped graphene. This catalyst exhibited a CO₂ reduction potential of 0.12 VRHE, exhibiting a considerable faradic efficiency of 94.1% at an overpotential of -0.27 V. Furthermore, the NH₃ yield rate of 1.4 μmol h⁻¹ cm⁻² in aqueous 0.1 M KOH electrolyte at a potential of -0.1 VRHE under continuous N₂ feeding conditions. The control experiments assert that the produced NH₃ molecules only emerge from the dissolved N₂ gas, reflecting the remarkable stability of the nitrogen–carbon framework during electrolysis. The DFT calculations showed the FeSAC-N-C catalyst to demonstrate a lower energy barrier during the rate-limiting step of the NRR process, consistent with the observed high activity of the catalyst. This study highlights the exceptional potential of single-atom catalysts for electrochemical NRR and offers a comprehensive understanding of the catalytic mechanisms involved. Ultimately, this work provides a facile synthesis strategy of FeSAC-N-C nano-sheets with high atomic dispersion, creating a novel design avenue of FeSAC-N-C that can vividly have potential applicability in the large spectrum of electrocatalytic applications.

5:00 PM EN09.08.11
3D Vertical Graphene Nanofibers with High Defect Density and Nitrogen Doping for Electrocatalytic Hydrogen Evolution Reaction TaoGeYeong Lim¹, Sang Ho Shin¹ and Ji Won Suk¹,²,³; Sungkyunkwan University, Korea (the Republic of);²Sungkyunkwan University Advanced Institute of NanoTechnology, Korea (the Republic of)

The production of clean hydrogen using water electrolysis is a crucial element in achieving sustainable energy production and utilization systems.[1] A key challenge in attaining sustainable hydrogen production via water electrolysis lies in the development of suitable electrocatalyst materials for the hydrogen evolution reaction (HER), aiming to replace conventional noble-metal-based electrocatalysts with earth-abundant alternatives.[2] Graphene-based materials have emerged as promising candidates for metal-free electrocatalysts due to their exceptional electrical conductivity, high specific surface area, and chemical stability.[3] The electrocatalytic performance of graphene-based materials has notably advanced with the introduction of heteroatom doping or defects.[4,5] In this study, we synthesized three-dimensional (3D) vertical graphene nanofibers (VGNFs) with unique 3D structures, serving as metal-free electrocatalyst for HER. The freestanding 3D VGNFs were synthesized via facile and scalable processes employing the electrospinning method combined with thermal chemical vapor deposition. The 3D VGNFs exhibited high defect
Capture and subsequent conversion of CO2 to value-added chemicals is a promising strategy to tackle the increase in CO2 concentrations in the atmosphere. CO2 electrosynthesis to CO is often the first step in such a conversion, necessitating the design of effective electrocatalysts that can not only produce CO with high selectivity but also do so energy-efficiently. The Ag-Nanoparticle-Ordered Ligand Interlayer (Ag-NOLI) catalyst produces CO at high selectivity. However, to achieve the catalytically active phase, the material needs to be biased to a large negative potential. Thus, any effort to create the catalytically active phase at lower magnitudes of negative potential can pave the way towards designing a more energy-efficient catalyst. We used density functional theory calculations to engineer the Ag surface by introducing vacancies, and Cu and Ag dopants, evaluated the relative energies of all the configurations, and computed the transition potentials needed to get to the catalytically active phase. We found that while introducing Ag vacancies and Cu dopants increase the magnitude of the transition potential, the opposite is seen with Au dopants, making Au dopants a suitable design modification. Moreover, while Cu increases the stability of all the phases compared to Ag, Au decreases it. The source of this Cu > Au effect is likely due to electronic factors, where Cu acts as a more prominent contributor compared to Au to other interactions in the system. Finally, we found that the trend in the ligand-surface interaction energy can be attributed partially to the intrinsic chemical interaction between the ligand and surface atoms, by investigating systems where the geometry of the topmost layer was kept fixed. Overall, this Cu < Ag < Au energy trend can be ascribed partially to the electronegativity differences with O, making it an important descriptor in the design of energy-efficient Ag-NOLI-based catalysts.

5:00 PM EN09.08.13
Thermodynamic Prediction of Gas-Solid Reactions for the Synthesis of Transition Metal Carbides Catalysts Sang-Ho Oh1, Dohun Kim2, Ji-Yong Kim3, Geosan Kang4, Jooyoung Jeon4, Miyoung Kim5, Young-Chang Joo6 and Dae-Hyun Nam7; 1Seoul National University, Korea (the Republic of); 2Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

Transition metal carbides have garnered significant attention due to their extensively adjustable physicochemical characteristics based on their structure, phase, and polymorph, making them highly versatile in a broad range of applications owing to their unique d-band electronic structures. Nevertheless, the synthesis of metal carbides and the precise control of their phases and structures present formidable challenges. In comparison to other metal compounds like oxides, sulfides, and phosphides, metal carbides exhibit the highest Gibbs free energy of formation (ΔG°), indicating the lowest inclination for synthesis. Additionally, the formation of metal carbides requires stringent processing conditions due to the preferential oxidation of metals in the presence of atmospheric oxygen. Typically, metal carbides are generated through carburization and carbothermic reduction using methane and graphite. However, the sluggish kinetics of carbon (C)–induced reactions demand elevated temperatures, leading to undesired sintering and aggregation. Moreover, an excessive supply of C sources inevitably results in coke encapsulation and precipitation.

In this work, we approach an alternative method for the optimization and synthesis of nanoscale carbide catalysts, achieved by steering the equilibrium reactions involving oxocarbons (carbon monoxide (CO) and carbon dioxide (CO2)) during the calcination process. Oxo carbons engage in two equilibrium reactions: the Boudourad reaction (2CO (g) ←→ CO2 (g) + C (s)) and the CO/CO2 redox reaction (2CO2 (g) ←→ 2CO (g) + O2 (g)). This phenomenon allows for concurrent C–O reactions (selective C combustion) and Mo–C interactions (Mo carbide formation) within the nanofibers, serving as a framework for the initiation and growth of Mo carbides. This process enables precise manipulation of the phases and structures of Mo compounds. Since inducing selective redox reactions in multi-atomic systems like Mo–C–O poses significant challenges, requiring considerable trial and error in experimentally determining process variables. Hence, the specific prediction of processing parameters becomes imperative.

We successfully established processing windows for nanoscale carbide synthesis through thermodynamically forecasting oxocarbon-mediated gas-solid reactions. By computing AG° for Mo compound formation, we present a method for discovering specific processing windows to control the phases of diverse Mo compounds. Concurrently, the extent of selective C combustion is anticipated through pO2 calculations to regulate the porosity of C nanofibers and diffusion behavior of Mo. By utilizing the thermodynamically predicted processing window, we not only controlled a wide range of Mo phases (MoO2, α-MoC1.48, and β-Mo2C) but also manipulated various nanostructures (nanoparticle, spike, stack, and core–shell) by steering diffusion during the phase synthesis process in the Mo compounds/C nanofibers. Moreover, to confirm the connections between material and properties in nanostructured Mo carbides, we examine their catalytic performance in the hydrogen evolution reaction (HER). Our results demonstrate a performance achievement, with an overpotential of 152 mV at 10 mA cm⁻², accomplished through the formation of active nano-spikes of MoC on C nanofibers. We expect that the predictions of element spontaneous and spontaneous reactions will offer valuable insights to researchers involved in the synthesis and structural manipulation of diverse catalysts based on transition metal compounds.

5:00 PM EN09.08.14
Ammonia-Fuelled Proton Ceramic Fuel Cells with Atomic Layer Deposited Palladium Catalysts Joon Hyung Shim; Korea University, Korea (the Republic of)

The study investigates the efficacy of protonic ceramic fuel cells (PCFCs) operating in an ammonia-fuel environment, focusing on enhancing their performance. PCFCs, known for lower operational temperatures, faced limitations in ammonia decomposition. The strategy for improving ammonia decomposition was to introduce a palladium (Pd) catalyst, which resulted in remarkable improvements. Compared to untreated counterparts, the treated PCFCs exhibited a substantial increase in performance, achieving a peak power density of 0.3 W/cm² at 500 °C, nearly doubling the output. The process involved depositing Pd catalysts via atomic layer deposition onto the anode surface, where a blend of nickel oxide and BaZr0.2Ce0.6Y0.1Yb0.1O3-δ facilitated Pd penetration into the porous interior. This treatment significantly enhanced current collection and notably reduced polarization resistance, particularly evident at lower temperatures, ultimately bolstering overall performance. Importantly, impedance analysis confirmed the catalyst’s role in augmenting the current flow and mitigating resistance, contributing to the observed improvements. Moreover, stability tests showcased the treated PCFCs’ superior durability compared to untreated samples, suggesting the catalyst’s role in enhancing long-term stability. These findings underscore the potential of this methodology as a promising avenue for achieving high-performance and resilient PCFCs in the context of ammonia injection environments. In summary, the study’s overall approach of introducing a Pd catalyst into PCFCs operating under ammonia injection demonstrates substantial enhancements in performance, particularly at lower temperatures. The catalyst deposition technique enhances current collection, reduces resistance, and significantly improves durability, marking a significant stride toward realizing high-performing and stable PCFCs in ammonia-based energy systems.

5:00 PM EN09.08.17
Plasma-Treated 1D Transition Metal Dichalcogenides for Efficient Hydrogen Evolution Reaction Alex Laikhtman1, Arie Borenstein2, Alla Zak1 and Asmita Dutta2; 1Holon Institute of Technology (HIT), Israel; 2Ariel University, Israel

Significant research endeavours have been dedicated to the search for highly efficient and cost-effective electrocatalysts for the Hydrogen Evolution Reaction (HER). Transition metal dichalcogenide (MoS2) nanotubes were previously demonstrated for electrocatalysis performances owing to their unique chemical structure and physical properties. In this study, we report a new method of surface modification through cold radiofrequency (RF) plasma. The effect of two plasma ions (D2+ and Ar+) on WS2 nanotubes has been investigated. The plasma-treated samples showed improved performances in HER electrocatalysis. Based on experimental results, both Ar and D2 plasma treatments, when performed separately, show similar effects on electrocatalysis performances with improved HER overpotentials of 348 and 343 mV at -10mA/cm² compared to 567 mV of the pristine WS2 nanotubes. On the other hand, combined treatment by Ar and then by D2 radio frequency plasma notably decreases the overpotential to 264 mV. Hydrogen is considered a promising alternative for energy production due to its high energy density, high calorific value, and zero environmental effect of combustion products. To avoid the risk of the continuous exploitation and increased consumption of fossil fuels, the efficient and sustainable electrocatalysts for HER is required. Among all the known HER catalysts, Pt-group metals have been utilized as the most effective electrocatalysts for HER in an acidic medium. However, the low abundance and high cost...
considerably limit its large-scale application. The preferred electrocatalyst material should lower the activation energy so the process consumes less energy at fast reaction kinetics of the HER. Two-dimensional transitional metal dichalcogenides (TMDs) are an emerging class of materials with advantageous properties for a wide range of applications such as nanoelectronics, nanophotonics, sensing, etc. Due to the very distinctive characteristics such as robustness, low cost, ease of intercalation, and accessibility to structural modification, this group of compounds exhibit excellent electrochemical characteristics. WS₂ is a representative member of the TMD family. One-dimensional (1D) WS₂ nanotubes are extensively studied for their unique structural and electronic properties. Among other applications, WS₂ nanotubes demonstrated efficient catalytic performance for HER. WS₂ nanotubes feature unique physical and chemical behavior originating from the lattice strain raised by the tubular curvature. Yet, this specific class of pristine morganic nanotubes possesses fewer active sites and thus eventually suffers from the low affinity of WS₂ nanotubes for proton adsorption. Among different methods, plasma treatment was reported to modify the surface of WS₂ nanoparticles effectively. Low-power RF plasma treatment increases the number of disordered sites at the surface layer and produces atom vacancies, thus significantly enhancing energy conversion performance. Herein, we demonstrate the surface modification of WS₂ nanotubes by plasma treatment. This plasma modified WS₂ nanotubes used as catalyst reveal improved HER performance. To summarise, we have successfully formed plasma-treated WS₂ nanotubes, which provides a high concentration of active catalytic sites for electrocatalytic reaction. As a result, the HER catalytic activity of all the treated samples significantly improved compared to pristine WS₂ nanotubes. Plasma treatment increases material modified performance for catalyzing defects and disorders of the nanotube surface. Additionally, RF plasma treatment helps the incorporation of oxides hydrophilic groups inside the system, which promotes fast electron transfer. The effective lowering of overpotential for HER activity was achieved due to the simple, scalable, cost-effective, and less time-consuming plasma treatment on of the semiconductive WS₂ nanomaterial, demonstrates efficient and stable HER electrocatalytic performance.

5:00 PM EN09.08.19
Enhancing Ammonia Production Rate from Electrochemical Nitrogen Reduction by Modifying Cu Catalyst and Three-Phase Boundary Jeehye Kim1,2, Il Hee Jung3, Mathieu Doucer1, Han Yu Wang4, Youn Jeong Jang5 and Jae Sung Lee6; 1Oak Ridge National Laboratory, United States; 2Ulsan National Institute of Science and Technology, Korea (the Republic of); 3Hanyang University, Korea (the Republic of)

Ammonia (NH₃) is a critical component in fertilizer and other essential industrial chemical production, making it the second largest synthetic chemical worldwide (> 200 million tons). However, the traditional Haber-Bosch process requires massive energy input and results in the emission of a large amount of carbon dioxide [1,2]. The electrochemical nitrogen reduction reaction (eNRR) driven by renewable electricity under mild condition emerges as a sustainable method for NH₃ production to minimize carbon footprint [3,4]. We are focusing on the development of an effective eNRR system using Cu-based electrocatalysts in gas diffusion electrode (GDE) system with modification of three-phase interfaces. To overcome the low affinity of Cu for N₂, phosphorus activation was applied to create electron-deficient Cu sites for better N₂ adsorption and activation. Additionally, we address the limited solubility of nitrogen in aqueous electrolytes by incorporating a GDE coated with polytetrafluoroethylene (PTFE). This setup optimizes the three-phase interfaces among water, gaseous N₂, and the catalyst. Our innovative approach in a flow-type cell achieves a Faradic efficiency of 13.15% and an ammonia production rate of 7.69 μg cm⁻² at -0.2 V_RHE. This represents a 59.2-fold increase in N₃H production rate compared to electrodeposited Cu electrodes, highlighting the potential of our strategies in practical systems [3].


5:00 PM EN09.08.20
Non-Noble Metal Oxide (WO₃), Sulfide (MoS₂) and Carbide (MoC) for Electro and Photoelectrocatalytic Hydrogen Evolution Reactions Jae-Jin Shim, Muhanned Shafi Parasseeri and Al Mahmud Abdullah; Yeungnam University, Korea (the Republic of)

Nonprecious transition metal electrocatalysts are cost-effective, possess catalytic solid performance, and are scalable for hydrogen generation via water splitting, which provides clean and sustainable energy. Developing an efficient catalyst for hydrogen evolution reaction (HER) based on metal oxide, sulfide, and carbide has been studied worldwide to replace the expensive noble metal Pt. In this work, selected oxide, sulfide, and carbide (WO₃, MoS₂, and MoC), together with other metal compounds, have been studied. The 2D molybdenum disulfide is a challenge because of the restacking of MoS₂ layers, which leads to insufficient access to active sites. In this study, the drawbacks of 1T MoS₂ catalyst were overcome by employing carbon nano-onion (CNO). This CNO-MoS₂ exhibited an excellent HER performance with an overpotential of 53 mV vs. RHE and a Tafel slope of 40.8 mV dec⁻¹ for over 25 h, showing it one of the best HER catalysts next to platinum. 3D core-shell heterostructures of WO₃/B₈MoO₉/Co-Pt and BiVO₄/MoS₂ were also synthesized using hydrothermal synthesis/ electrodeposition and electrodeposition/plasma-enhanced atomic layer deposition (PECALD). The former hetero-photocatalyst exhibited significantly high photoelectrochemical activity, where its photocurrent efficiency was 4.6 times greater than that of the constituent WO₃. For the BiVO₄/MoS₂ photoelectrode, an optimal thickness of the MoS₂ layer was controlled by the number of PEALD cycles. The highest photocurrent (2.1 mA cm⁻²) was produced from the electrode with a 6 nm layer-thickness, 2.4 times higher than the pristine BiVO₄. Thermal pyrolysis created a carbon-encased, nitrogen-rich γ-MoC/NiC composite that contains rGO. The overpotential at 10 mA cm⁻², of γ-MoC/NiC@rGO for HER is 185 mV, whereas it is 298 mV for OER. The Tafel slopes for HER and OER are relatively modest, at 78 and 80 mV dec⁻¹, respectively. This study highlights a new, highly stable, highly performing non-noble metal catalyst for electrochemical water splitting applications.

SESSION EN09.09: Batteries and Supercapacitors
Session Chairs: Nathalie Herlin-Boime and Cedric Tard
Thursday Morning, April 25, 2024
Room 337, Level 3, Summit

8:30 AM *EN09.09.01
Organic Chemistry—A Tool for Improved Performance of Lithium Secondary Batteries Charlotte Mallet; Hydro Quebec, Canada

Hydro-Quebec’s Center of Excellence in Transportation Electrification and Energy Storage has been a world-class innovation hub in the field of battery materials for electric vehicles as well as other energy storage applications for more than 40 years. The Center’s efforts are primarily focused on advanced lithium-ion batteries and solid-state batteries. Its know-how, extensive intellectual property portfolio and cutting-edge facilities draw interest from around the world and make it an essential partner for major industry players involved in the development of next-generation battery materials and technologies.

This presentation will outline our major breakthroughs in building our strong expertise in organic chemistry. By dint of multidisciplinary team, our work is rooted in understanding degradation phenomena of battery systems and aims to provide solutions based on the structure-property relationships of materials, which resulted in 40 patents with new concepts since 2015.

To tackle the challenges related with high voltage cathodes like LiMPO₄ or NMC, we developed new additives to protect electrolyte-cathode interface and limit degradation phenomena such as transition metal dissolution1,2 or electrolyte side reactions.3 In addition, we developed new binders or co-binders to improve low temperature applications, increase C-rate performance,4 and polymers to eliminate different types of gas by in-situ trapping.5 Our works include synthesis of new kind of salts for liquid and solid lithium batteries.6 We also developed new organic cathode materials with high operation voltage up to 4.5V, and high specific capacity of 692 mAh/g. The cycle life was tested with polymer electrolyte system at 40°C.7 Finally, another major project is protection of lithium metal anode by different organic compound deposition method like spray-coating or solution casting. This protective organic layer stabilized Li metal interface providing enhanced performance with various electrolyte chemistries such as liquid, polymer, and solid electrolyte.8 The organic and polymer chemistry team of center of excellence has developed a lot of creative solutions to address a wide range of issues such as stability, efficiency, low temperature performance and low cost.

Supercapacitors have drawn an extensive attention for their high power density and excellent cycling stability to meet a rapidly growing demand for high-capacity energy storage systems. Specifically, metal (e.g., Ni, Co, Fe, Al, Mn, and its combinations) layered double hydroxides (LDHs) have been integrated to supercapacitor electrodes owing to their seamless ion transport through interlayer. LDHs are often hybridized with conductive materials to facilitate charge transport since low conductivity of LDHs hinders the supercapacitors to reach their theoretical performance (e.g., ~3,000 F g⁻¹ for pristine NiCo LDH). Although diverse forms of LDH hybridized carbon electrodes are designed, it has not yet been systematically studied how morphology and composition simultaneously affect the performance of supercapacitors. Accordingly, we have systematically controlled the synthetic method/condition of growing metal LDHs on nitrogen doped porous carbons (NPCs) and studied their effects on electrical performance as hybrid electrodes of supercapacitors. In detail, various metals (i.e., Ni, Co, and NiCo) have been deposited on NPCs by either electrodeposition (i.e., 100, 300, 500, and 1000 mC) and solvothermal method. NPC was chosen as carbon electrodes since it can improve the rate performance as well as structural stability of electrodeposited LDHs owing to its higher conductivity, specific surface area, and hydrophilicity compared to other carbon-based materials with free-standing structure for electrodeposition compatibility. The supercapacitor with electrodeposited NiCo LDH@NPC electrodes exhibited higher specific capacitance than those of either Ni or Co LDH@NPC electrodes, since coexistence of metals shows a synergistic effect on storing higher energy via multiple reduction-oxidation (redox) reactions. Among NiCo LDH@NPC electrodes, the electrode with the total deposited charge of 500 mC (NiCo500 LDH@NPC) showed the highest capacitance of 3,155.52 F g⁻¹. These results might be ascribed to three main factors: (i) multiple redox reactions from Ni-Co coexistence, (ii) shortened hydroxide (OH⁻) ion diffusion length due to the uniform distribution of LDH in nanomesh structure, and (iii) facilitated OH⁻ ion accessibility into active materials owing to broader interlayer of LDH. Furthermore, an asymmetric supercapacitor (NPC||NiCo500 LDH@NPC) achieved energy density of 39.22 Wh kg⁻¹ at a power density of 913.87 W kg⁻¹ and 80.00% retention after 20,000 cycles.

9:15 AM EN09.09.03

Microwave Synthesis for Triimetallic Needle Structures coupled with N-Doped Carbon for Highly Boosted Bifunctional Oxygen Catalysts for Zn–Air Batteries

Hoyoung Jang, Youngsun Cha and Wonjoon Choi; Korea University, Korea (the Republic of)

Energy storage systems play a crucial role in expanding the capabilities of sustainable energy sources and addressing existing energy issues associated with environmental pollution concerns. While versatile renewable energy sources have been developed over the past decade, their large-scale implementation inherently requires the use of highly efficient yet robust energy storage solutions. Metal-air batteries have recently been attracting attention as a promising emerging candidate for next-generation storage cells due to their high theoretical capacity and eco-friendly use of oxygen. Among various types of metal-air batteries, the Zn-air battery has notably demonstrated a high theoretical energy density of 1860 Wh/kg, while ensuring cost-effective production, safety, and environmental compatibility. The primary emphasis in the development of rechargeable Zn-air batteries has been on improving stability and energy efficiency. The challenge of achieving high energy efficiency lies in the substantial overpotential of the constituent materials, which impacts the effectiveness of both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). Noble metal-based electrocatalysts such as Pt/C and Ir/C exhibit remarkable electrochemical performances in ORR and OER. However, its widespread application is limited due to its high cost and stability issue.

In this work, we report a facile synthesis route of trimetallic bifunctional catalysts with N-doped carbon, with their low overpotential and high stability comparable to precious metals. The formulation of the precursor solution is conducted by precisely mixing 0.3 M iron nitrate hexahydrate (Fe(NO₃)₃.6H₂O), 0.3 M nickel nitrate hexahydrate (Ni(NO₃)₂.6H₂O), 0.3 M cobalt nitrate hexahydrate (Co(NO₃)₂.6H₂O), 1.2 M urea (CO(NH₂)₂), and 0.4 M ammonium fluoride (NH₄F) in 100 ml of deionized (DI) water. The melamine foam was soaked in this solution and it was subjected to heating in an oven at 130 degrees celsius for a duration of 5 h as an integral step in the synthesis process. Then, the catalyst is directly fabricated using microwave heating for 20 seconds at 1000 W power. Scanning electron microscopy images illustrate the morphology transition of the catalysts at each stage of the synthesis process. Optimizing the microwave heating exposure leads to the creation of uniform metal oxides, as evidenced through transmission electron microscopy analysis. The composition and chemical state of the elements constituting the catalyst surfaces are precisely examined using X-ray photoelectron spectroscopy and X-ray powder diffraction.

The electrochemical performance of the developed catalysts is examined using a potentiostat in a three-electrode electrochemical cell with a rotating ring disk. The optimized trimetallic (Fe-Ni-Co) catalysts exhibit a low overpotential (0.071 V), similar to that of Pt/C and Ir/C. Under the full cell test, the catalysts obtain stable performances for 300 h in repetitive charge/discharge cycles for an hour interval, and the specific capacitance reaches 769 mAh g⁻¹ at 10 mA cm⁻². We believe that this rational synthesis strategy toward a facile fabrication process will contribute to developing novel active materials with mesoporous structure and large surface area, potentially useful for diverse electrochemical energy storage systems. Furthermore, the outcome of this work will inspire novel design of high performance electrocatalysts and other energy-related hybrid materials using transition metals.

9:30 AM *EN09.09.04

Confining Highly Redox-Active Aroms in Stable Insertion-Type Anode Materials for Alkali Metal-Ion Batteries

Dominic Bresser; Karlsruhe Institute of Technology, Germany

The unique combination of exceptional energy and power density along with the continuous decrease in cost have made lithium-ion batteries the electrochemical energy storage technology of choice for small-scale and large-scale applications. However, the use of graphite as active material for the negative electrode is intrinsically limiting the possibility to rapidly charge these batteries. Herein, a new class of active materials is presented that provides comparable charge storage capacities at much faster rates. This new class of materials is based on the introduction of highly redox-active atomic centers into stable metal oxide host structures. These host structures are well preserved upon continuous lithium cation insertion and deinsertion following a solid-solution-type mechanism, while the introduction of these highly redox-active atomic centers allows for the duplication and triplication of the charge storage capacity compared to the nanoparticulate metal oxide host structures alone. Remarkably, the redox centers are reversibly reduced to the metallic state at the atomic level without affecting the surrounding crystal structure. When replacing lithium cations by sodium or potassium cations, essentially the same mechanism is observed, apart from the expected “size effect”, highlighting the exceptional versatility of this new class of battery electrode materials.

References


10:00 AM BREAK

SESSION EN09.10: HER, OER and ORR Reactions I

Session Chairs: Dominic Bresser and Edmund Chun Ming Tse
Thursday Morning, April 25, 2024
Room 337, Level 3, Summit

11:00 AM EN09.10.03

Bifunctional Nickel Cobalt Phosphorus Sulfide Electro catalyst for Simultaneous Hydrogen Evolution and 5-Hydroxymethylfurfural Oxidation

Kuan-Mei Hung and Jih-Jen Wu; National Cheng Kung University, Taiwan

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
The replacement of the O$_2$ evolution reaction of electrocatalytic water splitting with a thermodynamically more favorable reaction has attracted considerable attention for simultaneous value-added feedstock formation coupled with H$_2$ production. The electrocatalytic oxidation of renewable biomass platform chemical 5-hydroxymethyl furfural (HMF) to 2,5-furandicarboxylic acid (FDCA), a valuable bio-monomer of polyethylene furanceate (PEF), has emerged as a promising sustainable route for biomass valorization. In this work, bifunctional nickel cobalt phosphorous sulfide nanosheet arrays (NCPS) were constructed on Ni foams as the electrodes of a two-electrode electrolytic H cell for simultaneous electrocatalytic hydrogen evolution and HMF oxidation (HMFOR) to FDCA in 0.1 m KOH. To overcome, mainly related to the slow kinetics of the acidic oxygen evolution reaction (OER) that occurs at the anode. Ruthenium (Ru)-based materials (e.g. RuO$_2$), which are much more abundant and have relatively high OER activity, are very attractive alternatives to rare iridium (Ir)-based materials such as IrO$_2$, the most commercialized acidic OER catalyst. Nonetheless, Ru has a critical drawback in that it is easily oxidized and dissolves as a soluble species (Ru$^{4+}$) under acidic OER operating conditions. Therefore, additional research is required to find solutions to this issue. In this study, we tried to develop a highly efficient and durable Ru-based acidic OER electrocatalyst, employing interfacial engineering. Ruthenium oxide (RuO$_2$) nanoparticles were coated on the surface of one-dimensional (1D) rutile TiO$_2$ nanosheets using a facile hydrothermal method. Introducing rutile TiO$_2$ as a support is advantageous in enhancing the OER stability and promoting an interfacial affinity with the catalyst due to its excellent corrosion resistance and the common crystal structure sharing with RuO$_2$. Notably, the size, morphology, and crystallinity of Ru species crystal grains on the TiO$_2$ surface changed depending on the pH conditions during the reaction process. When RuO$_2$ was grown in the form of a large nanosheet with high crystallinity through alkaline pretreatment (RT-Ns), it was less affected by strain effect and showed OER performance with no significant difference from general RuO$_2$. On the other hand, in the case of a sample composed of a small nanoparticle film on a TiO$_2$ support synthesized in an acidic solution (RT-NPs), the interfacial synergy with TiO$_2$ was maximized, showing excellent OER activity. Finally, we achieved enhanced acidic OER performance by improving stability through a low-temperature post-annealing process.

Acknowledgement:
This work is supported by the National Research Foundation of Korea (NRF) Grant funded by the Ministry of Science and ICT [NRF-2020R1A6A1A03045059].

1:45 PM EN09.11.02
Effective Catalysis Design for Selective OER in Seawater
Sarafadzeh Ghadami, Suraj Loomba, Muhammad Haris, Muhammad Waqas Khan and Nasir Mahmood; RMIT University, Australia

The oxygen evolution reaction (OER), a significant half-reaction in electrocatalytic water splitting to produce green hydrogen, has received considerable research attention. Currently, state-of-the-art water splitting technology utilises the expensive and scarce noble metal-based catalysts and freshwater, a limited resource, as it constitutes less than 1% of the world's total water. To this end, alternative feedstocks, such as seawater, need to be explored, which account for approximately 96.5% of the world's total water. As global concerns about crises such as climate change and fossil fuel depletion increase, the importance of hydrogen energy is being further emphasized. In particular, there is growing interest in the commercial feasibility of using polymer electrolyte membrane water electrolysis (PEMWE) for large-scale production of green hydrogen. However, there are significant obstacles to overcome, mainly related to the slow kinetics of the acidic oxygen evolution reaction (OER) that occurs at the anode. Ruthenium (Ru)-based materials (e.g. RuO$_2$), which are much more abundant and have relatively high OER activity, are very attractive alternatives to rare iridium (Ir)-based materials such as IrO$_2$, the most commercialized acidic OER catalyst. Nonetheless, Ru has a critical drawback in that it is easily oxidized and dissolves as a soluble species (Ru$^{4+}$) under acidic OER operating conditions. Therefore, additional research is required to find solutions to this issue. In this study, we tried to develop a highly efficient and durable Ru-based acidic OER electrocatalyst, employing interfacial engineering. Ruthenium oxide (RuO$_2$) nanoparticles were coated on the surface of one-dimensional (1D) rutile TiO$_2$ nanosheets using a facile hydrothermal method. Introducing rutile TiO$_2$ as a support is advantageous in enhancing the OER stability and promoting an interfacial affinity with the catalyst due to its excellent corrosion resistance and the common crystal structure sharing with RuO$_2$. Notably, the size, morphology, and crystallinity of Ru species crystal grains on the TiO$_2$ surface changed depending on the pH conditions during the reaction process. When RuO$_2$ was grown in the form of a large nanosheet with high crystallinity through alkaline pretreatment (RT-Ns), it was less affected by strain effect and showed OER performance with no significant difference from general RuO$_2$. On the other hand, in the case of a sample composed of a small nanoparticle film on a TiO$_2$ support synthesized in an acidic solution (RT-NPs), the interfacial synergy with TiO$_2$ was maximized, showing excellent OER activity. Finally, we achieved enhanced acidic OER performance by improving stability through a low-temperature post-annealing process.

Acknowledgement:
This work is supported by the National Research Foundation of Korea (NRF) Grant funded by the Ministry of Science and ICT [NRF-2020R1A6A1A03045059].
The initial oxidation state and composition of the calcined iridium oxides, as evidenced by XAS, XRD and XPS measurements. Regarding other types of porous materials, we have also been able to prepare hierarchical structures of IrO₂ based on Pearson’s hard and soft acid-base theory and characterize their outstanding activity toward the OER.[4]


2:30 PM BREAK

3:00 PM EN09.11.04
Investigation of Active Factors for Oxygen Reduction Reaction by Titanium Oxide Model Electrode Takahiro Saidai, Miyu Mashiyama and Takahiro Maruyama; Meijo University, Japan

Polymer electrolyte fuel cells (PEFCs) are one of the low-environmental-impact power sources. However, the broad commercialization of PEFCs has been slow. One reason for this is that the electrocatalyst of PEFCs is the high manufacturing cost and low durability. Titanium oxide-based catalysts have attracted attention as the candidate for low-cost and highly durable electrocatalysts. Titanium oxide-based catalysts need to address the drawback of poor catalytic activity.

Currently, introducing the oxygen vacancies and doping the other metal atoms are known to enhance the oxygen reduction-reaction (ORR) activity on titanium oxide. Generally, the catalytic reaction progresses at the low coordination site on the surface. Introducing oxygen vacancies leads to an increase in low-coordination sites, which means increasing the activity sites. As a result, the ORR activity of titanium oxide is improved by introducing oxygen vacancies. In addition, the oxygen vacancy changes the electron structure of titanium oxide and provides electron conductivity. From the results of the DFT calculation, it was reported that the low-coordination metal site, which was formed by oxygen vacancy, and the neighborhood structural oxygen played an important role in ORR. On the other hand, the structural analysis results using the pair distribution functions (PDFs) method using X-ray showed that the active site was related to the crystal distortion site and no confirmed oxygen vacancies. One of the problems in titanium oxide-based catalysts is that the active site and reaction mechanism are still unclear. For this reason, the design of new catalysts must rely on rules of thumb. Clarifying the active control factor for ORR on titanium oxide is one of the effective approaches to the high activity close to platinum-based catalysts.

In this study, a titanium oxide model electrode formed by a mono-layer of the titanium oxide nanosheets was used to separate the effects from the low coordination site and the crystal distortion. A titanium oxide nanosheet is composed of octahedrons centered on Ti atoms. Thus, the variation of Ti valence is linearly related to the number of low-coordination sites. The crystal distortion was evaluated by in-plane XRD and grazing-incidence XAFS measurements in synchrotron radiation facilities. In particular, the local coordination structure of the titanium-oxide model electrode was investigated from pre-peak before the adsorption edge and EXAFS region in the obtained XAFS spectrum. The Ti valence was estimated from the energy of half value at the edge jump intensity in the XAFS spectrum. The number of oxygen vacancies on a titanium-oxide model electrode was roughly controlled by the calcination temperature with hydrogen flow conditions. Electrochemical measurements were performed in a three-electrode cell with 0.1 M HClO₄ electrolyte.

The structure of the titanium-oxide model electrode was changed from the lepidocrocites structure to the anatase structure with increasing calcination temperature. The local coordinate structure was also transformed with increasing calcination temperature. At that time, the Ti valence was gradually elevated from 3.47 to 3.92. The ORR activity of the model electrode was enhanced by the calcination with hydrogen flow until the beginning of the phase transition to the anatase structure. The distortion of the crystal structure was most significant after the phase transition. However, the ORR activity was low compared to before the phase transition. Introducing the oxygen vacancies to the titanium-oxide model electrode clearly enhanced the ORR activity and gave its structure a very slight crystal distortion. At this time, it is forecasted that the crystal distortion is more effective in ORR activity on titanium oxide rather than the number of oxygen vacancies. However, the permissible crystal distortion rate may be narrow, and the phase transition probably leads to the degradation of the ORR activity.

3:15 PM EN09.11.06
MOF-Based Architectures towards Higher Activity Oxygen Reduction Reaction Catalysts Albert Enpstein, William A. Maza, Benjamin L. Greenberg, James Rideour, Bethany M. Hudak, Olga Baturina, Boris N. Feykelson and Brian Chaloux; U.S. Naval Research Laboratory, United States

The electrocatalyst responsible for carrying out the oxygen reduction reaction (ORR) at the hydrogen fuel cell (FC) cathode has a demanding task to perform in a highly acidic environment and under a corrosive potential. Despite its cost, platinum (Pt) has become the most common catalyst proven to have high activity and durability towards ORR catalysis. There is, therefore, a need to design and develop more cost-effective catalysts that can either replace or reduce Pt content. A key challenge in the design of ORR catalysts is maximizing the conduction and utilization of electrons, protons, and oxygen to the active sites on the electrode surface. For use in intermediate temperature hydrogen fuel cells, which operate above the boiling point of water, the ability to minimize transport barriers in the electrolyte material and optimizing the way it couples to the ORR catalyst is of great importance to maximize catalytic turnover and efficiency. To that end, we have set out to develop approaches toward using metal-organic frameworks (MOFs) as templates for high-surface-area platinum structures to develop high-performance ORR catalysts. As a proof-of-concept, we have chosen the highly robust and well-known UiO series, which among other benefits has the potential for pore-size tuning that should be conducive for effective gas transport. The MOF synthesis has been optimized to target well-defined, single crystalline MOF particles with shape control and narrow size distributions and scaled to multi-gram batches. Subsequently, we have explored different approaches to deposit Pt onto these MOF nanoparticles using methodologies that include colloid-derived methods, as well as solvothermal and atomic layer deposition (ALD) approaches. In this work we compare the different Pt deposition approaches by assessing the relative ORR activities and correlate the results to X-ray photoelectron spectroscopy (XPS) and the catalyst morphology as determined by high-resolution transmission electron microscopy (HR-TEM).

3:30 PM EN09.11.07
Current Density – Voltage (i-V) Dependence of Polymer Electrolyte Electrochemical Cells (PEEC) on The Cell Components of Gas Diffusion Layers (GDLs) and Cell Seatings Miyuki Nara, Katsumi Fujii, Takeharu Murakami, Takayo Ogawa and Satoshi Wada; RIKEN, RAP, Japan

Hydrogen production using water electrolysis in polymer electrolyte cells (PEEC) is an attractive technique. The PEEC is known to be relatively strong for input energy conversion into hydrogen and able to be used in many commercial applications. However, the current density characteristics as a function of PEEC voltage are critical for improving the efficiency of hydrogen production from renewable energies. Research is continuing to improve the performance of the PEEC by optimizing the way it couples to the ORR catalyst. The PEEC cell structure consists of endplates, gas diffusion layers (GDLs), catalyst-coated membranes (CCM), and gas and supplied water-sealing materials. These components were not considered to improve PEEC performance. However, these structures affect electron, water, and gas electron flows. Thus, the effect of these components on the PEEC performance is discussed here.

In this study, the influence of the GDL thickness and porosity was evaluated by current density-voltage (i-V) characteristics and electrochemical impedance spectroscopy (EIS). A PEEC with a thicker and higher porosity GDL improved the i-V characteristics. It was also found that the thickness of the seal has an appropriate relationship with the internal parts. The series resistance evaluated by EIS decreased with an improvement in the i-V performance. From these results, the reason for this i-V characteristic change is estimated to be changing the flow of electrons and/or the flows of the source material of water and/or of the produced gas oxygen or hydrogen.
obtained by different heat treatments. To facilitate the formation of grains, spherical seeds that are randomly located and oriented are introduced. Temperature dependence of the grain sizes of the obtained structures is investigated. Furthermore, the effects of the microstructural features on the band structure are computed using large-scale Density-Functional Tight-Binding calculations (DFTB). Differences in the electronic properties between ideal crystal and different grainy structures are compared.

8:15 AM EN09.12.02
Effects of Nanosizing of Zirconia and Bandstructure Modulation on Catalytic Activity: Insights from a Combined Density Functional Tight Binding – Order(N) Density Functional Theory Study Kexin Chen1, William Dawson2, Takahito Nakajima2, Aulia S. Hutama3, Keisuke Kameda3, Sergei Manzhos3 and Manabu Ihara1; 1Tokyo Institute of Technology, Japan; 2RIKEN Center for Computational Science, Japan; 3Universitas Gadjah Mada, Indonesia

Zirconia based materials are widely utilized in the electrodes of solid oxide fuel cells and electrolysis cells. Interactions of small molecules with zirconia surfaces are of key importance in these applications. Numerous theoretical reports have focused on periodic models, while the properties of materials at the nanoparticle or cluster scales may differ markedly from their bulk counterparts. However, ab initio level understanding of gas adsorption behavior on Zirconia at this scale remains limited. We will present a comparative analysis based on first principles and semiempirical calculations of cubic ZrO2 nanoparticles, varying in size from a few tens to a thousand atoms. This is achieved by combining density functional-based tight-binding (DFTB) and order-N DFT to balance computational cost and increase scalability. The band structure of the nanoparticles, which proves sensitive to oxygen deficiencies, exerts a significant influence on gas adsorption behavior. Notably, nanoparticles can exhibit intrinsic as well as p- and n-doped characteristics corresponding to O-rich or O-poor conditions. The n-type particles display heightened reactivity for the adsorption of CO and CO2 gases on their surfaces with promoted electron transfer from zirconia adsorbents to the adsorbed molecules, which is useful for their catalysis, with the effect strengthened by nanosizing. Our results suggest good potential of nanosizing and bandstructure engineering in zirconia nanoparticles to achieve enhanced gas adsorption and catalytic performance, thus presenting promising utilization prospects in energy devices.

8:30 AM EN09.12.03
Chemical Vapor Deposition of Ru/RuSe2 Catalyst for Electrolytic Hydrogen Evolution Reaction Daba D. Megera1, Gutema T. Gudena1, Youngho Kim2 and Hak K. Yu1,3; 1Ajou University, Korea (the Republic of); 2Korea University, Korea (the Republic of); 3Ajou University, Korea (the Republic of)

The current trend of synthesis in preparing catalysts for hydrogen evolution reaction (HER) is heavily dependent on solution processing which takes a great deal of time and is mostly not suitable to prepare supported structures. Solution processing has advantages to prepare controlled stoichiometry nano particles, while the prepared nano particles end up in another step of dispersing them into a solvent and coating onto desired substrate, which results in long process and sometimes poor adhesion of catalysts to the substrates. We believe chemical vapor deposition is less utilized in synthesis of supported catalysts for HER. In this regard the essence of this work was to provide a simple alternative synthesis route for catalysts used in HER. Therefore, this work demonstrates a one-step synthesis of highly stable Ru/RuSe2 nanoparticles (NPs) on carbon paper using low temperature and pressure chemical vapor deposition (CVD), resulting in a heterointerface with multiple active sites for catalysis. The catalyst exhibited outstanding performance for the hydrogen evolution reaction (HER) in an alkaline solution, with low overpotentials and fast hydrogen adsorption and desorption kinetics. The Ru/RuSe2-C nanoparticle structure has potential for large-scale production and can be used as an efficient catalyst for HER.

8:45 AM EN09.12.04
Transition Metal- Metal Carbide decorated N-Doped Carbon Framework as Efficient Dual Mott-Schottky Electro catalysts for Water Splitting Debanjan Das, Bidushi Sarkar, Shauvik Biswas and Karuna K. Nanda; Indian Institute of Science, India

Transition metal carbides (TMCs) have garnered significant attention as effective electrocatalysts for the hydrogen evolution reaction (HER), offering a highly active and stable alternative to precious metals like platinum, because of their d-band electronic structure resembling that of platinum. In this study, we address the challenge of developing a top-tier bifunctional electrolyte catalyst for efficient water splitting by employing a dual transition metal approach to electronically modify bimetallic carbides. Here, we have designed a composite structure through an in-situ fabrication process featuring N-doped carbon nanotubes (CNT) and graphene, which serve as anchors for Co/MoC, Co/WC, and Co/VC. This integrated pyrolysis technique promotes synergistic interactions among these components and creates dual Mott-Schottky junctions, resulting in a bifunctional catalyst capable of catalyzing both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) with exceptional activity in both acidic and basic environments. Furthermore, it demonstrates excellent performance in water splitting under basic conditions, requiring a relatively low cell voltage of approximately 1.686 V to generate a current of 10 mA/cm² while maintaining good stability. This superior performance is attributed to the cooperative electron transfer between the Co and MoC moieties and the defects induced by nitrogen doping in the graphene/CNT-based conductive network, distinguishing it from other recently reported Mo-based carbide materials.

8:50 AM EN09.12.09
Stabilization of PtRu Alloy Nanocatalysts by Encapsulation with Niobium Oxide Annabelle M. Hadley1, Fredoe Seland2 and Byron D. Gates1; 1Simon Fraser University, Canada; 2NTNU, Norway

The threat of climate change motivates us to reduce our reliance on fossil fuels and transition to renewable energy infrastructure. Direct methanol fuel cells (DMFCs), in which electrocatalysts harness electricity from the reaction of methanol and oxygen, are an attractive clean energy technology because of the high energy density and ease of transport and storage of methanol compared to hydrogen. However, there remains much to improve upon in terms of the durability, and as a consequence the economic viability, of DMFCs. This project focuses on the durability of the anodic electrocatalysts which facilitate the methanol oxidation reaction. A platinum-ruthenium alloy is the most commonly used electrocatalyst towards the methanol oxidation reaction due to its high performance. The high activity and selectivity of the platinum is additionally imparted high tolerance for poisoning byproducts of methanol oxidation [carbon monoxide (CO)] by alloying with ruthenium. Unfortunately, the ruthenium is known to dissolve from the alloy and reduce the CO tolerance of the catalysts. This project explored encapsulating the PtRu nanoparticle catalysts with porous niobium oxide to stabilize the PtRu alloy. Niobium oxide was chosen due to its high corrosion resistance and suitable to prepare supported structures. Solution processing has advantages to prepare controlled stoichiometry nano particles, while the prepared nano particles end up in another step of dispersing them into a solvent and coating onto desired substrate, which results in long process and sometimes poor adhesion of catalysts to the substrates. We believe chemical vapor deposition is less utilized in synthesis of supported catalysts for HER. In this regard the essence of this work was to provide a simple alternative synthesis route for catalysts used in HER. Therefore, this work demonstrates a one-step synthesis of highly stable Ru/RuSe2 nanoparticles (NPs) on carbon paper using low temperature and pressure chemical vapor deposition (CVD), resulting in a heterointerface with multiple active sites for catalysis. The catalyst exhibited outstanding performance for the hydrogen evolution reaction (HER) in an alkaline solution, with low overpotentials and fast hydrogen adsorption and desorption kinetics. The Ru/RuSe2-C nanoparticle structure has potential for large-scale production and can be used as an efficient catalyst for HER.

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SYMPOSIUM EN10

Novel Approaches to Synthesize and Characterize Stable Halide Perovskites and their Devices
April 22 - April 26, 2024
Minimizing energy loss and increasing the quality of crystalline perovskite films are keys to improve the performance and long-term stability of perovskite solar cells. To address these challenges, we have developed several multifunctional, nonvolatile additives that can be used to modulate the kinetics of perovskite film growth to enable large-sized grains and coherent growth of perovskites from bottom to surface to be achieved. The improved film morphology resulted in significantly reduced non-radiative recombination, helping enhance the power conversion efficiency (PCE) of inverted (p-i-n) device to ~26% with low energy loss and good stability. In addition, these multifunctional additives can also be applied to address one of the most challenging problems involved in large bandgap perovskites and their derived devices for single junction and tandem solar cells. The commonly observed halide segregation critically limits the stability of mixed-halide perovskites under device operational conditions. There is a strong indication that halide movement/oxidation is the primary driving force behind halide demixing. To alleviate this problem, we have developed a series of multifunctional mediators that can suppress these factors while simultaneously passivate defects through tailored substitution. These effects enable wide-bandgap (1.8 eV) perovskite solar cells to achieve an outstanding PCE >20%, with 95% of its initial PCE retained after tracking at maximum power point for 500 h. Integrating this layer into a monolithic perovskite-organic tandem solar cell as a wide-bandgap subcell afforded a record-high PCE of 26.1% and impressive long-term operational stability.

Challenges to upscaling metal halide perovskites (MHPs) include mechanical film stresses which accelerate degradation, dominate at the module scale, and can lead to delamination or fracture. In this work, we demonstrate open-air blade coating of single-step coated perovskite as a scalable method to control residual film stress after processing and introduce beneficial compression in the thin film with the use of polymer additives such as gelain gum and corn starch.

Given the strong link between residual stress and degradation, we assessed the stability of perovskite films with different residual stress states. Perovskite films on silicon and glass were stress engineered using additives to either be tensile or compressive and aged under either high heat or humidity conditions (85°C vacuum or 85% relative humidity). A control MAPbI3 film spin coated without additives was also added as a reference under 85% relative humidity. The samples were periodically removed, and the stress was remeasured in ambient conditions (22°C and 40% RH). The highly tensile samples experienced stress relaxation quickly in the humid environment due to moisture induced degradation. This effect was not observed for samples with compressive stress, which also did not experience visible degradation during the 100-hour exposure. We performed XRD measurements on these films to verify degradation and the tensile sample had PbI2 peaks after the aging experiment, whereas the compressive sample had lower intensity PbI2 peaks and still had MAPbI3 in the film. This confirms that perovskites are more structurally stable when exposed to environmental conditions while in compression. Samples were reannealed to ensure that trapped moisture was not the cause of the relaxation, and there was no change observed in the stress. Therefore, residual moisture is not the explanation for stress reduction.

A similar experiment was conducted for thermal stability at 85°C under vacuum to monitor the changes in stress under thermal aging. Once again, stress relaxation was observed for the highly tensile sample with gum. The improvement in stability was visually apparent since the tensile films turned completely yellow after being aged for 100 hours while the compressive one remained largely in the black photofactive phase. The samples with additives took longer to visibly degrade, which also points towards their improved stability. The tensile stress was therefore relaxing as the film degraded due to the strained bonds likely enabled the methylammonium cation to diffuse out, whereas a compressive stress showed better stability and unchanging stress under heat, similar to the effect observed with aging in high humidity.

A thermal cycling experiment was also conducted for a tensile and compressive sample to monitor the perovskite films as the temperature changes between -40 to 85°C. The experiment ran for 200 cycles and the results supported what was observed under high heat and humidity conditions. The tensile sample relaxed by 180 MPa and turned completely yellow. However, the compressive sample was stable both in terms of its appearance and film stress. A spin coated MAPbI3 film without additives (with tensile residual stress) was kept as the control sample. In all three aging conditions, films with residual tensile stress degraded significantly faster. The degradation also corresponded to stress relaxation in the perovskite film as the phase changed, marking the first time for which changes in stress have been directly mapped to stability. Stress relaxation has been observed in many other material systems (i.e., polymers and metals) when exposed to tensile stress. Perovskites therefore act similarly, and despite their brittle nature, share in this property.

This discovery of a new mechanism underpinning MHP degradation shows that film stress can be used as a parameter to screen MHP devices and modules for quality control before deployment as a design for reliability criterion.
Advancing Photovoltaic Performance and Stability of Perovskite Solar Cells Using a Solid-State Multi-Modal Electrochemical Approach

Juan F. Tirado, Mriganka Singh, Michel De Keersmaecker and Erin L. Ratcliff; University of Arizona, United States

Analysis and characterization of buried interfaces in metal halide perovskite (MHP) devices has always been a major challenge in advancing device performance and stability, particularly under conditions of operation including light bias and charge transport. Recently, our group has developed a solid-state electrolyte “peel and stick” spectro-electrochemistry methodology in order to directly study the energy levels and charge extraction capabilities of the buried interface between ITO/MHP under operando conditions. Moreover, this tool allows including redox probes in the solid electrolyte in order to measure near-gap and mid-gap defect densities of MHP with quantification limits around ~10^{14} cm^{-3}, which is below the space-charge limited current methodology or conventional spectroscopic techniques.

Our approach overcomes a major challenge to industrial adaptation and manufacturing at scale of printable electronics. Generally, interface modifications at charge-selective-layer/MHP bottom contacts are speculated to improve performance through correlations with indirect measurements and a demonstration of a change in power conversion efficiency. For instance, photoluminescence spectroscopies can only determine the chemical environment and energetics at the MHP surface, which is widely recognized to be dependent on buried interface chemistries that cannot be probed with subsequent layer deposition. Similarly, time-resolved photoluminescence spectroscopy is restricted to measuring the net total change in carrier lifetime but lacks exact information on charge extraction/injection at the buried interface with the MHP.

In this context, herein we extend the use of our “peel and stick” electrochemistry platform to assess the effect of partial device stacks comprised to transparent conductive oxide/hole-transporting-layer (HTL)/MHP interfaces, systematically modified using ionic liquids and phosphonic acids. Our approach is exquisitely sensitive to small changes in energetics, monitored through injection barriers, and charge extraction capabilities of HTL-MHP interface in a p-i-n Perovskite Solar Cells (PSCs) configuration. Remarkably, we demonstrate the correlation between interface charge extraction “quality” and photovoltaic response of p-i-n PSCs so that our solid-state electrochemical platform may advance the device performance by probing the buried interface.

Similarly, we take advantage of this powerful tool to explore MHP stability under thermal and illumination stress conditions and to measure the effect of HTL nature by quantifying the near-gap defect densities. Ultimately, by combining this approach with complementary spectroscopies, we are able to provide new insights into the degradation processes occurring in the MHP and corresponding devices. Thus, we highlight the potential of our solid-state electrochemistry methodology to become a very useful tool for advancing the behavior and stability of MHP and PSCs, which is necessary in order to find proper materials and interface treatments to increase PSCs stability to commercial level requirements.

Operando Trapped Carrier Dynamics in Perovskite Solar Cells Observed via Infrared Optical Activation Spectroscopy

Ziming Chen; Imperial College London, United Kingdom

Metal halide perovskites show promise for cost-effective and high-efficiency photovoltaics. Recent progress in perovskite solar cells (PeSCs) has achieved a certified power conversion efficiency (PCE) of approximately 26.0%. To push PeSCs closer to the Shockley-Queisser limit and enhance their performance, reducing non-radiative recombination caused by carrier traps is crucial under standard sunlight conditions. Understanding these trap states and trapped carrier dynamics is vital to minimise performance losses. To overcome the limitations of conventional spectroscopic techniques like time-resolved photoluminescence and transient absorption, which lack the necessary selectivity for detecting trapped carriers, we used a novel method called infrared optical activation spectroscopy, specifically optical pump-IR push-photo-current (PPPC), to monitor trapped carriers in real-time during PeSC operation. PPPC involves generating band-edge carriers with a visible ‘pump’ beam, followed by carrier trapping. Subsequently, trapped carriers absorb IR push' beam photons, returning them to the band states. IR-detrapped carriers contribute to additional device photocurrent, allowing us to assess trapped carrier concentration and dynamics based on the amplitude and behaviour of IR-induced photocurrent.

Here, we employed PPPC (both its time-resolved and quasi-steady-state versions) to investigate how the surface passivation process and strain of perovskite make an impact on the trapped carrier dynamics, respectively:

1) To study surface passivation effects, we fabricated FA_{0.99}Cs_{0.01}PbI_{3} PeSCs with and without surface passivation. Our device structure was ITO/SnO2/FA_{0.99}Cs_{0.01}PbI_{3}/(OAI)/Spiro-OMeTAD/Au, where n-octylammonium iodide (OAI) served as a passivator for both cation and halide vacancies at the FA_{0.99}Cs_{0.01}PbI_{3} surface. We found that bulk traps filled rapidly (within 10 ns) due to nearby photocarrier trapping, while surface trap filling was slower (tens to hundreds of ns) and involved band-edge carrier drift-diffusion to the perovskite surface. The filling of surface trap states created an interfacial charge layer that screened the internal field and slowed carrier drift-diffusion. This process was also influenced by device temperature. The surface-passivated device exhibited faster saturation of trapped carrier concentration compared to the pristine device with higher trap density. Our kinetic model estimated a ~50 times reduction in trap states after surface passivation. Notably, the activation energy of trap state bands (~280 meV) remained nearly identical in both devices, indicating that surface passivation reduced trap numbers without changing trap types.

2) To investigate the impact of strain, we fabricated two perovskite films with varying strain levels: MA_{0.95}Ga_{0.05}PbI_{3} with tensile strain and MA_{0.95}Ga_{0.05}Pb(F_{0.95}Br_{0.05}) with free strain due to Br (with smaller size) compensation in the lattice. We found that non-radiative recombination loss was suppressed in the strain-free perovskite, which resulted in better emission properties and higher device performance. Considering trap-assisted recombination is the main process accounting for the non-radiative recombination loss, again, the combination of both quasi-steady-state and time-resolved PPPPC measurements revealed that strain relaxation reduced trap density, shallowed trap depth, as well as prolonged trapped carrier lifetimes. Hence, this mitigated trap-assisted recombination losses in the strain-free device. This study represents the first explicit correlation between strain engineering and its effects on overall trap-assisted recombination processes.

Origin of Open-Circuit Voltage Losses from Energy-Level Misalignment between Metal Halide Perovskites and Hole Transport Layers

Jae Fun Lee1, Silvia G. Motti1,2, Robert D. Oliver1,3, Siyu Yan1, Henry J. Snailth1, Michael B. Johnston1 and Laura Herz1,4; 1University of Oxford, United Kingdom; 2University of Southampton, United Kingdom; 3The University of Sheffield, United Kingdom; 4Technical University of Munich, Germany

Metal halide perovskites (MHPs) show great potential in multijunction photovoltaics applications due to their tunable bandgaps through compositional mixing on the halide site. However, wide-bandgap MHPs (>1.7 eV) typically suffer from greater open-circuit voltage (V_{OC}) losses compared to their narrow-bandgap counterparts (~1.6 eV) owing to energy-level misalignment with charge extraction layers. Herein, we investigate the origin of such losses, focusing on the energy level misalignment between the valence band maximum and the highest occupied molecular orbital (HOMO) for a commonly employed combination of perovskite with various halide compositions and hole transport layers.[1] Our research combines time-resolved photoluminescence spectroscopy and numerical modelling to reveal the origin of V_{OC} losses, which stem from the accumulation of holes in the HOMO of hole transport layers, followed by subsequent non-radiative across-interfacial recombination via interfacial defects. By simulating an ideal choice of hole transport material to pair with a mixed-halide MHP whose 1.8-eV bandgap is optimized for tandem solar cells, we demonstrate a potential reduction in V_{OC} losses originating from energy level misalignment. Our findings underscore the need for tailored charge-extraction materials with improved energy level alignment to enhance the efficiency of solar cells based on wide-bandgap mixed halide MHPs.


3:00 PM BREAK

SESSION EN10.02: Stability I
Session Chairs: Tim Kodalle and Yuanyuan Zhou
Monday Afternoon, April 22, 2024
Room 347, Level 3, Summit

3:30 PM EN10.02.01
Advancing Perovskite Solar Cell Development and Stability Using In-Line Electrochemical Methodologies
Erin L. Ratcliff; University of Arizona, United States

This talk will discuss established (spectro)electrochemistry-based measurement science approaches to quantify the distribution and energetics of donor and acceptor defects in prototypical perovskite solar cell materials and partial device stacks.
We utilize a solid-state electrolyte top contact that equilibrates with the perovskite film to create “half-cells” of device-relevant material stacks and study them under solar cell-relevant electric fields. This allows us to spectroscopically assess onsets in valence and conduction bands under *operando* conditions, as well as quantify near-band edge defects using redox-active hole or electron capturing molecular probes. The combination of spectroscopy and electrochemistry characterizes the energetics distribution of donor defect states at an energy resolution of <10 meV in “stoichiometric” triple cation, mixed halide perovskite thin films (Cs0.05FA0.79 MA0.16)Pb(0.87Br0.13)3 or CsFAMA, under device-relevant electric fields (i.e., electrochemical biasing). Limits of detection are at the 10^14 defects/cm^2. Such detection limits are better than spectroscopic, electronic and photoemission protocols, with speciation (anion versus cation defects) not available in those other approaches.

The technique is exquisitely sensitive, allowing for detection of clear differences in buried perovskite/metal oxide interfaces to better understand photovoltaic performance. Ongoing efforts to characterize defects and distributions include both nickel oxide nanoparticles and sputtered nickel oxide hole-transport contacts, modified with molecular species. Advancements towards development of in-line characterization (i.e., roll-to-roll) and connections to stability will also be described and benchmarked with respect to photoluminescence and photocurrent spectroscopies.

4:00 PM EN10.02.02
Multifunctional Polymeric-Nanofiber Reinforcement of Perovskite Solar Cells for Improved Mechanical Stability without Performance Trade-Off [Adam Printz, Anton Samoylov, Kenneth Lang, Patrick Lohr, Matthew Dailey, Yanan Li and Euan McLeod; University of Arizona, United States]

Metal halide perovskites have been demonstrated to be extremely fragile materials that can fracture at low applied stresses. Previous efforts to mechanically reinforce perovskite films have focused on the extrinsic mechanical shielding such as polymer scaffolding, but these implementations demonstrated to date either have performance trade-offs or require complex manufacturing steps. I will discuss a perovskite-polymer nanofiber composite that increases the mechanical toughness without an efficiency tradeoff. The fracture energy, Gc, of this nanocomposite is 500% higher (2.34 ± 1.67 J m^-2) than in pristine perovskite (0.40 ± 0.16 J m^-2). The nanocomposites were observed via scanning electron microscopy (SEM) and atomic force microscopy (AFM) to be homogeneous in the vertical direction, and X-ray diffraction (XRD) showed that the films were of similar quality to pristine perovskite (no lead iodide growth), but with a decrease in orientation. Furthermore, we show that there is no trade-off in device efficiency despite the integration of the insulating nanofibers, which we show is likely due to beneficial light scattering that increases current generation.

4:15 PM EN10.02.03
Increasing Halide Perovskite Scalability and Stability with Food Additives [Carsenl Cartledge, Muneeza Ahmad and Nicholas Rolston; Arizona State University, United States]

In this work, we report on a polymeric additive endemic to the food industry, gellan gum, as a means of enabling scalable, open-air manufacturing of halide perovskites with improved stability characteristics under high heat and humidity conditions.

As the global demand for scalability escalates, traditional perovskite inks designed for small scale fabrication in inert environments like spin coating have been found to produce pinholed, incomplete, and shunted films when utilized in more scalable open-air processes like blade coating. Interestingly, gellan gum enables viable films through the critical transition of well-studied manufacturing steps. I will discuss a perovskite-polymeric nanofiber composite that increases the mechanical toughness without an efficiency tradeoff. The fracture energy, Gc, of this nanocomposite is 500% higher (2.34 ± 1.67 J m^-2) than in pristine perovskite (0.40 ± 0.16 J m^-2). The nanocomposites were observed via scanning electron microscopy (SEM) and atomic force microscopy (AFM) to be homogeneous in the vertical direction, and X-ray diffraction (XRD) showed that the films were of similar quality to pristine perovskite (no lead iodide growth), but with a decrease in orientation. Furthermore, we show that there is no trade-off in device efficiency despite the integration of the insulating nanofibers, which we show is likely due to beneficial light scattering that increases current generation.
contributing to an enhancement of open-circuit voltage of the devices. Furthermore, TMA-TFSI enhances resistance of the HTL against harsh environmental conditions, such as humidity and high temperature, owing to suppressed ion migration and hydrophobic nature. Resultingly, the TMA-TFSI-based devices demonstrate superior stability under high temperature (~85 degrees Celsius) and maximum-power-point tracking compared to those based on Li-TFSI.

5:00 PM EN10.02.06

Reduced Recombination via Tunable Surface Fields in Perovskite Solar Cells

Dane W. DeQuilettes1,2, Jason J. Yoo1, Roberto Brenes1, Felix U. Kosash1, Madeleine Laitz1, Benja Dou1, Daniel Grahan4, Kevin Ho4, Yangwei Shi4, Seong Sik Shin5,6, Caterina Ducati2, Mounig G. Barwendi1,1, Massachusetts Institute of Technology, United Kingdom; 2Optigon Inc., United States; 3University of Cambridge, United Kingdom; 4University of Washington, United States; 5Korea Institute of Science and Technology, Korea (the Republic of); 6Sungkyunkwan University, Korea (the Republic of)

The ability to reduce energy loss at semiconductor surfaces through passivation or surface field engineering has become an essential step in the manufacturing of efficient photovoltaic (PV) and optoelectronic devices. Similarly, surface modification of emerging halide perovskites with quasi-2D heterostructures is now ubiquitous to achieve PV power conversion efficiencies (PCEs) > 22% and has enabled single-junction PV devices to reach >26%, yet a fundamental understanding to how these treatments function is still generally lacking. This has established a bottleneck for maximizing beneficial improvements as no concrete selection and design rules currently exist. Here we uncover a new type of tunable passivation strategy and mechanism found in perovskite PV devices that were the first to reach the > 25% PCE milestone, which is enabled by surface treating a bulk perovskite layer with hexylammonium bromide (HABr). We uncover the simultaneous formation of an iodide-rich 2D layer along with a Br halide gradient achieved through partial halide exchange that extends from defective surfaces and grain boundaries into the bulk layer. We demonstrate and directly visualize the tunability of both the 2D layer thickness, halide gradient, and band structure using a unique combination of depth-sensitive nanoscale characterization techniques. We show that the optimization of this interface can extend the charge carrier lifetime to values > 30 μs, which is the longest value reported for a direct bandgap semiconductor (GaN, InP, CdTe) over the past 50 years. Furthermore, we show that this heterostructure is well suited for a host of optoelectronic devices where we achieve a new benchmark for perovskite/charge transport layer surface recombination velocity with values < 7 cm s⁻¹. Importantly, this work reveals an entirely new strategy and knob for optimizing and tuning recombination and charge transport at semiconductor interfaces and will likely establish new frontiers in achieving the next set of perovskite device performance records.

5:15 PM EN10.02.07

Light Makes Right: Laser Polishing for Surface Modification of Perovskite Solar Cells

Mayank Kedia1,2 and Michael Saliba1,2; 1University of Stuttgart, Germany; 2Forschungszentrum Jülich GmbH, Germany

Interface engineering is a common strategy for passivating surface defects to attain open circuit voltages (Voc) in perovskite solar cells (PSCs). Although a large volume of reports highlights the potential of chemical passivation, an additional solvent-based processing step increases the challenges of upscaling and reliability. Moreover, as the library of chemical passivators consistently expands, there is no consensus on the result risking that each perovskite composition needs its tailor-made solution. Hence, a solvent-free, up-scalable, and one-size-fits-all approach is desirable.

In this work, we introduce the concept of polishing a perovskite thin-film surface using a nanosecond (ns) pulsed ultraviolet laser to reduce surface defects, such as dangling bonds, undesirable phases, and suboptimal stoichiometry. Careful control of laser energy and scanning speed improves the photophysical properties of the surface without compromising the thickness. A detailed and complementary analysis of the perovskite top layer and the full device using photoluminescence imaging and Kelvin Probe Force Microscopy reveal the removal of dark spots that act as traps for photogenerated carriers, resulting in surface homogeneity and narrowing of the band gap. Using laser polishing, a record Voc of 1.21 V is achieved for planar PSCs with a triple cation composition (Eg ~ 1.61 eV), showing an improved perovskite/hole transport layer interface by mitigating surface recombination losses. We measure an efficiency boost from 18.0% to 19.3% with an improved stability of up to 1000 h. The polishing effect on the MAPbI3 perovskite is also studied to explore the versatility of this method.

Furthermore, the same laser is employed to fabricate ultra-thin perovskite films up to 50 nm achieving a Voc of 1.15 V, which is one of the highest reported so far for such semi-transparent PSCs. These results open the door to a new class of surface modification without any structural damage using lasers for interface passivation and semi-transparency in well-controllable, automated, scalable, and solvent-free surface treatments.

5:30 PM EN10.02.08

Highly Efficient Perovskite Blue Light-Emitting Diodes

Jian Mao1,2 and Samuel D. Stranks1; 1University of Cambridge, United Kingdom; 2Fudan University, China

Lead halide perovskite has attracted extensive attention during the past decade for applications in light-emitting diodes because of its wide emission tunability, high color purity, high quantum yield, and easy solution processibility. Despite the exciting progress of perovskite green, red, and near-infrared LEDs, fabrication of perovskite blue LEDs with high external quantum efficiency (EQE), high brightness, and high color purity remains a considerable challenge. Here, we report efficient perovskite blue LEDs with a world-record EQE of surpassing 22%, a peak luminance above 7000 cd/m², and a full width at half maximum of 15 nm. Besides, the devices exhibit a stable electroluminescence spectrum at constant elevated current injection. This performance is achieved by carefully manipulating the growth of perovskite into thin films with homogeneously isolated grains, which not only improve the light outcoupling efficiency but also enhance the spectrum stability.

5:45 PM EN10.02.09

Dual Strategies with Defect Suppression and Hole Transporting Bilayer for Inverted Perovskite Solar Cell (PCE ~24%) 

Hyunji Shin, Hyoemgmin Park, Hyeon Jun Jeong, Yongjae In and Urasawadee Amornkitbamrung; Sungkyunkwan University, Korea (the Republic of)

A growing interest in inverted structure perovskite solar cells (i-PSCs) is underway due to their higher stability and potential applications in tandem structures. Typical organic/polymeric hole-transporting layers (HTLs) often faced limitations in improving stability due to intrinsic hygroscopic nature, acidity, intrinsic instability, and non-uniform coating. On the other hand, self-assembled monolayers (SAMs) have demonstrated better stability and higher device performance. Nevertheless, challenges persist, such as non-uniform coating and the hydrophobicity, when perovskite’s layers were fabricated on the top of SAMs. Inorganic hole transport layers like NiO can offer better stability and higher performance compared to organic HTLs, but surface defect-related undesirable reactions have been reported. In this study, an ultra-thin NiO (4nm) using atomic layer deposition (ALD) was applied, forming an ALD-NiO/SAMs bi-layer HTL. The use of ALD-NiO showed superior uniformity compared to traditional sol-gel and nano-particleulate films’ preparation methods, ensuring uniformly formed bi-layers with SAMs. Together with bi-layer perovskite’s layers were fabricated on the top of SAMs. Inorganic hole transport layers like NiO can offer better stability and higher performance compared to organic HTLs, but surface defect-related undesirable reactions have been reported. In this study, an ultra-thin NiO (4nm) using atomic layer deposition (ALD) was applied, forming an ALD-NiO/SAMs bi-layer HTL. The use of ALD-NiO showed superior uniformity compared to traditional sol-gel and nano-particleulate films’ preparation methods, ensuring uniformly formed bi-layers with SAMs. Together with bi-layer perovskite’s layers were fabricated on the top of SAMs. The polishing effect on the MAPbI3 perovskite is also studied to explore the versatility of this method.

High-Throughput Experiments and a Machine-Learning-Driven Analysis to Characterize the Stability of Halide Perovskites

11:00 AM EN10.03.02

High-Throughput Experiments and a Machine-Learning-Driven Analysis to Characterize the Stability of Halide Perovskites

Marina S. Leite; University of California, Davis, United
Reverse-Bias Resilience of Monolithic Perovskite/Silicon Tandem Solar Cells

In this work, we demonstrate that by employing a monolithic perovskite/silicon tandem structure, the perovskite subcell can be effectively protected by the silicon subcell under reverse bias, owing to the low reverse-bias diode current of the silicon subcell. As a result, the tested perovskite/silicon tandem devices show superior reverse-bias resilience compared to perovskite single-junction devices in both long-term reverse voltage biasing tests at the single-cell level and partial shading tests at the module level. These results highlight that, compared to other perovskite technologies, monolithic perovskite/silicon tandems are at a higher technology readiness level in terms of tackling the reverse-bias and partial shading challenge, which is a considerable advantage towards commercialization.

Rational Design of Photoelectrochemical Perovskite-BiVO₄ Tandem Devices for Stable Fuel Production

Metal halide perovskites have rapidly enabled a range of high-performance photovoltaic technologies. However, catastrophic failure under reverse voltage bias hinders their commercialization. In this work, we develop a rational design strategy for photoelectrochemical perovskite-BiVO₄ tandem devices that enables stable fuel production under reverse-bias conditions. The developed tandem devices exhibit superior reverse-bias resilience compared to perovskite single-junction devices, making them promising candidates for sustainable energy conversion applications.
Advances in Materials and Process for Sustainable Perovskite Solar Cells

3:30 PM

Unveiling Non-Fullerene Routes: Strategic Design of Wide Bandgap Inverted Perovskite Solar Cells with SnO2 Layers

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Recently, metal halide perovskites have garnered attention in photovoltaic research, experiencing a substantial increase in efficiency, achieving an impressive 26.1%. Within this realm, the inverted perovskite solar cell structure is notable for avoiding stability issues associated with the transport layer, such as Spiro-MeOTAD in regular perovskite solar cells. However, the majority of high-efficiency inverted structures employ fullerene derivatives like C60 and PCBM as Electron Transport Layers (ETLs), posing difficulties in commercialization due to their long-term stability and cost-related challenges. Consequently, inorganic materials like SnO2, TiO2, and Nb2O5 have emerged as potential ETL candidates, with SnO2 being the most extensively used material in n-i-p structures due to its high electron mobility, wide bandgap, and low cost.

We report achieving a high efficiency of 18.3% at a 1.77eV bandgap, utilizing synthesized SnO2 nanoparticles, dispersed in a non-damaging solvent, as an Electron Transport Layer (ETL) in an inverted structure. This efficiency is the highest achieved using SnO2 in inverted structures, even without considering the bandgap. In order to mitigate defects originating from the expanded SnO2 surface area attributed to the small particles, ethylenediamine (EDA) was employed for passivation. Notably, EDA exhibited a bifunctional role between the perovskite and SnO2 layers.

An appropriate encapsulation technique can extend the device lifetime to a few days under operation in aqueous media. To this end, we replace low melting alloys with graphite epoxy paste as a conductive, hydrophobic and low-cost encapsulant. The combined advantages of these approaches are demonstrated in a perovskite-BiVO4 tandem device archiving selective unassisted CO2 reduction to syngas. These design principles are successfully applied to an underexplored BiOI light absorber, increasing the photocathode stability towards hydrogen evolution from minutes to months. Finally, we take a glance at the next steps required for scalable solar fuels production, showcasing our latest progress in terms of device manufacturing. A suitable choice of materials can decrease the device cost tenfold and expand the device functionality, resulting in flexible, floating artificial leaves. Those materials are compatible with large-scale, automated fabrication processes, which present the most potential towards future real-world applications. Such PEC systems approaching a m2 size can further take advantage of the modularity of artificial leaves.

References

2:45 PM


4. E. Erdenebileg, et al Solar RRL, 2022, 6, 2100842


2. J. Li et al., Joule 2020, 4, 1035


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2. J. Li et al., Joule 2020, 4, 1035
4. E. Erdenebileg, et al Solar RRL, 2022, 6, 2100842
7. E. Erdenebileg et al., Material Today Chemistry, 2023, 30, 101575
Correlating Halide Segregation with Iodide Oxidation via In-Situ Opto-Gravimetric Analysis
Zhaoqian Xu and Barry P. Rand; Princeton University, United States

Halide oxidation plays an important role in halide segregation and degradation of metal halide perovskites. However, a direct and quantitative measurement of halide oxidation in solid-state perovskite samples is still required to fully understand and evaluate the effect of halide oxidation. In this work, we employed a quartz crystal microbalance to achieve an in-situ opto-gravimetric measurement of solid-state perovskite films and quantify the iodide loss rate under light excitation. Combining photoluminescence, X-ray photoelectron spectroscopy, X-ray diffraction, and in-situ opto-gravimetric measurements on a series of mixed-halide perovskites, we are able to explain the degradation mechanism of mixed-halide perovskite under prolonged light illumination (photolysis of iodine), and demonstrate an identical compositional threshold for both light-induced halide segregation and iodide oxidation. These results not only reveal the correlation between light-induced halide segregation and iodide oxidation, which experimentally proves the photoelectrochemical origin of light-induced halide segregation, but also provide a powerful tool to quantitatively study halogen loss and degradation kinetics of metal halide perovskites.

5:00 PM EN10.06.02
Utilizing Machine Learning and Diode Physics to Optimize Photovoltaic Performance in Sequentially Processed Perovskite Solar Cells
Jeongbeom Cha and Min Kim; Jeonbuk National University, Korea (the Republic of)

Organic-inorganic lead halide perovskite photovoltaics are well-known for their exceptional solution processability. However, achieving uniformly crystalline perovskite films often requires complex deposition methods. To solve this challenge of the perovskite deposition method, several studies have been performed to utilize deposition parameters such as concentrations of the annealing temperatures, precursor solution, and spin-coating speeds. Unfortunately, most of these studies have been conducted on trial-and-error approaches, which are resource-intensive and time-consuming. Nowadays, machine learning techniques have considered as powerful tools for utilizing complex experimental parameters and predicting the device performance, making more efficient analysis of parameter spaces.

In our study, we combined Shockley diode-based numerical analysis with machine learning techniques to analyze the photovoltaic characteristics of the device and utilize their photovoltaic performance by considering experimental variables. The application of the Shockley diode equation allowed us to extract photovoltaic parameters and predict power conversion efficiency, contributing to our understanding of device recombination and device physics. Using machine learning techniques, we trained a machine learning model using current-voltage curves that are sensitive to changes in manufacturing conditions. This enabled us to identify the optimal settings for improved device performance.

Our harmonized approach not only reveals the relationship between experimental conditions and device performance, but also simplifies the optimization process, reducing the need for extensive trial-and-error experimentation. This methodology shows great promise in advancing the development and fine-tuning for next-generation perovskite solar cells.
channel layer to be susceptible to common solvents used in lithography, which is challenging for complex circuit integration, large-area or micro-scale electronics. Here, we present thermally evaporated metal halide perovskite, caesium-tin-iodide, as a channel layer for high-performance p-channel thin-film transistor. While thermal evaporation is a mature fabrication technique, the low crystallinity of deposited thin-films, when compared with those from solution-process, was a fundamental bottleneck. The chemical reaction can take place by overcoming high energy barrier for diffusion and solid-solid interaction, unlike fast ionic reactions of the solution-process.4,5 By incorporating chloride-based additives that accelerate the solid-state diffusion under high thermal energy and alkali metal iodide additives that modulate the formation of nucleation sites, we achieved a highly crystalline film and high-performance thin-film transistor with field-effect hole mobilities over 30 cm²V⁻¹s⁻¹ and on/off current ratios exceeding 10⁸. High reproducibility and operational stability were attained in large-area wafer-scale to micro-scale devices, accentuating the highly promising and industry-ready thermally evaporated metal halide perovskite thin-films transistors.


5:00 PM EN10.06.06
Process Optimization of Chemical Vapor Deposition of MAPbBr₃ for Optoelectronic Applications

Jona Riedel¹, Franziska E. Muckel², Michael Heuken¹,³, Andrei Vescan¹ and Holger Kalisch³; ¹RWTH Aachen University, Germany; ²Universität Duisburg-Essen, Germany; ³AIXTRON SE, Germany

With growing commercial interest in halide perovskite (HP) thin-film applications, the question which deposition techniques can meet the requirements of industrial scalability and reproducibility becomes increasingly important. At the current time, solution-based methods which are prominent in research are limited to small areas, low reproducibility and are not able to meet special requirements such as deposition on structured substrates. Promising alternatives are vapor-based techniques like vacuum thermal evaporation (VTE) or chemical vapor deposition (CVD) which are well established in the field of semiconductor manufacturing.

At CST (RWTH Aachen University), we have designed and built a custom showerhead-based CVD tool for the deposition of HP thin films by thermal evaporation of halide salts into a heated carrier gas stream. The usage of an inert carrier gas such as N₂ at low vacuum around 5-10 l/h allows for the simultaneous or alternating evaporation of both metal-halide as well as organo-halide salts in a single process. The latter materials are typically difficult to use in high-vacuum techniques like VTE due to their large vapor pressures and low sticking coefficients. In addition, unlike quartz furnace CVD setups found in research literature, our tool features separate sources for different precursor salts. Temperature-controlled substrates are mounted in a heated showerhead-based reactor chamber allowing for uniform deposition on areas up to 100 cm².

While different HP materials have been successfully prepared in our tool, benchmarks for both LEDs and solar cells are lagging behind those of devices based on HP films prepared by spin coating. A typical feature of our CVD films is a reduction of photoluminescence (PL) intensity compared to spin-coated reference samples by 2-3 orders of magnitude. Times-resolved PL spectroscopy indicates the presence of a fast, non-radiative recombination channel in CVD samples absent in their solution-processed counterparts, which likely impedes efficient operation of both LEDs and solar cells. By sequential deposition of PbBr₂ and MAI or MABr to form MAPbBr₃ using combinations of CVD and solution deposition, we investigated the influence of both precursors and processes. We observed that spin-coated PbBr₂ layers can be easily converted to MAPbBr₃ layers with strong PL intensity using CVD-MABr, while simultaneously grown CVD-MABrPbI₃ films converted by either CVD-MABr or MABr solutions share a low PL intensity. This is in accordance with literature which comprises numerous reports on the conversion of lead-halide precursor films from solution to VTE or MABr-CVD, but lacks reports on the usage of lead halide salts as separate precursors under low vacuum. Unlike reports from high-vacuum evaporation, we observe strong evidence for the dissociation of thermally evaporated PbBr₂. Notably after prolonged evaporation of PbBr₂ precursor material, metallic residues can be found in the crucible. This indicates an at least partial dissociation of PbBr₂ into elemental Pb and volatile Br₂. Due to the high vapor pressure of Br₂, the deposition conditions inside our reactor can be expected to be Br-rich. This could facilitate the formation of intrinsic defects related to excess Br, like Br interstitials, and give a reason for the low PL intensity found when evaporated PbBr₂ is part of the process. Nevertheless, we were able to increase the PL intensity of MAPbBr₃ by 1-2 orders of magnitude by thermal annealing of PbBr₂ precursor layers for up to 3 h at 200-310 °C in N₂. A similar effect can be observed by increasing the substrate temperature during PbBr₂ deposition from 100 °C to above 200 °C, supporting the assumption of a volatile species like Br poisoning our HP. The combined results show a clear path to directly avoid the suspected negative impact of PbBr₂ dissociation in CVD of HPs.

5:00 PM EN10.06.07
Structure and Properties of Novel Mixed Organics Hybrid Lead-Halide Phase (1-NA)(1-MQ)Pb₂I₆

Megan Cassingham, Peter Djurovich, Mark E. Thompson and Brent Melot; University of Southern California, United States

Low dimensional hybrid organic-inorganic lead-halide structures are gaining interest due to their structural flexibility and tunability compared their parent 3-D perovskite structure. By combining the tunability of organic chromophores and the desirable optical properties of perovskites, we aim to develop a new portfolio of hybrid organic-inorganic lead-halide materials. In order to achieve a mixed organics hybrid lead-halide phase structure, several 1-naphthylamine isomers were used to synthesize new 1-D hybrids to screen for similar crystal structures to the known 1-D hybrid, 1-naphthylammonium lead iodide (1-NA)PbI₃, 1-methylnilinium iodide (1-MQ)PbI₃ has a similar structure, and a mixed organics hybrid phase, (1-NA)(1-MQ)Pb₂I₆, is successfully synthesized. (1-NA)(1-MQ)Pb₂I₆ shows clear ordering of the organics, which is the first we are aware of in these systems. We will discuss the optical and dielectric properties of the end members, (1-NA)PbI₃ and (1-MQ)PbI₃, as well as the mixed organics hybrid phase, (1-NA)(1-MQ)Pb₂I₆, and how that relates to their respective structures.

5:00 PM EN10.06.08
Direct Photo-Patterning of Perovskite Nanocrystals with Siloxane Resin Showing Highly Stable Luminescence

Yang Goh, Megan Cassingham, Peter Djurovich, Mark E. Thompson and Brent Melot; University of Southern California, United States

Silvia Colella

1, Franziska E. Muckel², Michael Heuken¹,³, Andrei Vescan¹ and Holger Kalisch³; ¹RWTH Aachen University, Germany; ²Universität Duisburg-Essen, Germany; ³AIXTRON SE, Germany

Herein, we report highly stable PeNCs (green emitting MAPbBr₃/resin composites) patterns encapsulated in siloxane resin which is synthesized by the sol-gel reaction between methoxy groups of (3-methacryloxypropyl) trimethoxysilane (MPTS) and hydroxyl groups of diphenylsilanediol (DPSD). The synthesized siloxane resin provides physical protection to core materials by coating. A typical feature of our CVD films is a reduction of photoluminescence (PL) intensity compared to spin-coated reference samples by 2-3 orders of magnitude. Times-resolved PL spectroscopy indicates the presence of a fast, non-radiative recombination channel in CVD samples absent in their solution-processed counterparts, which likely impedes efficient operation of both LEDs and solar cells. By sequential deposition of PbBr₂ and MAI or MABr to form MAPbBr₃ using combinations of CVD and solution deposition, we investigated the influence of both precursors and processes. We observed that spin-coated PbBr₂ layers can be easily converted to MAPbBr₃ layers with strong PL intensity using CVD-MABr, while simultaneously grown CVD-MABrPbI₃ films converted by either CVD-MABr or MABr solutions share a low PL intensity. This is in accordance with literature which comprises numerous reports on the conversion of lead-halide precursor films from solution to VTE or MABr-CVD, but lacks reports on the usage of lead halide salts as separate precursors under low vacuum. Unlike reports from high-vacuum evaporation, we observe strong evidence for the dissociation of thermally evaporated PbBr₂. Notably after prolonged evaporation of PbBr₂ precursor material, metallic residues can be found in the crucible. This indicates an at least partial dissociation of PbBr₂ into elemental Pb and volatile Br₂. Due to the high vapor pressure of Br₂, the deposition conditions inside our reactor can be expected to be Br-rich. This could facilitate the formation of intrinsic defects related to excess Br, like Br interstitials, and give a reason for the low PL intensity found when evaporated PbBr₂ is part of the process. Nevertheless, we were able to increase the PL intensity of MAPbBr₃ by 1-2 orders of magnitude by thermal annealing of PbBr₂ precursor layers for up to 3 h at 200-310 °C in N₂. A similar effect can be observed by increasing the substrate temperature during PbBr₂ deposition from 100 °C to above 200 °C, supporting the assumption of a volatile species like Br poisoning our HP. The combined results show a clear path to directly avoid the suspected negative impact of PbBr₂ dissociation in CVD of HPs.

5:00 PM EN10.06.07
Devices Session Chairs: Jin-Wook Lee and Michael Saliba

8:00 AM EN10.07.01
Insights into Hybrid Perovskites Ink Reactivity and Evolution to Polytypes

Silvia Colella¹,², Jona Riedel¹, Franziska E. Muckel², Michael Heuken¹,³, Andrei Vescan¹ and Holger Kalisch³; ¹RWTH Aachen University, Germany; ²Universität Duisburg-Essen, Germany; ³AIXTRON SE, Germany

By introducing the siloxane resin, PeNCs patterns demonstrate high photoluminescence quantum yield (PLQY) in various harsh conditions: in DI water (> 100 days), ambient conditions (> 150 days) and under 40 °C RH 70% (> 8 hours) without additional encapsulation process, since the siloxane resin suppresses hydrolysis of PeNCs and controls permeation of H₂O molecules moderately. Moreover, direct optical patterning with siloxane resin can be applied to various inorganic light emitting materials (red emitting CdSe QDs/resin composites). We believe that our material design, which combines MAPbBr₂ and CdSe QDs with siloxane resin, will offer a universal solution, demonstrating high levels of pattern stability in harsh conditions while enabling direct optical patterning without the need for ligand crosslinkers, simultaneously.
Metal halide perovskite (MHP) semiconductors are excellent candidates for contemporary optoelectronics innovation, particularly for photovoltaics. The advantages of this class of materials derive from their hybrid nature, allowing for straightforward fabrication processes, and from their unique optoelectronic properties. A typical 3D organic-inorganic perovskite has a chemical formula of ABX3, where A is an organic cation (such as MA [methylammonium] or FA [formamidinium]), B is a metal cation (such as Pb2+), and X is a halogen anion (such as I or Br). However, recent advances have also explored more complex compositions embedding diverse cations/anions. These materials are prepared by simple and straightforward solution processing, the material precursors dissolved in a solvent undergoes self-assembly and a polycrystalline film structure during spin-coating onto a substrate under mild thermal annealing. As the technology continues to mature, this still is a key advantage, allowing for affordable and scalable processing. Understanding perovskite ink properties is therefore a fundamental requirement towards industrialization, especially with regards to the evolution of this material. It has been demonstrated that for the simplest system, the precursor solution is a complex – and dynamic – dispersion which contains not only solvated ions but also lead halide complexes, colloids and aggregates of different natures and dimensions. In these complex dispersions, multiple chemical species are present and can interact – or react – between each other or with the solvent. We have proved the existence of a reactivity between two of the perovskite components – MA and FA – in the precursors solutions, that leads to the formation of a novel condensation product, methylformamidinium (MFA). We have studied different parameters that affects such reactions kinetics therefore modifying the ink composition over time, and proposed solutions to overcome these issues. With the aim of correlating the solution chemistry with the film structural properties, through the synergic use of solution Nuclear Magnetic Resonance (NMR) spectroscopy, X-ray Diffraction and Density Functional Theory (DFT) calculations, we have recognized and explained for the first time a correlation between the aging of perovskite precursor solutions, the presence of MFA species in solution and the emergence of photoinactive hexagonal polytypes (hH4 and hH4) starting from the known reactivity of the chemical species present in ink solutions, we outline the directions towards which future research efforts should be directed. References: [1] Jeong, J., Kim, M., Seo, J., Lu, H., Ahlawat, P., Mishra, A., Yang, Y., Hope, M.A., Eickenmeyer, F.T., Kim, M., et al. (2021). Pseudo-halide anion engineering for α-FAPbI3 perovskite solar cells: Nature Materials, 59, 381–385. [2] Snait, H.J. (2013). Perovskites: The emergence of a new era for low-cost, high-efficiency solar cells. Journal of Physical Chemistry Letters 4, 3623–3630. [3] McMeekin, D.P., Sadoughi, G., Rehman, W., Eperon, G.E., Saliba, M., Hörantner, M.T., Haghighirad, A., Sakai, N., Korte, L., Reich, B., et al. (2016). A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells. Science 351, 151–155. [4] Valenzano, V., Cesari, A., Balzano, F., Milella, A., Fracassi, F., Listorti, A., Gigi, G., Rizzo, A., Ucellio-Barretta, C., and Soli, C. (2021). Methylammonium-formamidinium reactivity in aged organometal halide perovskite inks. Cell Reports Physical Science 2, 100432. [5] Gianluca Bravetti, Nicola Taurisano, Anna Moliterni, Jose Manuel Vicent-Luna, Davide Altamura, Federica Aiello, Nadir Vanni, Agostina Lina Capodilupo, Sonia Carallo, Giuseppe Gigli, Gloria Ucellio-Barretta, Federica Balzano, Cinzia Giannini, Shuxia Tao, Silvia Colella, Aurora Rizzo (2023). Solution Aging Promotes Hexagonal Polypeptide Formation in Mixed Cation/Halide Perovskites, accepted. [6] Rizzo A., Listorti A., Colella S. (2022). Chemical insights into perovskite ink stability. Chem, 8, 1, 31–45.
Unlocking Versatility: Innovative Crystallization Strategies for Metal Halide Perovskites and Their Application Potentials

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Metal halide perovskite crystals in the macro and nano scales can leverage the huge versatility of the perovskite family. They present exceptional optoelectronic properties that make them attractive for a variety of applications. However, these structures usually depend on complex synthesis processes, where the ligands play a dominating role, or are limited by growth form factor and surface losses. We present crystallographic insights that enable less demanding synthesis processes, such as a promising sol-gel approach [1] for humidity-triggered nanoparticle crystallization or a contactless surface passivation technique for large crystals. The particularity of these systems can be adapted to specific applications such as memristive devices or downconversion films with efficiencies >95%, which also serve as a platform to characterize the fundamental working mechanisms of these materials.

The combination of the crystallization control with additive engineering also opens new routes for lead-free perovskite photovoltaics, improving their ambient and operational stabilities.

References


Acknowledgment

The work was partially funded by MCIN/ AEI through project TEC2021-136006-C32, by Generalitat Valenciana via Pla Gent-T (grant CIDEXG/2022/34) and by the research project no. PID2020-119628RB-C31 funded by MCIN/ AEI /10.13039/501100011033.

10:45 AM EN10.08.03

Light-Induced Halide Sublimation and Diffusion in 2D Halide Perovskites

Yaqing Liao1, Shuchen Zhang2, Jia-Shiang Chen3, Xuedan Ma4, Ke Ma5, Junying Deng6, Yi Jiang7, Luxi Li8, Barry Lai9, Si Chen10, Sarah Wiegold11 and Letian Dou12; 1Argonne National Laboratory, United States; 2Purdue University, United States

To address stability challenges in two-dimensional (2D) perovskite semiconductor materials, an improved understanding of the degradation origins and pathways under external stimuli is needed. Here, we investigate the evolution of halide redistribution within various 2D halide perovskites (n = 1 to 3) lateral heterostructures using in-situ synchrotron nanoprobe X-ray fluorescence (nano-XRF) microscopy. The heterostructures comprise distinguishable iodine (I) and bromine (Br) regimes laterally. Continuous UV exposure leads to iodine sublimation in high-dimensional 2D perovskites and a visible amount of Br diffusion to the previously iodine-rich regime. In contrast, bromine is relatively more stable than iodine in n = 2 and 3 heterostructures, with no significant change in total Br concentration. Additionally, combining nano-XRF structural mapping and X-ray absorption spectroscopy, we found a reduction of dimensionality in the previously iodine-rich regime in crystals with n > 1 after UV exposure, indicating significant structural reconfiguration beyond ion migration. These findings provide new insights into the photo-induced ion migration and degradation mechanisms of 2D perovskite materials and shed light on future materials design.

11:00 AM EN10.08.04

3D Printing of Vertical Heterostructures of Two Dimensional Halide Perovskites

Sixin Cao and Ji Tae Kim; The University of Hong Kong, Hong Kong

The integration of different 2D perovskite heterostructures allows for the manipulation of interfaces and electronic structures, playing a crucial role in various modern electronics and optoelectronics applications, such as solar cells, light-emitting diodes, lasers, self-powered photodetectors, transistors, and large-scale electronic circuits1-3. Two-dimensional (2D) halide perovskites have gained significant attention due to their superior optoelectronic properties and high stability, making them promising candidates for next-generation multifunctional devices4,5. The heterostructures formed by 2D halide perovskites exhibit high tolerance to lattice mismatch and low intrinsic anionic diffusion at the interface, thanks to the presence of the organic layer in the 2D quantum well, which enhance their stability and performance in optoelectronic integrated device6. However, achieving controllable integration of 2D perovskites remains a challenge due to their mobile and fragile crystal lattice7. Solution and gas-solid phase intercalation have been reported for fabricating 2D perovskite-based lateral and vertical heterostructures8,9. Nevertheless, these methods suffer from limitations, including a lack of scalability and limited control over the morphology of the resulting heterostructures, which hinders large-scale production and integration of 2D perovskite nanowire heterostructures into practical devices. In this work, we propose a novel approach for fabricating freestanding layer perovskite nanowire heterostructures using a 3D printing method. This method of control ensures uniformity and reproducibility, facilitating the deterministic fabrication of arbitrary vertical heterostructures and multi-heterostructures using 2D perovskites. Our fabricated perovskite nanowires showed an excellent stability with suppressed anionic diffusion at the interface. By offering structural degrees of freedom, our approach allows for the precise definition of the electronic structures of the heterojunctions.

References


11:15 AM EN10.08.05

Enhancing Crystallization Kinetics in Glass-Forming Halide Perovskitites Using Organic Cation Isomers

Akash Singhi, Yi Xie, Curtis Adams III and David B. Mitzi; Duke University, United States

The recent exploration of glass-forming hybrid metal halide perovskites (MHPs) has opened new possibilities to extend their applications beyond the well-established realm of optoelectronic research, which primarily focuses on their crystalline variants. In this regard, it is imperative to diversify the range of glass-forming MHP compositions and manipulate their crystallization kinetics through synthetic structural engineering. Herein, we conducted a comparative study involving two MHPs that possess subtly different structural characteristics, utilizing isomer organic cations while maintaining the same chemical composition. Our investigation sheds light on how these alterations in the position of functional groups profoundly influence the kinetics of both glass formation and cold crystallization. One of the MHPs, [(S)-1-(1-naphthyl)ethylammonium lead bromide (S(1-1)NPB), exhibits a lower melting point (Tm) of 193°C, and readily transforms into a glassy state at a critical cooling rate (CCR) of 20 °C/min. In contrast, (S)-1-(2-naphthyl)ethylammonium lead bromide (S(1-2)NPB) displays a higher Tm of 210°C, and requires a CCR of 150,000°C/min, necessitating the use of ultrafast calorimetry for glass formation. The examination of the underlying crystallization kinetics, performed using iterative calorimetry and the Kissinger modeling technique, further indicates a small activation energy barrier (EA) for crystallization in S(1-2)NPB.

We also investigate the interplay between structural and thermodynamic features that engenders distinct glass formation and crystallization behavior using a comprehensive analysis of the organic-inorganic hydrogen bonding interactions in the crystalline state and a careful examination of the enthalpy and entropy balance across the melting transition. These analyses highlight the strengthened hydrogen bonding in S(1-2)NPB and the reduced entropy of melting as the key factors contributing to the higher Tm and CCR, as well as a lower EA observed in comparison to S(1-1)NPB. The results presented in this study establish a framework for evaluating structural elements on the kinetics of glass formation and crystallization, serving as a new material design strategy to diversify the family of glass-forming MHPs and extending their potential applications in areas demanding faster switching speeds such as memory, computing, metamaterials, and reconfigurable photonic devices.

11:30 AM EN10.08.06

A Templating Approach to Controlling the Growth of Co-Evaporated Halide Perovskites

Siuw Yau1, Jay Patel1, Jee Eun Lee1, Karim Elmestekawy1, Sinclair R. Ratnasingham1, Qiming Yuan1, Laura Herz1,2, Nakita K. Noel1 and Michael B. Johnston1; 1University of Oxford, United Kingdom; 2Institute for Advanced Study, Technical University of Munich, Germany

Metal halide perovskite semiconductors have shown significant potential for use in photovoltaic devices. While fabrication of perovskite thin-films can be achieved through a variety of different techniques, thermal vapour deposition is particularly promising, allowing for high-throughput fabrication and large-scale production. However, the ability to control the nucleation and growth of these materials, particularly at the charge-transfer layer (CTL)/perovskite interface, is critical to unlocking the full potential of vapour-deposited perovskite photovoltaics, since the surface of the substrate material exerts a substantial impact beyond the interface, leading to alterations in the morphology of the entire film. As a result, for vapour-deposited perovskites, it is crucial to choose the right CTLs to ensure uniform deposition of alkylammonium halides and appropriate crystallization of the perovskite material. This not only limits the range of available substrates, but also requires extensive experimentation to optimize the evaporation parameters for different types of substrates. This issue limits the economic feasibility of industrial
Robustness and Versatility of CsPbBr₃ Perovskite Detectors in Extreme Radiation Environments

EN10.09.01
1:45 PM

Two-Dimensional Hybrid Halide Perovskite as Highly Efficient Metal Halides were employed. The carefully selected filters were inserted into them, enabling the combined radioluminescence (RL) to span the entire visible range (350 nm to 800 nm) devoid of the sublimation of substances. Liquid scintillators pose challenges in terms of manufacturing, transportation, storage, and handling due to their vulnerability to oxygen and flame. 

perovskites are known to exhibit higher light yield and faster scintillation decay compared to three-dimensional (3D) perovskite owing to higher exciton binding energy. Moreover, long-range polarization effects and discover their correlation with deep defects generated by intense radiation. Importantly, we find that the polarization can be mitigated by stronger applied electric fields and reduced carrier traps. Additionally, we employ thermally stimulated current spectroscopy to identify trap states and their impact on performance. Our findings suggest that CsPbBr₃ detectors fabricated with low defect concentrations (<1 x 10¹⁴ cm⁻³) show appreciable performance and stability. Another remarkable aspect of our research is the use of solution-processed perovskites for hard X-ray and gamma-ray detection. These solution-grown CsPbBr₃ detectors display excellent photocurrent linearity and sensitivity, even under ultrahigh x-ray fluxes, substantiating their wide applicability in high-flux environments. Comparisons between solution-grown and melt-grown crystals reveal comparable performance in terms of defect concentration and overall detector efficacy. There is a compelling case emerging for the use of CsPbBr₃-based detectors in a variety of high-stress applications, ranging from industrial settings to space explorations while highlighting strategies for further optimizing these promising materials.

The burgeoning field of radiation detection has witnessed a significant interest in semiconductors that can operate under harsh conditions and high photon fluxes. We present a comprehensive study on CsPbBr₃, a perovskite-based semiconductor, showcasing its potential as a robust and cost-effective alternative to conventional Cd¹₋ₓZnₓTe (CZT) detectors. Our research reveals that CsPbBr₃ detectors demonstrate minimal degradation even after exposure to 1 Mrad of Co-60 gamma radiation, maintaining high energy resolution and hole mobility. Many of these detectors also continue to function after a 10 Mrad dose over 3 days, indicating that device failure is more likely related to electrode-material interactions rather than intrinsic material degradation. We will also present the behavior of these detectors under extreme x-ray flux conditions. Utilizing ultrahigh flux synchrotron x-rays and advanced pump-and-probe techniques, we examine the polarization effects and discover their correlation with deep defects generated by intense radiation. Importantly, we find that the polarization can be mitigated by stronger applied electric fields and reduced carrier traps. Additionally, we employ thermally stimulated current spectroscopy to identify trap states and their impact on performance. Our findings suggest that CsPbBr₃ detectors fabricated with low defect concentrations (<1 x 10¹⁴ cm⁻³) show appreciable performance and stability. Another remarkable aspect of our research is the use of solution-processed perovskites for hard X-ray and gamma-ray detection. These solution-grown CsPbBr₃ detectors display excellent photocurrent linearity and sensitivity, even under ultrahigh x-ray fluxes, substantiating their wide applicability in high-flux environments. Comparisons between solution-grown and melt-grown crystals reveal comparable performance in terms of defect concentration and overall detector efficacy. There is a compelling case emerging for the use of CsPbBr₃-based detectors in a variety of high-stress applications, ranging from industrial settings to space explorations while highlighting strategies for further optimizing these promising materials.

known to facilitate the absorption and release of energy, has not yet been developed as a scintillator.

Herein, we developed blue-emitting 2D hybrid halide perovskites and evaluated its scintillation properties under various types of radiation. More specifically, ammonium derivatives from organic scintillators (i.e. anthracene, naphthalene, or stilbene) were employed as cations, where aromatic rings effectively serve as centers for the absorption of radiation energy. The synthesized 2D perovskite exhibited a photoluminescence (PL) peak centered at 410 nm, along with a notably high PL quantum yield of 64.5%. Furthermore, it demonstrated highly efficient scintillation property under X-ray and β-ray (C–14, Ni–63). In this study, we proposed a new strategy to enhance scintillation efficiency by incorporating organic scintillator cations into 2D hybrid halide perovskites, thereby paving a way for applications in future nuclear radiation monitoring devices.

3:30 PM *EN10.10.01

**Perovskite Light-Emitting Diodes for Next-Generation Data Communications**

Wei Zhang; University of Surrey, United Kingdom

Light-emitting diodes (LEDs) are ubiquitous in modern society. However, future applications of light-emitting diodes (LEDs) will not be limited to the fields of lighting and displays. As billions of Internet of Things (IoT) devices are already connected, the demand for data communication systems with low-cost and low-power consumption is dramatically increasing. It has been widely expected that LED-based links will act as key elements in the next-generation data communication systems. The conventional III-nitride micro-LEDs have the potential to provide a promising solution for such applications. However, the development of high-performance light-emitting diodes (LEDs) for this purpose has been hindered by the high fabrication costs and the lack of scalability.

Metal halide perovskites are emerging classes of semiconductors that have recently shown great potentials in the optoelectronic devices such as high-performance photovoltaics, photodetectors and LEDs. Their wide tunable properties such as bandgap and electronic energy levels can be tailored through synthesis and composition engineering. This distinct advantage is that these emerging materials can be solution-processed and deposited on different types of substrates under ambient conditions which are attractive for low-cost high-throughput industrial-scale fabrication. These fascinating features make metal halide perovskites promising materials for LED applications. Although prior research has progressed substantially in optimizing their external quantum efficiency for the applications in lighting and displays, the modulation characteristics of perovskite LEDs remain unclear.

In this talk, I will review the challenges that exist in developing practical high-speed LEDs, and highlight the most recent advance in the development of emerging LED materials—organic semiconductors, colloidal quantum dots and metal halide perovskites—for use in optical communications. I will then introduce a holistic approach that we developed most recently for realizing fast perovskite photonic sources on silicon based on tailoring halide perovskites cations in perovskite systems. Under optimal conditions, we achieved device modulation bandwidths of 42.6 MHz and data rates above 50 Mbps, with further analysis suggesting that the bandwidth may exceed gigahertz levels. Finally, I will summarize the general principles that will support the future development of perovskite light sources for next-generation data-communication architectures, which might open up new possibility of integration with micro-electronics platforms.

References

4:00 PM *EN10.10.02

**Molecular Interface Engineering and Optical Design for High-Efficiency Perovskite LEDs**

Hin-Lap Yip; City University of Hong Kong, Hong Kong

Metal halide perovskite light-emitting diodes (PeLEDs) have the potential to significantly impact next-generation lighting and display technology. However, their full promise has yet to be unlocked, particularly for blue and white PeLEDs. These devices face unique challenges such as maintaining stability, achieving high efficiency, and obtaining pure color emission, especially for blue light, due to the inherent material and device-related difficulties.

Our research tackles these issues through a multifaceted strategy designed to optimize the performance and efficiency of PeLEDs. We commence with interfacial engineering, introducing a self-assembled monolayer (SAM) with functional hole injection properties between the NiOx and poly(9-vinylcarbazole) hole injection layers. This approach effectively mitigates common obstacles such as weak interfacial adhesion, high interfacial trap density, and mismatched energy levels. The introduction of the SAM has successfully led to blue PeLEDs with external quantum efficiencies (EQEs) exceeding 15% and green devices with EQEs of 26.0%. In addition to enhancing efficiency, the introduction of the SAM also augments the device response speed by reducing interfacial capacitance and resistance. These advancements together pave the way for the development of more efficient, brighter, and faster responding perovskite LEDs, thereby broadening their potential applications in various fields.

Furthermore, we have developed an advanced device structure that optically couples a blue PeLED with a red-emitting perovskite nanocrystal layer, leading to the creation of efficient white PeLEDs. This innovative strategy utilizes near-field effects to facilitate the extraction of trapped blue photons’ optical modes to the red perovskite layer, resulting in white PeLEDs achieving EQEs over 12% - a significant advancement in white PeLED performance.

4:30 PM En10.10.03

**Semitransparent OLEDs with Ultrathin Light Emitting Layer and Extraordinarily Thick Perovskite Hole Transport Layer**

Michele Forzatti, Sang-Hyun Chiu, Daniel Tordera and Henk J. Bolink; Universitat de Valencia, Spain

Organic light-emitting diodes (OLEDs) have had a huge gain in popularity by virtue of their simple fabrication process, thin structure and for the possibility to devise transparent devices. However, the production of stable, cheap and efficient devices remains a challenge. Ultrathin nondoped emitting layers have been investigated as a way to simplify fabrication process and lower material consumption, but the consequent reduction in thickness may decrease device stability. Overcoming this issue with thicker transport layers is alluring but tough, as organics have intrinsically low charge-carrier mobilities. On the other hand, metal halide perovskites (MHPs), promising materials in many fields of optoelectronics, have also been used as charge transport materials, where their transparency in the visible region and high hole conductivity make it possible to increase the thickness of the layer to the micrometer-scale without increasing the operating voltage or reducing luminous efficiency.

In light of this, we developed a semitransparent OLED having a thick cesium lead chloride-all-inorganic perovskite hole transport layer, an ultrathin (<0.1 nm) Ir(ppy)₃acac film as emission layer and a semitransparent top indium-tin oxide contact deposited on top of a thin metallic layer. The resulting devices have a thickness exceeding 1 µm, a combined peak luminance of over 1000 cd m⁻², a current efficiency of 34 cd/A and a transparency in excess of 60% over the visible spectrum above 480 nm. The hole transporting CsPbCl₃ layer includes two thin (2 nm) CsCl layers at the interfaces, which are designed to be passable interfacial halide vacancies, improving the photoluminescence and reducing exciton quenching in turn. The nature of the ultrathin layer was investigated by means of contact angle measurement, which confirmed that the molecules forming the LEL are not in the form of a neat layer. The metallic layer could be deposited with little damage to the underlying organic layers but despite its low thickness, essential to guarantee transparency, it still protected towards the final ITO sputtering deposition. The combination of transparent top electrode, thick perovskite HTL and ultrathin LEL, described herein for the first time, entails a reduction in material and fabrication costs and is promising towards future cheap and stable semitransparent OLEDs.

4:45 PM En10.10.04

**Overcome Charge Transfer Barrier via Electrostatically Stabilized CsPbBr₂ Nanocrystals for Efficient Perovskite Light-Emitting Diodes**

Min-Gi Jeon, Artavazd Kirakosyan, Kim Joonsok, Subin Yun and Jhoon Choi; Chonnam National University, Korea (the Republic of)

Electrically insulating organic ligands with long hydrocarbon chains cause bottlenecks, which hinder efficient charge injection and transportation in CsPbBr₂ nanocrystal (NC)-based light-
Elevating Perovskite Solar Cells: Advances in Scalable Thin Film Deposition and Degradation Insights

Randall Headrick, Seid Yimer Abate, Pramod Baral, Gary E. Carver, and Richards G. Miller

In the rapidly evolving landscape of perovskite solar cells (PSCs), two pivotal challenges take center stage: (i) pioneering scalable thin film deposition techniques and (ii) unraveling degradation mechanisms. This presentation converges groundbreaking research encompassing scalable thin film deposition, high-efficiency solar cells, in-situ synchrotron X-ray diffraction studies, spatially resolved photoluminescence analysis, and accelerated degradation investigations under maximum power point tracking conditions.

At the heart of this presentation lies the development of scalable thin film deposition techniques, with a special emphasis on the innovative Verde Slot Coater [Ref 1]. Engineered to bring perovskite solar cells closer to commercial viability, the Verde Slot Coater represents a significant leap forward. It addresses the challenges of achieving uniform coating and effectively bridges the gap between scalability and control over crystallization that we call Restricted Area Printing (RAPID). RAPID prints films from confined volumes (between a superstrate and substrate) in a continuous process.

Film growth with RAPID can be tuned by controlling the working parameters that dictate the nucleation and growth—confinement gap, residence time, and temperature. We will show the influence of the solvent evaporation rate, distance between substrate/superstrate, and surface chemistry on both the substrate and superstrate on the nucleation and growth of perovskite thin films. Finally, we will demonstrate RAPID-printed perovskite thin films with domains greater than 20 μm and no lead iodide can be achieved in ambient conditions without the need for post-processing.

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Perovskite solar cells (PSCs) have attracted much attention because of the fast progress of their power conversion efficiency (PCE), from 3.8% to 25.7% in the past 14 years [1]. However, the toxicity of Pb effectively hinders its large-scale commercial production of PSCs. Therefore, researchers have turned their attention to Sn-based perovskite due to their similar or even superior optoelectronic properties, such as optimum band gap, high carrier charge mobility, and low exciton binding energy [2–3]. However, the stability of the Sn-based PSCs is low compared to Pb-based PSCs, which limits the practical use of the solar cells. One of the reasons for this low stability is the rapid crystallization, which results in inhomogeneous films with a lot of pin holes. Another reason is the easy oxidation of Sn²⁺ to Sn⁴⁺, which leads to high nonradiative recombination of carriers, low efficiency, and low stability. According to recent studies, Sn²⁺ oxidation is more dominant on the perovskite surface [2].

To enhance the quality of perovskite film, additive engineering is a well-known process for Sn-based PSCs to slow down the crystallization rate [3]. Recently, polydentate additives have shown effectiveness in modulating the growth of Sn-based perovskite films [4]. However, the stability of perovskite film is dependent on crystallinity and pin-hole-free large-grain compact films. Highly oriented crystal offers smooth charge transfer, whereas the larger grain reduces the grain boundaries, which are regarded as the recombination centers for the charges. In this work, we used a bifunctional additive in Sn precursor solution that acted as a modulator to dictate the growth of perovskite film and were able to fabricate highly crystalline and stable uniform perovskite film.

The additive-fused FASnI₃ film showed large and compact grains without any pinholes. This is because the bifunctional additive had a strong interaction with SnI₄ through hydrogen bonding, which delayed the fastSnI₃ crystal growth. At the same time, the bifunctional groups helped to create strong adherence between perovskite and PEODOT:PSS and dictated the growth of perovskite crystals in a preferred orientation. The XRD pattern of the modified FASnI₃ film remained unchanged for up to 3h when exposed to air, which indicates that the addition of this bifunctional additive to the precursor solution significantly enhanced the environmental stability of the FASnI₃ film.

With the addition of a bifunctional additive, the PCE jumped from 10.0% to 13.2%. It is important to state that the addition of the additive significantly improved the open circuit voltage (V_OC) from 0.85 V to 0.95 V as well as the short circuit current (I_SC) from 16.5 mA/cm² to 18.2 mA/cm². The enhancement of V_OC may be due to the suppression of leakage current with the addition of additives in the precursor solution, as we confirmed from our dark current measurement. This modification also reduced the charge recombination center, such as Sn⁴⁺ content in the film, as we observed from the XPS result. The PCE of the modified PSC retained its 90% initial PCE even after 100h. As a result, we achieved a certified (AIST, Japan) PCE of over 12% with superior device stability for Sn-based PSCs.

References
NREL Best Research-Cell Efficiency Chart. [https://www.nrel.gov/pv/cellefficiency.html]

5:00 PM EN10.11.05
p-Type Doping of Cs₂Sn₃Halide Perovskites Using Charge Transfer Donuts Alex Kratzer and Shubhra Bansal; Purdue University, United States

Perovskite solar cells (PSCs) have shown remarkable progress in recent years, surpassing the efficiency of conventional thin-film photovoltaic (PV) technologies such as CdTe and CIGS. The recent discoveries in organic-inorganic hybrid perovskites resulting from synergistic optimization of the perovskite absorber layer have generated remarkable development in device efficiency from 3.8% in 2009 to the present state-of-art 25.7%. Organic-inorganic halide perovskites have also shown 31.3% efficient tandem devices with Si bottom cells. Mixed-halide and mixed-cation systems have demonstrated high efficiency improvements in stability and reduced hysteresis. The emergence of 2D perovskite optoelectronics and 2D/3D heterojunctions, have shown promise by enhancing the long-term stability of Pb-based halide PSCs, however, addressing toxicity challenge is crucial for large scale adoption.

AZBX6 is a defect variant of the general perovskite structure ABX₃ where half of the vacant B-cations results in corner-sharing octahedron of anions [BX6]²⁻ and A-cation occupying the sites between the octahedron in 12-fold coordination. Alteration and substitution of B-cations and/or halogen anions (Cs₂TeI₆, Cs₂PtI₆, Cs₂PbI₆, Cs₂TiBr₆, Cs₂AgI₆, Cs₂AgBr₆, etc.) offer a multitude of features in these double perovskite structures with enhanced thermal and moisture stability.

Cs₂SnI₆ double perovskite has emerged as a promising light absorber, with a 4.0-eV bandgap and high efficiency in free-standing form. Cs₂SnI₆ has a direct bandgap of 1.3-1.6 eV, and the closed-packed halide framework results in dispersed conduction and valence bands leading to low electron effective mass of 0.48m₀ for electrons and 1.32m₀ for holes. Cs₂SnI₆ exhibits electron and hole mobilities of 310 cm²V⁻¹s⁻¹ and 42 cm²V⁻¹s⁻¹, respectively, and is believed to be an ambipolar material due to formation of n-type iodide vacancies/tin interstitials or p-type cesium vacancies. Devices up to 5% PCE have been demonstrated with enhancements such as CsI, Rb, Ag, In doping; ZnO nanorod electron transport layer (ETL); ethylene diamine post-deposition treatments. However, state-of-art Cs₂SnI₆ devices show high bulk and interface recombination as indicated by low carrier lifetime and high dark saturation current. Power conversion efficiency of 1.7 eV). We identify the ideal energy offset between the hole extraction and the wide bandgap perovskite layers and modulate the band gap function to this ideal using novel halide self-assembled monolayers (SAMs) as interface modifiers. Mixing these SAMs allows for selective tunability of both wettability and work function.

Using a two-step SAM-perovskite deposition, we have not found a clear correlation between improved performance of the SAM-modified ITO-perovskite interface and improved V_OC in solar cell devices. However, we found that mixing the SAMs into the perovskite precursor solution using a one-step deposition method improves their solar cell performance. This suggests that interfacial chemistry, including SAM functionalization and SAM interactions with perovskite in solution, may supersede energy alignment as the primary factor currently limiting V_OC.

Understanding their respective roles will enable the development of efficient wide gap perovskite devices for Si-tandem applications.

5:00 PM EN10.11.07
Efficient and Stable Perovskite Quantum Dot Photovoltaics enabled by Using Dopant-Free Hole Transport Materials with Rigidal Segments Seyeong Lim, Sungryong Kim and Taiho Park; Pohang University of Science and Technology, Korea (the Republic of)

CsPbI₃ quantum dots (QDs) with ideal optoelectronic properties offer high thermal stability for photovoltaics. In device fabrication, a ligand exchange process is required to enhance electrical coupling within QDs. However, this dynamic ligand exchange is imperfectly performed, resulting in surface traps and inevitable exposure of QDs to external conditions containing H₂O or O₂. So far, most QD photovoltaics (QDPVs) have adopted Spiro-OMeTAD as hole transport material (HTM), which requires deliquescent dopants to enhance its hole mobility, resulting in moisture that penetrates the perovskite crystal and greatly accelerates the decomposition of QDs.

In this point of view, hydrophobic HTMs on the QD surface are crucial for achieving high device stability. Conjugated polymeric HTMs basically have strong molecular packing for efficient charge transport, but excessive intermolecular interactions degrade film-forming properties in perovskites, which causes interfacial nonradiative recombination. In this respect, side chain engineering (e.g., extended-, polar-, and asymmetric-side chains) is developed for wide bandgap compositions relevant to tandems (E_g > 2.5 eV). However, state-of-art Cs₂SnI₆ devices show high bulk and interface recombination as indicated by low carrier lifetime and high dark saturation current. Power conversion efficiency of higher than 5% has been demonstrated for planar p-i-n Cs₂SnI₆ devices; however, to increase the device efficiency further robust methods of defect passivation and improved doping density are needed.

Here we will present the results of a controlled study on charge transfer doping using molecules such as F4TCNQ for Cs₂SnI₆. When applied to MAPb₀.₅Sn₀.₅I₃, the electrical conductivity increased by 5 orders of magnitude, the hole density increased by 1 order of magnitude, and the passivation of charge carrier traps increased the carrier recombination lifetime. The molecular dopant F4TCNQ also fits the criteria to be an effective p-type dopant for Cs₂SnI₆ due to its lowest unoccupied molecular orbital (LUMO) value being less than the valence band maximum (VBM) value, so as to facilitate effective charge transfer for holes. Data in film processing, doping and carrier lifetime will be presented for Cs₂SnI₆ processed by doctor blade method with and without molecular dopants. The effect of the dopants on phase stability, absorption bandgap will also be studied.

5:00 PM EN10.11.08
Electrochemical Impedance Spectroscopy on Perovskite Inks to Probe Ion Pairing in Solution Keenan W. Wyatt, Marder2 and David S. Ginger1; 1University of Washington, United States; 2University of Colorado Boulder, United States

Open circuit voltage losses (V_OC) in the perovskite top cell remain a significant challenge for the commercialization of perovskite tandem solar cells. We show through simulations that common hole transport materials like PTAA and Me-4PAc are energetically mismatched with the perovskite active layer which lowers the quasi-Fermi level splitting and limits V_OC particularly for wide bandgap compositions relevant to tandem (E_g > 1.7 eV).

We identify the ideal energy offset between the hole extraction and the wide bandgap perovskite layers and modulate the anode work function to this ideal using novel halide self-assembled monolayers (SAMs) as interface modifiers. Mixing these SAMs allows for selective tunability of both wettability and work function.

Using a two-step SAM-perovskite deposition, we have not found a clear correlation between improved alignment of the SAM-modified ITO-perovskite interface and improved V_OC in solar cell devices. However, we found that mixing the SAMs into the perovskite precursor solution using a one-step deposition method improves their solar cell performance. This suggests that interfacial chemistry, including SAM functionalization and SAM interactions with perovskite in solution, may supersede energy alignment as the primary factor currently limiting V_OC.

Understanding their respective roles will enable the development of efficient wide gap perovskite devices for Si-tandem applications.

Hybrid perovskite solar cells (PSCs) are a disruptive technology with their rapid improvement in power conversion efficiencies over the last decade. At the laboratory scale, solution processed

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Mechanism of the Anomalous Dependence between Spin–Orbit Coupling and Dimensionality in Lead Halide Perovskites

Yuming Xian, Xiaoming Wang and Yanfa Yan; University of Toledo, United States

The spin–orbit coupling (SOC) effect of lead (Pb) atoms is a consequential attribute of the unique optoelectronic and defect properties of lead halide perovskites (LHPs). It has been found that the SOC effect varies significantly as the structural dimensionality changes with an anomalous dependence; i.e., while the SOC strength monotonically decreases as structural dimensionality decreases from three-dimensional (3D) to structural dimensionality (2D) and then to one-dimensional (1D), the zero-dimensional (0D) SOC strength is greater than the 1D SOC strength. The underlying mechanism of such a SOC dimensionality dependence anomaly remains elusive. In this work, we show that Pb 6p energy splitting increases from 3D to 2D and to 1D LHPs due to the increased degree of distortion, leading to a reduced SOC strength. However, the degree of distortion decreases for the 1D to 0D transformation, resulting in reverse SOC enhancement. The mechanism described in this work can be employed to regulate the SOC effect in the design of perovskite materials.

Understanding the Structure-Property Relationship of Two-Dimensional Metal Halide Perovskites

Yumeng Song, Philip C.Y. Chow*; Department of Mechanical Engineering, The University of Hong Kong, Hong Kong SAR, China

Two-dimensional (2D) metal halide perovskites have emerged as promising materials for next-generation solar cells and light-emitting diodes thanks to their outstanding optoelectronic properties, facile tunability, and superior stability over their 3D counterparts. However, the detailed structure-property relationship of 2D perovskites underlying their optoelectronic properties has remained unclear. In this project, we design and synthesize a variety of 2D perovskite single crystals, in both Ruddlesden-Popper and Dion-Jacobson phases. We then use a combination of steady-state and time-resolved optical spectroscopy methods to characterize the exciton properties and dynamics, specifically focusing on how they are affected by changes in structural properties. Our results will help us develop a fundamental understanding of 2D perovskites and enable rational material design and development.

Mitigating Iodine Diffusion by a MoO3-Organic Composite Hole Transport Layer for Stable Perovskite Solar Cells

Jisu Hong1, Zhaojian Xu1, Dominique Lungwitz2, Jonathan Scott1, Holly Johnson1, Yun-Hi Kim1, Antoine Kahn1 and Barry P. Rand1; 1Princeton University, United States; 2Gyeongsang National University, Korea (the Republic of)

Halide perovskite solar cells (PSCs) exhibit commercialization potential, but long-term stability still has to be addressed. Among various products of perovskite decomposition, iodine species are of considerable concern due to their high vapor pressure and corrosive nature. To address this, a small-molecule hole transport layer (HTL), 4,4',4''-tris[(3-methylphenyl)phenylamino]triphenylamine (m-MTDATA), is used, and p-doped using molybdenum trioxide (MoO3) to prevent an alternative oxidation reaction with iodine species that are released from iodide perovskites upon degradation. The resulting m-MTDATA:MoO3 composite HTL demonstrates high conductivity and suppressed iodine permeation. We demonstrate that m-MTDATA:MoO3 HTLs employed in PSCs improve stability under both thermal and voltage bias stress compared to devices with a conventional doped 2,2',7,7'-tetakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) HTL.

Halide Choice is Critical for The Formation of 2D/3D Perovskites and Their Performance in Solar Cells

Randahl F. Moral1,2, Carlo Andrea Riccardo Perini3, Tim Kodal1, Alyoun Kim1, Finn Babbe1, Nao Harada4, Philip Schult2, Naomi S. Ginsberg2, Ruipeng Li3, Shaal Aloni1, Craig Schwartz2, Juan-Pablo Correa-Baena2 and Carolin M. Sutter-Fella1; 1Lawrence Berkeley National Laboratory, United States; 2University of Nevada, Las Vegas, United States; 3Georgia Institute of Technology, United States; 4L'Institut Photovoltaïque d'Île-de-France, France; 5Centre National de la Recherche Scientifique, France; 6University of California, Berkeley, United States; 7Brookhaven National Laboratory, United States

2D/3D perovskite solar cells (PSCs) hold great promise for photovoltaics applications.1 The key to the development of stable and efficient devices is the synergy between the higher ambient stability of 2D phases and the outstanding electrical and optical properties of 3D perovskites. These materials also have high versatility in terms of composition, allowing for different material design and engineering strategies. The vast list of molecules (spacers cations) that can be used for the synthesis of the 3D phases also poses a challenge to the development of these materials.2 Each of these spacer cation presents a different reactivity with the underlying 3D perovskite, encouraging trial-and-error approaches rather than a rational design of stable 2D/3D interfaces.3 For example, the choice of the halide anion, both in the spacer cation and in the 3D perovskite, greatly influences materials' photovoltaic and device properties.4 To provide more insights into the formation and ionic dynamics of these complex interfaces, we examined the impact of halide choice (I and Br) in 3D perovskites treated with phenylethyliammonium/ammonium salts (PEAI and PEABr, respectively).

We evaluated the formation of layered perovskites using PEAI and PEABr salts on top of 3D perovskites with pure iodine and mixed halides, Cs0.17FA0.83PbI3 and Cs0.17FA0.83PbI2.5Br0.5, respectively, before, during, and after annealing at 65 °C for 30 minutes. Through various spectroscopic techniques, we revealed that PEABr reacts less readily with the 3D film compared to PEAI to form the 2D phases. As a consequence of this lower reactivity, PEABr can diffuse through the grain boundaries as an ionic pair, and this behavior was revealed by X-ray photoelectron spectroscopy (XPS). Also, the mixed-halide 3D perovskite is less reactive than its pure-iodine counterpart. The lower reactivity of PEABr may be attributed to the higher lattice energy of ammonium bromides in comparison to ammonium iodides, and similar reasoning applies to the mixed-halide 3D perovskite. Consequently, PEAI presents higher passivation ability than...
PEABr, and the best device performance and reproducibility were achieved with PEAI-treated Cs₉₁\textsubscript{0.17}FA₈₀.₈₃Pb\textsubscript{₃.} Our work provides valuable insights into the fundamental properties and formation mechanisms of 2D/3D perovskites, which is crucial for advancing these photovoltaic devices.

9:00 AM EN10.12.04
Preventing Metal Shunting in Perovskite Solar Cells during Reverse Bias

Daniel A. Morales and Michael McGehee; University of Colorado Boulder, United States

Perovskite solar cells (PSCs) are emerging as promising materials for photovoltaic energy conversion due to their rapidly increasing power conversion efficiencies and cost-effective fabrication procedures. Many research efforts are currently dedicated to investigating external stressors that perovskite solar cells experience in the field – oxygen, elevated temperatures, and moisture/humidity. However, there remains a knowledge gap concerning the behavior of this technology when subjected to another real-world external stressor for solar panels – reverse bias.

PSCs typically exhibit low breakdown voltages in reverse bias (<5V), making the integration of traditional bypass diodes used in Si arrays difficult due to the increased production costs\(^1\)[2]. Therefore, numerous efforts have been made to identify and address the root causes of reverse bias-induced degradation of PSCs. These breakdown mechanisms of PSCs have been directly correlated with voltage-induced ion migration and the formation of hotspots when using metal electrodes\(^2\)[3]. The diffusion of metallic species in PSCs has been recorded during regular operation, but is accelerated under reverse bias conditions as elevated electric fields facilitate ion migration and initiate interactions between mobile ions and metal species at the contacts.

We have studied a wide variety of strategically chosen perovskite solar cells under reverse bias, and we observe the formation of these metallic shunts in PIN architectures with metal electrodes. We employed metals with various electrochemical reactivities (Ag, Au, Cu, & Al) and found that metal shunting is most prominent in silver metal electrodes, one of the most popular contact materials used in perovskite solar cells. Metal diffusion/shunting most-often results in catastrophic failure of the device when returned to normal operating conditions. We attribute this metal shunting behavior to the preferred oxidation state of the metals and the increased activation energy for these metal ions to diffuse through the perovskite device architecture. We show that metal shunting/diffusion in our inverted perovskites can be prevented by simply using higher oxidation-state metals (Au, Cu, & Al). We also investigate the application of interlayer additives, including barrier layers deposited via atomic layer deposition (ALD), chromium (Cr), benzo triazole (BTA), and other chelating agents commonly employed in water treatment facilities to address metal accumulation.


9:15 AM EN10.12.05
All Inorganic Layer Perovskite Solar Cells Based on Oxide/Halide/Oxide Architecture

Soo Woong Jeon, Min Ju Jeong and Jun Hong Noh; Korea University, Korea (the Republic of)

Inorganic CsPbI\textsubscript{2}Br perovskite has outstanding thermal stability and substantial potential for semi-transparent solar cells. However, Cesium-based perovskite solar cells (PSCs) exhibit phase instability due to the perovskite film's moisture penetration. Therefore, 2,2\',7,7\'-tetrakis(N,N-di-p-methoxyphenylamino)-9,9\'-spirobi fluorene (spiro-OMeTAD) has been commonly used as hole transporting layers (HTLs) in high-performance PSCs. However, achieving precise stoichiometry with multiple sources is challenging when using a co-evaporation process. Herein, we report all inorganic layer PSCs based on oxide/halide/oxide architecture for the high stability and performance of PSCs. We introduced nickel oxide (NiO\textsubscript{x}) nanoparticles overlayer on the perovskite layer as HTLs. As a result, the all-inorganic layer device shows an improved thermal stability and power conversion efficiency (PCE) of 16.67%. In addition, we fabricated the semi-transparent devices by sputtering the tin-doped indium oxide (ITO) as an electrode, which achieved an average visible transmittance higher than 20%. All inorganic layer PSCs with oxide/halide/oxide also showed superior storage stability without encapsulation under 10% relative humidity, retaining over 85% of initial PCE for 1000 h. We believe that this architecture with n-type oxide/inorganic perovskite/p-type oxide represents a cornerstone for the high stability of PSCs.

9:30 AM EN10.12.06
Irreversible Performance Degradation Driven by Lithium-Ion Migration in FAPb\textsubscript{1-x} Perovskite Solar Cells

Seung-Gu Choi and Jin-Wook Lee; Sungkyunkwan University, Korea (the Republic of)

The typical n-i-p structured perovskite solar cells (PSCs) incorporate 2,2\',7,7\'-Tetrakis (N,N-di-p-methoxyphenylamine)-9,9\'-spirobi fluorene (spiro-OMeTAD) as a hole transporting material. The chemical doping process of the spiro-OMeTAD involves a redox reaction with bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI) accompanying complex side reactions of which impact on device performance is not fully understood. Here, we investigate correlation between aging dependent device performance of widely used formamidinium lead tri-iodides (FAPb\textsubscript{I₃}) based PSCs and migration of lithium ion (Li\textsuperscript{+}) generated from Li-TFSI. The cross-sectional Kelvin probe force microscopy unraveled aging time dependent change in hetero-interface energetics in PSCs, which was correlated with progressive migration of Li\textsuperscript{+} ions generated from Li-TFSI confirmed by Time-of-flight secondary ion mass spectroscopy. Comprehensive analysis revealed that the Li\textsuperscript{+} migrate from spiro-OMeTAD to perovskite, SnO\textsubscript{2}, and their carrier extraction interfaces to induce phase back conversion of α-FAPb\textsubscript{I₃} to δ-FAPb\textsubscript{I₃} with local microstrain, and consequent generation and migration of iodine defects and dedoping of the spiro-OMeTAD. The rapid performance drop of PSCs even aging under dark conditions was attributed to a series of these processes. Our work unraveled the hidden side effect of Li\textsuperscript{+} ion migration in FAPb\textsubscript{I₃} based PSCs that can guide further work to maximize the operational stability of the PSCs.

9:45 AM EN10.12.07
Effective Addition of Cation and halides in FAPb\textsubscript{1-x} Perovskite Solar Cells by Multiple Thermal Co-Evaporation

Ha Kyung Park and William Jö; Ewha Womans University, Korea (the Republic of)

Metal halide perovskite solar cells (PSCs) have rapidly advanced as a next-generation solar cells with high efficiency over 25%. Among the various fabrication methods for the perovskite, thermal evaporation stands out as a suitable option for scaling up commercialization. However, achieving precise stoichiometry with multiple sources is challenging when using a co-evaporation method due to the varying volatility. In this study, multiple co-evaporation method was designed to fabricate the stoichiometrically mixed cation and halides PSCs using two sources. Formamidinium iodide (FAI) and lead iodide (PbI\textsubscript{2}) were co-evaporated followed by the co-evaporation of methylammonium iodide (MAI) and PbI\textsubscript{2} or methylammonium bromide (MABr) and lead bromide (PbBr\textsubscript{2}). The deposition rates and thickness of secondly co-evaporated layer were controlled to achieve stoichiometry of mixed cations and halides precursors. After that, samples were annealed to form FAPb\textsubscript{1-x} (FA,MA)Pb\textsubscript{1-x} and (FA,MA)PbBr\textsubscript{1-x} films. The completed PSCs were semi-film vacuum-deposited, except for the hole transport layer. Among the samples, (FA,MA)Pb(FA,MA)Br\textsubscript{2} solar cells showed the highest performance of 11.38% efficiency with improved open-circuit voltage of 25 mV and current-voltage hysteresis. Herein, band gap of MA and Br added FAPb\textsubscript{1-x} slightly increased indicating only small amount of MAPb\textsubscript{1-x} and MAPbBr\textsubscript{1-x} phases formed. Still, mixed cations samples showed improved absorbance compared to CA cation only sample. In conclusion, multiple co-evaporation is effective method for mixing cations and halides in PSCs.

10:00 AM BREAK

SESSION EN10.13: Strain and Single Crystals
Session Chairs: Silvia Colella and Carolin Satter-Fella
Thursday Morning, April 25, 2024
Room 334, Level 3, Summit

10:30 AM EN10.13.02
How The Dynamics of Attachment to The Substrate Influence Stress in Metal Halide Perovskites

Gabriel McAndrews\textsuperscript{1,2}, Boya Guo\textsuperscript{3}, Daniel Morales\textsuperscript{1}, Aram Assamian\textsuperscript{3} and Michael D. McGehee\textsuperscript{1,3,}\textsuperscript{*}; University of Colorado Boulder, United States; \textsuperscript{2}National Renewable Energy Laboratory, United States; \textsuperscript{3}North Carolina State University, United States

Metal halide perovskites, hereon referred to perovskites for simplicity, are a promising class of semiconductors eagerly researched for their use in photovoltaic and optoelectronic applications.
Despite low fabrication cost and superb initial efficiencies, improvements to the operational stability of perovskites would aid extensive deployment in both terrestrial and space applications. Mechanical stress is an important, but often misunderstood factor impacting chemical and structural degradation as well as reliability during extreme temperature cycling. Tension has been shown to be a significant contributor to chemical and structural degradation, leading to a reduction in device performance.

Here, we show that a simple application of the CTE mismatch equation inaccurately predicts residual stress in perovskite films. For example, despite similar CTEs, there is a 60 MPa stress difference between narrow bandgap “SnPb Perovskite” (Cs0.25FA0.75Sn0.5Pb0.5I3) and popularized “Triple Cation Perovskite” (Cs0.05MA0.16FA0.79Pb(I0.83Br0.17)3). We probe the cause of residual stress variation in metal halide perovskite with a combination of in situ absorbance and substrate curvature measurements during the spin coating, anneal, and cooldown procedures. This reveals that the degree of partial attachment prior to the anneal can reduce residual tension following cooldown. Additionally, we demonstrate the dynamic nature of stress in perovskite with evidence of tensile stress relaxation which is accelerated by the presence of moisture and oxygen. In turn, we propose a new framework to understand the relationship between stress and degradation as films with tension are driven to uptake moisture and oxygen to release stress. Finally, we present a critical perspective on stress engineering strategies based on high CTE buffer or interlayers which are claimed to modify thermal stress in the perovskite.

We show that these strategies are not grounded in thin-film mechanics as the stress in the perovskite in response to temperature changes is dominated by the thickest, stiffer layer, such as glass.


10:45 AM EN10.13.03 Suppressing Trap-Assisted Recombination in Perovskite Solar Cells via Strain Relaxation Peier Hu; Imperial College London, United Kingdom

Intraband trap states can be formed unavoidably during the solution-processed fabrication of perovskite solar cells (PeSCs). Their existence contributes to non-radiative recombination loss via trap-assisted recombination pathways in PeSCs, leading to insufficient power conversion as well as a higherIntraband trap states can be formed unavoidably during the solution-processed fabrication of perovskite solar cells (PeSCs). Their existence contributes to non-radiative recombination loss via trap-assisted recombination pathways in PeSCs, leading to insufficient power conversion as well as a higherIntraband trap states can be formed unavoidably during the solution-processed fabrication of perovskite solar cells (PeSCs). 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11:15 AM EN10.13.05 Advancing Perovskite Single Crystal Fabrication: Enhanced Crystallinity and Reproducibility through Feedback Control of Linear Growth Rate Yuki Haruta, Antoine Pavesic Junior and Makhshud Saidaminov; University of Victoria, Canada

Lead halide perovskites have gained significant attention in recent years thanks to their excellent photon absorption capabilities and charge transport properties, raising high expectations for diverse device applications such as solar cells and x-ray detectors. However, their instability presents a major challenge that demands resolution. Notably, perovskite single crystals are known to exhibit substantially higher durability compared to polycrystalline films, with an even higher degree of crystallinity suggesting enhanced stability. Nevertheless, conventional methods for synthesizing perovskite single crystals have often been relatively straightforward, yet challenging to consistently produce high-quality single crystals. In light of this, our research focused on controlling the linear growth rate of the single crystals which has been likely overlooked in the conventional methods. Methylammonium lead triiodide (MAPbI3) single crystals are fabricated as a case study. Our novel approach combines in-situ imaging techniques to monitor crystal growth rates with a conventional solvent evaporation method. When the crystal growth deviates from the desired rate, our system provides feedback to adjust growth conditions accordingly. Through this approach, we successfully maintain a constant linear growth rate for over 60 hours, leading to the reproducible synthesis of single crystals with enhanced crystallinity.

The degree of crystallinity is quantified by measuring the rocking curves of the (100) plane of the obtained MAPbI3 single crystals. This work uncovers the critical role of controlling the linear growth rate, rather than the mass growth rate, in achieving superior crystallinity and reproducibility. MAPbI3 single crystals grown with a linear growth rate of less than 0.3 mm h-1 exhibit narrow rocking curves, with a full width at half maximum (FWHM) of 19.0±2.7 arcsec (n=17), while growth rates exceeding 0.3 mm h-1 results in a FWHM of 27.9±10.0 arcsec (n=15). The best crystal achieves a remarkable FWHM of 15.3 arcsec, the narrowest reported for MAPbI3 single crystals, comparable to a commercial silicon wafer. Note that these excellent FWHM are achieved with centimeter-scale single crystals. This research emphasizes the pivotal importance of linear growth rate control in single crystal growth.

11:15 AM DISCUSSION TIME

SESSION EN10.14: Beyond Photovoltaics

Session Chairs: Sascha Feldmann and Carolin Sutter-Fella
Thursday Afternoon, April 25, 2024
Room 334, Level 3, Summit
Lead-halide perovskites have emerged as important semiconducting materials suitable for a variety of optoelectronic applications. Further advances in the field will rely on establishing the unique potential of perovskites to address the first experimental realization of the intrinsic (not dominated by defects) charge conduction regime in metal-halide perovskite field-effect transistors (FETs). The advance has been enabled by: i) a new vapor-phase epitaxy technique that results in large-area single crystalline all-inorganic cesium lead bromide (CsPbBr3) films with excellent structural and surface properties, including atomically-flat surface morphology, essentially free from defects and traps at the level relevant to device operation; ii) an extensive materials analysis of these films using a variety of thin film and surface probes certifying the chemical and structural quality of the material; iii) the fabrication of nearly ideal (trap-free) FETs with textbook FET characteristics superior to any reported to date. These devices have allowed the investigation of the intrinsic carrier mobility as a function of temperature via both FET and gated Hall-effect measurements. The intrinsic mobility of our CsPbBr3 FETs was found to increase on cooling from ~ 30 cm²/Vs at room temperature to ~ 250 cm²/Vs at 50 K. The combination of photo-Hall, gated Hall, and FET measurements reveal the intrinsic band transport occurring in these devices, with the mobility limited only by phonon scattering. The outstanding quality of these devices is largely due to the atomically flat, single crystalline morphology of the epitaxial CsPbBr3 films achieved over macroscopic length scales, as confirmed by comprehensive structural, morphological, and surface analysis.

The epitaxial CsPbBr3 FETs exhibit no degradation over a long storage regime in air (as tested for up to several months) or during extended electric measurements (that sometimes run for several weeks on end), with the exceptions of driving the FETs into a saturation regime or micro crack formation at low temperatures. While the encapsulation of the perovskite in parylene may have contributed to the excellent operational stability of our FETs, our as-grown uncoated perovskite films did not exhibit noticeable degradation during a prolonged storage in the regular laboratory air (ranging in duration from days to weeks).

Establishing the intrinsic (phonon-scattering limited) mobility can not only serve as a rigorous test for theoretical models of carrier transport but can also reveal the ultimate fundamental limits of mobility in these materials, as well as to point a pathway for future innovation to still newer and improved perovskite systems. Additionally, our findings suggest that epitaxial perovskites offer an ideal platform for fundamental studies on charge transport in this class of materials. The robust, simple, and effective method for fabricating perovskite FETs that exhibit stable and ultimately efficient intrinsic charge transport paves a way for a plethora of new perovskite-based devices, such as light emitting FETs, electrically pumped injection lasers, better radiation detectors, sensors and memories.

Reference


2:00 PM EN10.14.03
High-Resolution Multicolor Transfer Printing of Perovskite Nanocrystals for Ultrathin Skin-Attachable Displays. Gwang Heon Lee1, Jong Il Kwon2, Gyuri Park3, Jae Hong Jang4, Iwoong Yang2 and Moon Kee Choi1,1 Ulsan National Institute of Science and Technology, Korea (the Republic of); 2Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

Over the past decade, the development of wearable displays with ultrahigh definition has garnered considerable attention in the information technology. Wearable displays exhibit mechanical deformability, allowing them to conformally attach to various objects with curvilinear surfaces. Technological advances to achieve deformable form factors enable mechanical changes such as bending, rolling, and twisting. In parallel to the advanced at form factors, high-definition red-green-blue (RGB) subpixels are crucial for visualizing diverse information on the compact surface of wearable displays. Despite the recent advancements in display technology, the development of high-definition full-color wearable light-emitting diodes (LEDs) remain an unresolved problem.

Metal halide perovskites have gained attention as promising light-emitting materials due to their narrow full-width half-maximum, high photoluminescence, and color tunability. Furthermore, the extremely thin construction of perovskite light-emitting diode (PeLEDs) (~1 μm, excluding the thickness of the substrate) make them highly promising for applications in ultrathin and deformable displays. With recent advances in synthesis and device engineering, progress in this field has led to impressive external quantum efficiency (EQE) values, with red, green, and blue PeLEDs achieving 25.8%, 28.9%, and 18%, respectively. Most previous studies predominantly centered on optimizing PeLED performance via monochromatic perovskite nanocrystal (PeNC) films produced by spin-coating techniques. However, most full-color displays on the commercial scale require the development of patterning methods to ensure the seamless integration of RGB subpixels within the ultra-thin and conformable (EL) devices.

Conceptually, the RGB patterning of PeNCs have several requirements: 1) Preservation of device layer integrity and no contamination during the patterning process; 2) high reproducibility; and 3) high-resolution patterning capabilities, particularly at the sub-micrometer scale. Unfortunately, conventional patterning methods (e.g., photolithography and inkjet printing) of perovskite materials are unsuitable for the fabrication of highly efficient PeLEDs. Photolithography suffer from the degradation of perovskite materials by ultraviolet(UV) light, moisture and polars solvents, owing to their ionic bonding nature. Ink jet printing is applicable to multicolor pixelation of PeNCs through additive patterning. However, the additives (i.e., polymer matrix, surfactant, and viscosity modifier) suppress the EL device performance. Dry transfer printing employing a viscoelastic stamp represents a strategic choice for producing high-definition PeNC pixels for EL devices. This method circumvents the use of wet chemicals, mitigating concerns about solvent compatibility and cross-contamination between different colored pixels. Nonetheless, this approach has shown limited application in the case of PeNCs. The low interaction energy among PeNCs can lead to internal film cracking during the transfer process. Here, we demonstrate high-resolution dry transfer printing for ultrathin wearable displays. Specifically, we employ a simple and effective double-layer transfer printing method with an additional organic ligand between PeNCs and a poly(dimethylsiloxane) (PDMS) stamp to prevent internal cracks in the transferred PeNC films. Furthermore, the pressure applied during the transfer printing process reduces the interparticle distance in the transfer-printed PeNC layers, enabling the highly efficient PeLEDs, which exhibit peak EQE of 15.3%, 14.8%, and 2.5% for red, green, and blue PeLEDs, respectively. Finally, we demonstrate ultrathin, skin-attachable PeLEDs based on this patterning method. The realization of high-resolution RGB patterns using double-layer transfer printing may open up unique opportunities for wearable displays with various form factors.

2:15 PM EN10.14.04
Halide Perovskites as Thermoelectric Materials. Oliver Fenwick; Queen Mary University of London, United Kingdom

Halide perovskites are well known as promising candidates for photovoltaics and light-emitting diodes. Additionally, promising thermoelectric performance has been reported for a small number of halide perovskites, with this class of materials offering ultralow thermal conductivity, good Seebeck coefficients and potential advantages in processing and sustainability. However, there is not yet a good understanding of how thermoelectric performance of halide perovskites can be optimised. This talk will cover the origins of ultralow thermal conductivity and compare both the Lorentz number and the thermal boundary resistance in [3] in polycrystalline films. Extrinsic doping and self-doping will be discussed as methods to optimise the thermoelectric figure of merit zT, with values of zT reaching 0.14 in CsSnI$_3$. [2] The case of self-doping by Sn-oxidation in CsSnI$_3$ will be examined in detail and strategies to improve performance and control the rate of oxidation by modification of deposition procedures, or by using mixed halide and mixed metal stoichiometries will be presented. Thin-film vapour deposition, single crystal growth [1] and solid-state synthesis of pellets will be discussed, along with doping techniques to improve stability and conductivity.

[2] Liu, T; Zhao, X; Li, J; Liu, Z; Liscio, F; Milita, S; Schroeder, BC; Fenwick, O Enhanced control of self-doping in halide perovskites for improved thermoelectric performance, Nature Communications, 2020, 11(2), 13590.
[3] Liu, T; Yue, SY; Ratnamahingam, SR; Degoues, T; Varsani, PR; Briccely, J; McLachlan, MA; Hu, M; Fenwick, O Unusual thermal boundary resistance in halide perovskites: A way to tune ultralow thermal conductivity, ACS Applied Materials and Interfaces, 2019, 11 (50), 47507–47515.
Degradation Mechanism of Colloidal Perovskite Nanocrystals and its Stabilization Strategy

Qingsen Zeng, Huanyu Zhou and Tae-Woo Lee; Seoul National University, Korea (the Republic of)

SESSION EN10.15: Emission
Session Chairs: Jack Jasieniak and Carolin Sutter-Fella
Thursday Afternoon, April 25, 2024
Room 334, Level 3, Summit

3:30 PM EN10.15.01
Light Emission from Localization in Halide Perovskites – Composition, Doping, Dimensionality
Sascha Feldmann; Harvard University, United States

Halide perovskites are fascinating semiconductors for light-emitting applications. Compared to conventional inorganic covalent semiconductors like silicon or GaAs, perovskites are structurally soft and often more disordered. Understanding the consequences of this remains a key challenge for commercialization.

Here I will present our recent mechanistic insights from spectroscopy on the role of composition, doping and dimensionality to control light emission through localization in these materials, including the introduction of a new method of doping halide perovskites at room temperature and its impact on excitation dynamics.

4:00 PM EN10.15.02
Tailoring The Optoelectronic Properties of Tin-Based Perovskite Light-Emitting Diodes
Jae Eun Seo; University of Naples Federico II, Italy

Two-dimensional perovskite thin films have shown tremendous potential as active materials for light-emitting diode (LED) applications, thanks to their remarkable optoelectronic properties and high environmental stability compared to their three-dimensional counterparts. However, achieving precise control over their composition and morphology remains a significant challenge.

To overcome these issues, a strong coordinating agent, several functionalized bulky cations, and an increasing number of precursor materials have been applied. In this study, we investigate the influence of additives on the growth and performance of 2D tin-based perovskite thin films in nonoxidative solvent. We employed advanced characterization techniques such as UV-Vis absorption spectroscopy, X-ray diffraction, scanning electron microscopy, and photoluminescence spectroscopy to understand its effect. By systematically varying the processing parameters, including the amount of additive and the deposition conditions, we gain insights into the underlying mechanisms governing the film formation and properties. As a result, the 2D tin-based perovskite LED device had a low turn-on voltage of 1.75 V, and a maximum external quantum efficiency of ~2.2% in a nonoxidative solvent. The optimized thin film compositions and processing conditions from this research will facilitate the development of good-performance tin-based perovskite LEDs with enhanced external quantum efficiency, stability, and color purity.

Furthermore, this work will contribute to the advancement of additive engineering strategies for the scalable fabrication of perovskite-based LEDs, fostering their integration into next-generation solid-state lighting technologies.

4:15 PM EN10.15.03
How Pinholes in Perovskite Films Create Stealthy ETL-HTL Diodes that Slightly Reduce Efficiency and Dramatically Enhance Reverse Bias Shunting
Samuel A. Johnson and Michael D. McGehee; University of Colorado, Boulder, United States

Solution processing metal halide perovskites has advantages for scaling up manufacturing, but reproducibility and reliability are complicated by physics dictating coating (e.g. surface tension and dewetting). Void defects and pinholes form via tension created by volume reduction during the drying phase. We systematically investigate the origin and impacts of ‘void defects’ and reveal five common defect formation mechanisms that can result in points where the intrinsic perovskite absorber is missing. At most of these sites, metal- electron transport material (ETM) - hole transport material (HTM) - metal defects exist. We determine how much current can pass through these defect diodes by making diodes without the perovskite layer and measuring the current-voltage curve. We found that the current turned on between 0.4 and 0.8 V depending on which contact layers we used. Dark Lock-in Thermography (DLIT) of a perovskite solar cell shows localized regions begin to heat under forward bias, but only above the turn-on voltage of transport-layer diodes indicating diode-like defect response in real devices. An important consequence of this behavior is that the defect diodes do not pass current near 0 V where the shunt resistance is typically measured by taking the slope of the current-voltage curve. They do, however, pass significant current at the maximum power point and the open circuit voltage. Consequently, they have a more detrimental effect on device performance than most people realize.

These defects have even more important consequences when the cells are operated in reverse bias, which can happen when a panel is partially shaded. These defects enable breakdown at lower voltages and shunt current, resulting in local ohmic heating, followed by the melting and propagation of burning metal shunts across the surface. This effect produces catastrophic degradation of the solar module. It is therefore critical to mitigate such defects for widespread implementation of perovskite PV. We demonstrate optical profilometry and PL-mapping as high-throughput detection methods for these defects as well as improved particle control and solution wetting as possible preventative measures. Elimination or passivation of these defects will prevent localized loss and enhance long-term reliability of perovskite solar cells, paving the way for successful commercial perovskite solar cell production.

4:30 PM EN10.15.04
Bismuth: An Infrared-Emitting, Deep-Level Trap in CsPbBr3
Kyle Sendzikowski1, Brendon T. Jones2, Michael H. Stewart1, Barbara A. Marcheschi1, Todd H. Brittlinger1, John Lyons1 and Sarah Britman1; 1U. S. Naval Research Laboratory, United States; 2Florida State University, United States

Halide perovskites have already demonstrated impressive optoelectronic performance in applications ranging from photovoltaics, to light-emitting diodes and lasers, to X-ray and gamma-ray detectors and scintillators. Understanding how extrinsic dopants behave in this class of materials is a critical next step to gaining greater control over the stability and performance of this versatile class of materials.

While Bi3+ was originally proposed as a potential n-type dopant in lead halide perovskites, experiments and theory clearly demonstrate that it is a deep-level trap that gives rise to broad near-infrared emission. We synthesized a series of crystals of CsPbBr3 doped with Bi content ranging from 0.01 to 0.32 atomic percent, as quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES). The absorption edge shifts redder with Bi incorporation, but density function theory (DFT) calculations show that this increased absorption comes from the electronic structure of Bi as a deep-level trap, not from a shift in the CsPbBr3 band edge. Indeed, all doped crystals emit both narrow band-edge (2.37 eV) and broad defect-level (1.12 eV) photoluminescence at room temperature, consistent with our theoretical prediction. We also apply STEM-EDS to the most heavily doped samples to characterize the spatial uniformity of the Bi incorporation within the CsPbBr3 crystals. Our combined results demonstrate the power of current theoretical approaches to predict defect behavior in halide perovskites, which will be invaluable in guiding the development of these materials.

4:45 PM EN10.15.05
Photoluminescence Enhancement of Perovskite Quantum Dot@Polymer Nanocomposite via Silver Epoxy Paste Treatment for Time-And Environment-Dependent Optical Encryption
Jaeheok Ryu, Jiyoon Lee, Dongjun Kim and Jiwon Kim; Yonsei University, Korea (the Republic of)

While Bi3+ was originally proposed as a potential n-type dopant in lead halide perovskites, experiments and theory clearly demonstrate that it is a deep-level trap that gives rise to broad near-infrared emission. We synthesized a series of crystals of CsPbBr3 doped with Bi content ranging from 0.01 to 0.32 atomic percent, as quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES). The absorption edge shifts redder with Bi incorporation, but density function theory (DFT) calculations show that this increased absorption comes from the electronic structure of Bi as a deep-level trap, not from a shift in the CsPbBr3 band edge. Indeed, all doped crystals emit both narrow band-edge (2.37 eV) and broad defect-level (1.12 eV) photoluminescence at room temperature, consistent with our theoretical prediction. We also apply STEM-EDS to the most heavily doped samples to characterize the spatial uniformity of the Bi incorporation within the CsPbBr3 crystals. Our combined results demonstrate the power of current theoretical approaches to predict defect behavior in halide perovskites, which will be invaluable in guiding the development of these materials.
In an increasingly digital and interconnected world, advanced information encryption techniques became imperative for ensuring the confidentiality, integrity, and availability of data. The integration of perovskite quantum dots (QDs) with polymers has garnered considerable attention in the field of optical encryption for their eminent photoluminescence (PL) property and improved stability. Herein, we have designed a time- and environment-dependent optical encryption/decryption method based on the PL enhancement of CsPbBr₃ QDs/polydimethylsiloxane (PDMS) nanocomposite film using a conductive Ag epoxy paste. Ag epoxy paste treatment was conducted by a thermal treatment subsequent to applying the Ag epoxy paste on the surface of the nanocomposite film, followed by the removal of cured paste with ease. The Ag⁺ ions from the Ag epoxy paste diffuse into the PDMS matrix and passivate the surface defects of CsPbBr₃ QDs, resulting in enhanced PL properties (e.g., intensity, lifetime, PL quantum yield (PLQY)) of the nanocomposite film.

In order to enhance the image contrast for an optical encryption, surface defects have further been generated by ligand purification of CsPbBr₃ QDs during the synthesis of nanocomposite film. By controlling the treatment duration and external environment, Ag epoxy paste treatment was utilized as a time-dependent information encryption/decryption method via regulation of the PL intensity. Specifically, an encrypted information was initially concealed under daylight and disguised by a fake information under UV light, which was decrypted over time owing to the differences in the degradation rates of PQDs. Once the information had been confirmed by an intended receiver, the leakage of information was further avoided with a subsequent water immersion, in which the decrypted information permanently reverts to the initial fake information via PL intensity inversion between treated and untreated region. In this work, we propose novel applications of commercially available Ag epoxy paste as a method for surface defects passivation in PQDs embedded in polymer matrix and as a strategy for optical encryption/decryption, providing a high level of security with multiple encryption states and a straightforward decryption.

5:00 PM EN10.16.01
Beginner’s Guide to Visual Analysis of Perovskite and Organic Solar Cell Current Density-Voltage Characteristics Albert Theiss¹,², ¹Institute for Materials Electronics and Energy Technology, Germany; ²Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

The current density-voltage characteristic (JV) is a critical tool for understanding the behaviour of solar cells. In this poster, I will present an overview of the key aspects of JV analysis and introduce a user-friendly flowchart that facilitates the swift identification of the most probable limiting process in a solar cell, based mainly on the outcomes of light-intensity-dependent JV measurements. The flowchart was developed through extensive trial-and-error simulations and a rigorous review of the literature, with a specific focus on perovskite and organic solar cells. Moreover, the flowchart proposes supplementary experiments that can be conducted to obtain a more precise prediction of the primary performance losses. It therefore serves as an optimal starting point to analyse performance losses of solar cells.

5:00 PM EN10.16.04
Trap Density and Energy States in Organic-Inorganic Halide Perovskite Thin Films: A Study of Thickness Variations Using Drive Level Capacitance Profiling and Admittance Spectroscopy Jaegwan Sin¹, JaeKim², Gisung Kim³, Mijung Kim¹, Moonho Kim¹, Hyoung Kim² and Jung Yung Yang¹, Kunsan National University, Korea (the Republic of); ¹The Institute of Basic Science, Korea (the Republic of)

Recently, organic-inorganic halide perovskite (OHIP) materials have gained significant prominence in various applications, especially in renewable energy and semiconductor technology, such as photovoltaic and thin film transistor (TFT) devices. Thickness of the OHIP film is an important factor in determining device characteristics. For example, an OHIP thin film thickness of approximately 30 nm must be achieved in order to attain optimum on/off ratios and high mobility for TFT devices. Despite its critical importance, the relationship between halide perovskite film thickness and trap density has not been comprehensively explored. In this research, drive-level capacitance profiling (DLCP) and temperature derivative admittance spectroscopy (TAS) were used to investigate changes in trap energy and density depending on the thickness of the OHIP film. The DLCP and TAS methods were employed to explore the intricate relationship between OHIP film thickness and trap characteristics, providing insights into their impacts on charge transfer dynamics and overall stability. From the DLCP and TAS analysis, it was observed that as the OHIP film thickness decreases, the trap density rapidly increases from 10¹⁵/cm³ to 10¹⁷/cm³ at the 0.35 eV trap energy level, due to the increasing influence of the interface caused by the reduction in OHIP film thickness. The defect energy level of 0.35 eV appears as an iodine interstitial defect, and we were able to improve device performances by applying an interface passivation process to remove iodine interstitial defects. We believe that this study provides a detailed analysis of the complex relationship between OHIP film thickness and trap states and can provide key research directions for OHIP-based photovoltaic and semiconductor devices and provide guidance for device optimization.

5:00 PM EN10.16.05
Damage-Free Process of Metal Electrode Using Plasma-Assisted Vapor Deposition for Halide Perovskite Devices Gisung Kim¹,², Mijung Kim², Jaegwan Sin³, Hyoung Kim², Kang-il Lee¹, Yongsup Choi³ and Jung Yung Yang¹,²,³, Kunsan National University, Korea (the Republic of); ³Kunsan National University, Korea (the Republic of); ²The Institute of Basic Science, Korea (the Republic of)

In response to fossil fuel depletion and global warming, research and development of new and renewable energy are recognized as crucial tasks worldwide. Solar cells, which utilize unlimited solar energy to generate electricity in an environmentally friendly manner, are at the forefront of new renewable energy technologies. Solar cells, which utilize unlimited solar energy to generate electricity in an environmentally friendly manner, are at the forefront of new renewable energy technologies. Solar cells, which utilize unlimited solar energy to generate electricity in an environmentally friendly manner, are at the forefront of new renewable energy technologies. Solar cells, which utilize unlimited solar energy to generate electricity in an environmentally friendly manner, are at the forefront of new renewable energy technologies. Solar cells, which utilize unlimited solar energy to generate electricity in an environmentally friendly manner, are at the forefront of new renewable energy technologies. This unprecedented optoelectronic performance, perovskite-based detectors are poorly stable under operation, falling by far the market requirements. Various technological approaches have been proposed to overcome the instability problem caused by the migration of halide ions, which, while delivering appreciable incremental improvements, are still far from a market-proof solution. Here, we demonstrate that a zero-dimensional PEA₂ZnI₄ induces more robust surface passivation on 2D perovskite single crystal and stronger n–N isotype two-dimensional/zero-dimensional heterojunctions than its lead-based counterpart. The 0D/2D forms an exceptional gradually-organized multi-dimensional interface that yields up to 30% external quantum efficiency which 8 % higher than 2D perovskite device. Our device maintains 100 % initial efficiency after 1000 on-off cycles and after >70 hours under continuous illumination of 178.7 μg/s and an applied voltage of 10V. In addition, the unencapsulated device exhibited zero performance loss under normal measured and storage conditions (temperature: 25 °C, humidity: 20 to 60%) in 2 months. Our findings expand the material library for low-dimensional interface engineering and open an opportunity for the timely commercialization of perovskite x-ray detectors.

5:00 PM EN10.16.06
Controllable Synthesis of 0D/3D Perovskite Heterostructure for High-Performance and Stable X-Ray Detection Devices Thanh Hai Le, Los Alamos National Laboratory, United States

Despite the impressive optoelectronic performance, perovskite-based detectors are poorly stable under operation, failing by far the market requirements. Various technological approaches have been proposed to overcome the instability problem caused by the migration of halide ions, which, while delivering appreciable incremental improvements, are still far from a market-proof solution. Here, we demonstrate that a zero-dimensional PEA₂ZnI₄ induces more robust surface passivation on 2D perovskite single crystal and stronger n–N isotype two-dimensional/zero-dimensional heterojunctions than its lead-based counterpart. The 0D/2D forms an exceptional gradually-organized multi-dimensional interface that yields up to 30% external quantum efficiency which 8 % higher than 2D perovskite device. Our device maintains 100 % initial efficiency after 1000 on-off cycles and after >70 hours under continuous illumination of 178.7 μg/s and an applied voltage of 10V. In addition, the unencapsulated device exhibited zero performance loss under normal measured and storage conditions (temperature: 25 °C, humidity: 20 to 60%) in 2 months. Our findings expand the material library for low-dimensional interface engineering and open an opportunity for the timely commercialization of perovskite x-ray detectors.

5:00 PM EN10.16.07
Conductivity Analysis of a Polypyrrole/Carbon Nanotube Composite for use in Electrosyn Photovoltaics and Flexible Electronics Luke J. Suttey¹, Dennis J. Moritz², John Borkowski², Jessica M. Andrichio¹ and Jack L. Skinner¹, Montana Technological University, United States; ²Montana State University, United States
In recent years, conductive electrospun (ES) microfbers have gained traction for use in flexible electronics and perovskite photovoltaics. ES fbers are attractive for their large surface-area-to-volume ratio and relative strength. Conductivity in ES microfbers has been accomplished using conductive or semiconducting polymers. Alternatively, conductivity in polymer thin fms can be accomplished through addition of carbon nanotubes (CNTs) or graphene.

Previously, we have formed hybrid perovskite crystals enanced in ES fbers in situ that demonstrated improved stability in humid conditions. In other work, we used melt electrospinning to produce conductive graphene-doped polymer fbers. Additionally, we have utilized the previously established method of multiwalled CNT (MWCNT) dispersion by using combined hydroxyl-functionalized and unfunctionalized MWCNTs in polycaprolactone (PCL) matrix to fabricate a conductive PCL/MWCNT composite. Thin fms of the composite were measured using a four-point probe and demonstrated a maximum conductivity of 0.3765 S/cm. In the present work, the hydroxyl-functionalized and unfunctionalized MWCNTs will be replaced with hydroxyl-functionalized and unfunctionalized metallic single-wall carbon nanotubes (MSWNTs) to achieve larger conductivity values in the composite material in preparation for electrosprinning of a multi-layer solar cell structure.

Triaxial ES will be used to form the multi-layer solar cell structure described. In the design, a conductive PCL core will be coated with the previously established perovskite-polymer composite. The exterior layer of the solar cell fiber structure will consist of a polymeric electron transport layer (ETL). In this work, each layer of the device will be characterized. Conductivity of a PCL thin film doped with a mixture of functionalized and unfunctionalized MSWNTs will be evaluated for conductivity via a non-destructive four-point probe method. Conductivity characterization will be used to determine the percolation threshold and preferable ratios for the MSWNT-doped PCL composite used as the core of the functional fbers proposed. MSWNT dispersion in the composite as a function of sonication time will be characterized through crystallinity analysis via Raman spectroscopy and electron microscopy.

Presented work will include conductivity characterization of the PCL/MSWNT composite material and fabrication methods of a four-layer thin film photovoltaic system consisting of the conductive MSWNT/PCL composite, a polymer-encapsulated hybrid perovskite layer, a polymeric ETL, and a transparent conductor. This work will provide the foundational preliminary data for future fabrication of an ES perovskite solar cell. The design is achieved without a hole transport layer, which has previously been established as non-consequential to perovskite solar cell performance. After adequate conductivity is achieved, the conductive ES microfbers will be used as a central electrode in a concentric, triaxial ES photovoltaic cell.

5:00 PM EN10.16.09
High-Performance Photodetector and Angular-Dependent Random Lasing from Long-Chain Organic Diammonium Sandwiched 2D Hybrid Perovskite Non-Linear Optical Single Crystal Rajesh Kumar Ulaanathang1, Pradip Kumar Roy2, Raghavan Chinnambedu Murugesan3, Ambika Subramanian4, Chu-Yang Lin4, Chi-Te Liang5 and Raman Sankar1, 2, 3, 4, 5 Academia Sinica, Taiwan; 2National Taiwan University, Taiwan; 3Aston University, United Kingdom; 4Chang Yuan Christian University, Taiwan

3D organic-inorganic metal halide perovskites are excellent materials for optoelectronic applications due to their exceptional properties, solution processability, and cost-effectiveness. However, the lack of environmental stability highly restricts them from practical applications. Herein, a stable centimeter-long 2D hybrid perovskite (N-MPDA)[PbBr4] single crystal using divalent N1-methylpropane-1,3-diammonium (N-MPDA) cation as an organic spacer, is reported. The as-grown single crystal exhibits stable optoelectronic performance, low threshold random lasing, and multi-photon luminescence/multi-harmonic generation. A photodetector fabricated using (N-MPDA)[PbBr4] single crystal exhibits an excellent photoresponsivity (≈124 AW−1 at 405 nm) that is ≈4 orders of magnitude higher than that of monovalent organic spacer-assisted 2D perovskites, such as (BA)2PbBr4 and (PEA)2PbBr4, and large specific detectivity (≈1012 Jones). As an optical gain media, the (N-MPDA)[PbBr4] single crystal exhibits a low threshold random lasing (≈6.5 µJ cm−2) with angular dependent narrow linewidth (≈0.1 nm) and high-quality factor (Q = 2673). Based on these results, the outstanding optoelectronic merits of (N-MPDA)[PbBr4] single perovskite will offer a high-performance device and act as a dynamic material to construct stable future electronics and optoelectronic-based applications.

5:00 PM EN10.16.11

Following advancements to increase the efficiency of perovskite solar cells, the current emphasis is mainly on enhancing their operational stability. Various methods of encapsulation have been employed to safeguard perovskite solar cells from environmental factors and preserve their efficiency. Recent research studies have primarily focused on using organic/inorganic multilayers to create a more robust barrier against the degradation of perovskite solar cells. However, the commercial feasibility of employing inorganic materials might be limited due to their high-cost fabrication process and low flexibility. The encapsulation techniques using polymers stand out for their versatility in material selection and functionality, making them suitable for manufacturing flexible devices. Polymers efficiently act as encapsulants, preventing the infiltration of water and oxygen into the perovskite layer while also inhibiting the release of perovskite composition. One such polymer, parylene-C, offers cost-effective extrinsic protection against environmental harm, mainly humidity and oxygen, to uphold the performance and reliability of perovskite solar cells. In our study, we utilized a multilayer deposition of parylene-C with a high light and low water vapor transmission rate, uniformly applied across the surface of the perovskite solar cells. To assess the operational stability of these devices, we employed ISOS-D1 and D2 protocols including conditions such as ambient/ambient and 85/ambient, pertaining to temperature/relative humidity. The obtained results underscore the durability of parylene-C coated perovskite solar cells compared to their unencapsulated counterparts.

5:00 PM EN10.16.12
Novel 3D Cubic Topology in Hybrid Lead Halides with a Symmetric Aromatic Triammonium Exhibiting Water Stability Eugenia S. Vasileiadou1, Imra S. Tajuddin1, Michael C. De Siena1, Vladislav V. Kleopov1, Mikael Kepenekian2, George Volonakis3, Jacky Even2, Lukasz Wojtas3, Ioannis Spanopoulos1, Xiuxuan Zhou1, Abisher Iyek3, Julie L Fenton4, William Dichtel1 and Mercouri K. Kanatzidis1, 2, 3 Northwestern University, United States; 4Univ. Rennes, France; 5University of South Florida, United States; 6The Pennsylvania State University, United States

The limitations of three-dimensional (3D) perovskite hybrid metal halides [(Et4)2PbI6]3− one-dimensional (1D) chains embedded with (T-Et6)3+ cations, affording an overall 3D topology. The constituent [(Et4)2PbI6]9− chains include (T-Et6)3+ cations as an organic spacer. Herein, we report a new family of 3D could be used for polarized photodetectors and LEDs. The bands are highly dispersive along Pb-Br chains and nearly flat along other directions, leading to a factor of 100 in conductivity as calculated by Boltzmann transport. We find an indirect gap and a direct gap which is just slightly higher in energy. Our GW/Bethe-Salpeter equation calculations using BerkeleyGW show strong anisotropy in absorption, especially in the lowest exciton which has a binding energy of 0.83 eV [Smale Stroube, 2203378 (2023)]. We calculate excited-state forces based on these results and our vibrational calculations to find the coupling of excitons and phonons, from which we can predict exciton self-trapping and get insight into mechanisms of broadband emission.

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Towards Semi-Opaque Perovskite Solar Cells via Molecular Templates

Over the past decade, we have witnessed the emergence of metal halide perovskites as a most formidable building block for emergent solar cells with record-breaking performances. Recently, 2D/3D materials that combine these ABX₃ (3D) metal halide perovskites with their layered (2D) counterparts, have enabled the fabrication of photovoltaic devices that are both stable and highly efficient. [1] Yet, it is well-known that layered perovskites exhibit poor charge carrier transport in comparison with 3D perovskites. [2] To date, the underlying mechanisms behind the reported reduced mobilities remain elusive. In this work, we employ a combination of state-of-the-art ab initio approaches [3] and symmetry analysis to explore the electron-phonon coupling mechanisms in layered halide perovskites. We start from the three-dimensional perovskite CsPbBr₂ and model the cases of layered n = 1 (Cs₈PbBr₁₄) and n = 2 (Cs₉Pb₂Br₁₄). We show that the diminished charge carrier mobilities in layered systems primarily originate from differences in the carrier's lifetimes. We identify the vibrational modes contributing to charge carrier scattering and associate them with polar-phonon scattering mechanisms arising from long-range Fröhlich coupling and non-polar optical deformation potential scattering processes. Furthermore, we show that the charge carrier mobilities are not only reduced by the increased polar-phonon interactions but also by an abrupt increase in the electronic density of states near the band edges. Our findings uncover the electron-phonon coupling mechanisms that intrinsically limit the charge carrier transport of layered metal halide perovskites, which is critical for their application in any optoelectronic device, such as solar cells.

JE acknowledges the support of the MErnet project Plantastic.


Photon Management for Efficient and Stable Large-Area Perovskite Solar Cells via Luminescent Thin Films of Platinum(II) Complexes

Metal halide perovskites semi-transparent perovskite solar cells (ST-PSC) have drawn great interest for applications in building integrated photovoltaics (BIPV), such as solar windows. Conventionally, ST-PSC are realised by thinning the perovskite absorber layer to allow partial light transmission, while also replacing the opaque back electrode with one that is transparent. This approach has been shown to produce efficient and stable cells, with window-grade levels of transparency (>30%). However, their main drawback is the unavoidable perceived colour (typically red to yellow) due to the optical bandgap laying within the visible range, which lowers the colour-rendering index (CRI) and therefore impedes their application in BVP. A possible path to overcome this hurdle is by patterning the solar cell in a way that selected regions are entirely transmissive, while others remain fully absorbing. Such semi-opaque configurations can support greater efficiencies and color purity levels than ST-PSC. Towards this technological evolution, here, we explore a low-cost and efficient method for patterning metal-halide perovskites via stamping of a hydrophobic template on substrates. The facile approach is demonstrated to be scalable and suitable for both flexible and rigid substrates. It further removes the need for post-processing, thus minimizing potential lithographic steps, and the burden of the substrate. The use of such patterned perovskite solar cell configurations, highlighting the challenges and the major opportunities that such patterned films and this form of solar cell architecture present.

Integrated numbers of optical materials with different band gaps forms the basis of a multispectral technology. While step-by-step integrations are the prevailing manufacturing approach, realizations of complex patterns with increasing numbers of material units by high definition and reproducibility remain challenging, preventing the wide implications of the multiplexed platform. Here, we report optical lithography to spatially control the optical band gaps of semiconductor alloys by composition modulations with a single-shot exposure. Luminescent patterns with intrinsic emission wavelengths, spanning the entire visible-spectral range are designed to realize functional multispectral films. With programmed correlations between spatial and spectral information, we fabricate multivariate optical filters for dispersive optics-free spectroscopy with a high spectral resolution and wavelength-selective encoding patterns for encryptions with precise spectral programming. The fabrication is at room temperature, and compatible with various device platforms for monolithic integrations.

As a representative photon management strategy converting high-energy photons into low-energy ones, photon downshifting in photovoltaic applications can be realized by introducing strongly luminescent materials that are properly designed to have spectral overlap with the corresponding light absorbers. Especially for perovskite solar cells (PSCs), photon downshifting has been suggested as an effective way to overcome UV-related problems such as exciton loss, thermalization, and catalytic decomposition of the photoactive layers. However, it is still challenging to achieve thin-film photon downshifting layers (PDLs) with high photoluminescence quantum yields (PLQYs) and versatility for fabrication, considering upcoming high-performance and large-area PSCs. Herein, to enhance UV stability without any loss in photocurrent generation, a highly blue-emissive Pt(II) complex is developed for effective photon management in high-performance PSCs. Thin PDLs based on the Pt(II) complex are fabricated on glass substrates of PSCs using ultrasonic spray deposition, leading to significant improvement in PLQY and facile production of large-area PSCs with an active area of 25 cm². Owing to their long-range photon downshifting and associate them with polar-phonon scattering mechanisms arising from long-range Fröhlich coupling and non-polar optical deformation potential scattering processes. Furthermore, we show that the charge carrier mobilities are not only reduced by the increased polar-phonon interactions but also by an abrupt increase in the electronic density of states near the band edges. Our findings uncover the electron-phonon coupling mechanisms that intrinsically limit the charge carrier transport of layered metal halide perovskites, which is critical for their application in any optoelectronic device, such as solar cells.

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optoelectronic devices.

10:00 AM BREAK

SESSION EN10.19: Lead-Free, Lead-Reduced, Perovskite-Like Materials
Session Chairs: Sascha Feldmann and Raphael Moral
Friday Morning, April 26, 2024
Room 334, Level 3, Summit

10:30 AM EN10.19.01
Material and Device Stability of Lead-Tin Perovskite Solar Cells
Florence Rombach and Henry J. Snaith; University of Oxford, United Kingdom

Narrow bandgap perovskite solar cells based on mixed lead-tin perovskites tend to suffer from poor stability under operating conditions. This impedes the successful development of all-perovskite tandems. We explore the causes of this instability under extended periods of combined 65°C thermal and 1 sun illumination stressing, using a range of structural, optical, and electronic characterization techniques on lead-tin perovskite films, half-stacks and devices.

We show that the phase, absorbance, morphology and mobility of lead-tin perovskite films are stable on timescales that exceed those of device degradation, although we reveal an interesting pattern of phase segregation after stressing for much longer amounts of time. Additionally, we observe only a slight increase in background carrier density and a moderate decrease in charge carrier lifetime during the first few hundred hours of stressing. We simulate the impact of these properties on device performance using SCAPS, and argue that these changes can only partially account for the observed device degradation.

A close investigation of the EQE and J-V characteristics of devices reveals the formation of a charge extraction barrier in aged devices. We find that the impact of this barrier is hugely decreased in very fast J-V scans, suggesting that mobile ions contribute significantly to device degradation. We quantify the increasing impact of mobile ions on device performance during aging, and furthermore reveal that the extent of this impact is strongly related to the hole transport layer used in devices.

Ultimately, we identify a rapidly worsening impact of mobile ions during aging as the major cause of the observed device performance degradation. The segregation of a non-perovskite CsSnI3 degradation phase and an increasing defect density are also expected to limit the stability of lead-tin perovskite solar cells over longer timescales. Finally, we propose solutions related to both bulk perovskite composition and device architecture to overcome these challenges.

10:45 AM EN10.19.02
Highly Efficient and Stable Thermal Evaporated Lead-Tin Perovskites
Heeun Jin and Henry J. Snaith; University of Oxford, United Kingdom

Multi-junction tandem solar cells, utilizing complementary bandgaps, offer the potential to surpass the detailed balance limit for single-junction perovskite solar cells (PSCs). Through the tunability of perovskite bandgaps and recent advancements in mixed lead-tin (Pb:Sn) narrow bandgap PSCs, it is now possible to create highly efficient multi-junction solar cells solely using perovskites, achieving certified PCEs of up to 26.4% in all-perovskite tandem solar cells.

However, there are two main challenges when using Pb:Sn perovskites. Firstly, methylammonium (MA) has been traditionally used in the most efficient Pb:Sn PSCs, but its thermal and chemical stability concerns prompt the search for MA-free alternatives. Second, conventional solution processing methods remain prevalent in lab-scale Pb:Sn PSCs fabrication. There were many attempts to thermal evaporate Pb:Sn as this method presents significant advantages, including high-quality thin film fabrication, precise thickness control, elimination of toxic solvents, large-scale compatibility, and reproducibility. Vacuum evaporation can also be applied to the fabrication of all-perovskite tandem solar cells without damaging underlying layers. Although vacuum deposition has proven successful in achieving high efficiency and large-area PSCs for Pb-based perovskites, its application to Pb:Sn perovskites is less explored. Ball et al. and Igal-Munoz et al. are among the few to report Pb:Sn PSCs using vacuum evaporation.

In this work, we demonstrate that through careful control of the environment and some fine-tuning, it is possible to deposit Pb:Sn perovskite films of high quality through thermal evaporation. We compare devices made using this method to those made from similar state-of-the-art solution processed methods. Our work demonstrates that it is possible to approach the performance of solution processed devices within a workable processing window using vacuum evaporation. Our champion devices reach PCEs of 17%, surpassing previously set records of 14% for thermally coevaporated Pb:Sn devices. This was done without requiring additional passivation or bulk additive, which are used in the previous reports.

11:00 AM EN10.19.03
Local Background Hole Density Drives Non-Radiative Recombination in Tin Halide Perovskites
Robert J. Westbrook1, Margherita Taddéi1, Rajiv Girdharagopal1, Meihuizi Jiang2, Shaun Gallagher1, Kathryn Guy1,3, Aaron Warga1, Saif Haque2 and David S. Ginger1,3; 1University of Washington, United States; 2Imperial College London, United Kingdom; 3Pacific Northwest National Laboratory, United States

Tin halide perovskites, with the general formula ABX3 [A = Formamidinium (FA), B = Sn, X = Br, I], offer a narrower bandgap (~1.3 eV) than their lead counterparts, making them suitable candidates for the light-absorbing semiconductor in single-junction photovoltaic devices. Moreover, this attribute makes tin halide perovskites integral to all-perovskite tandems, with the best-performing cells incorporating a 50-50 Sn-Pb composition in the low bandgap component. Nevertheless, record-breaking pure-Sn devices still exhibit severe losses in both open-circuit voltage (VOC) and short-circuit current (JSC), keeping power conversion efficiencies well below theoretical limits.

Non-radiative voltage loss is directly linked to decreases in the photoluminescence quantum yield (PLQY), and thus the prevalence of non-radiative recombination.[1] This picture is complicated in Sn perovskites given that the presence of Sn4+ impurities in the precursor solution leads to both the introduction of background hole dopants (serving to increase radiative recombination rates) and an increasing defect density with the introduction of background hole dopants (serving to decrease radiative recombination rates).[2]

We observe the use of pseudo-first order photoluminescence (PL) decay kinetics in Sn perovskite films to establish a method for characterizing the hole dopant level and non-radiative voltage loss.

In this work, we demonstrate that through careful control of the environment and some fine-tuning, it is possible to deposit Pb:Sn perovskite films of high quality through thermal evaporation. We compare devices made using this method to those made from similar state-of-the-art solution processed methods. Our work demonstrates that it is possible to approach the performance of solution processed devices within a workable processing window using vacuum evaporation. Our champion devices reach PCEs of 17%, surpassing previously set records of 14% for thermally coevaporated Pb:Sn devices. This was done without requiring additional passivation or bulk additive, which are used in the previous reports.

11:15 AM EN10.19.04
Quantifying Spatiotemporal Signal in Photothermal Heterodyne Imaging of Metal-Halide Perovskites
Lauren Cisneros and Matthew Crane; Colorado School of Mines, United States

Resonant pump-probe spectroscopies like photothermal heterodyne imaging have emerged as promising approaches to selectively measure the distribution of chemical species with high spatial and temporal resolution. In photothermal heterodyne imaging, a pump resonant with an electronic or vibrational transition of the species of interest heats the sample, and a higher energy probe measures differential reflectance (or transmittance) due to heating. For materials research, pump-probe photothermal spectroscopies thus offer an attractive and unique tool to evaluate the spatial distribution of “dark” species including, e.g. defects or molecules without significant radiative transitions. However, the conditions under which signal is optimized in thin films, including metal-halide perovskites, is not well understood, and approximations are frequently used to describe differential reflectance or transmittance signal. Here, we develop a multiphysics simulation implemented with a finite-difference method to quantify transient photothermal heating and the resulting differential reflectance signal. Using this approach, we investigate the conditions that optimize spatiotemporal resolution in alloyed methylammonium and formamidinium metal-halide perovskite thin films and evaluate these simulations.
Halide Perovskites based Indoor Photovoltaics: Role of Composition Tuning and Interfacial Layers

1:30 PM

Javel L. Li, Yang Wang, Sanatana Saha, Zhihengyu Chen, Jason Misleh, Karen Chapman, Jeffrey Reimer, Marina R. Fibl and Hemamala Karunadasa; Stanford University, United States; University of California, Berkeley, United States; University of Oxford, United Kingdom; Stony Brook University, The State University of New York, United States

ABX₃ [A = Cs, FA, MA; B = Pb, Sn, Ge; X = Cl, Br, I] metal halide perovskites have dominated the research landscape since the first demonstration of MAPbI₃ as an absorber layer for dye-sensitized solar cells. Since then, developments in this space have realized perovskites for widespread applications in LEDs, photovoltaics, sensing, radiation detection, lasing, and more. The ubiquity of perovskites today is partly due to facile synthesis via multiple routes, their high defect concentrations, and highly tunable composition whereby properties can be defined. Of late, low-dimensional perovskite-based materials, alloys, or high entropy systems (with multiple elements at the same site) have brought renewed interest.

Wideband deployment of ABX₃ perovskites has been slowed by the inclusion of the toxic heavy metal Pb, and material instability to heat and moisture. An attractive method for promoting the formation of the desired phase(s) while limiting degradation involves site-mixing. A- and X-site mixing is currently applied to materials in state-of-the-art compositions for the current best-performing prototype solar cells. Only limited examples showing mixing at the B-site have appeared and most involve Pb-Sn derivatives that only reduce Pb content in the material, without completely eliminating it. Sn-Ge mixed perovskites have received some attention, and exhibit improved stability and solar cell performance than previous Ge-based perovskites. A detailed understanding of the phenomena leading to such improvements using a suite of bulk spectroscopic and diffraction methods can provide insight into the mechanisms at play. Specifically, NMR spectroscopy offers atomic-level precision of the local chemical environment and has been used with much success for studying challenging and interesting perovskite materials. Together, this toolkit can provide the means for rational design of new materials for advanced solar absorbers.

Our work explores new systems of mixed B-site mixed Sn-Pb-Ge perovskites.

References

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Among lead-free alternatives, tin perovskite solar cells (Sn-PSCs) have the highest PCE (>14%) due to their narrow band gap (1.4 eV), low exciton binding energy, and high carrier mobility. Despite the vigorous efforts to improve the efficiency of Sn-PSCs, thermal stability is still a critical issue that has not been solved. Inverse devices using poly(3,4-ethylenedioxythiophene) polystyrene sulphonic acid (PEDOT:PSS) as the hole transport layer (HTL) are commonly used for highly efficient Sn-PSCs. However, the PEDOT:PSS layer has hygroscopic and acidic properties that reduce the stability of the solar cell. Therefore, Sn-PSCs without PEDOT:PSS is an important research item in terms of stability. In addition, the diffusion of iodine ions within the tin perovskite layer reduces device stability. Therefore, preventing iodine ion diffusion is also important to improve the stability of Sn-PSCs.

Previous studies have reported that ALD-SnOx (x = 1.7-1.8) can act as HTLs in tin-lead perovskite solar cells. Furthermore, our previous study demonstrated that SnOx (x = 1.7-1.8), obtained by plasma oxidation of metallic Sn, can serve as HTLS in Sn-PVK-PV with PCEs exceeding 14%. We have also found that tin oxide nanoparticle layers, which are commonly used as electron transport layers (ETLs) in Pb-PSCs, can operate as HTLs in Sn-PSCs. These SnOx layers are partially composed of Sn2+ rather than Sn3+ and exhibit bipolar carrier transport. Sn-PSCs with tin oxide nanoparticle HTLs exhibit higher stability than PEDOT:PSS HTL devices. Therefore, tin oxide HTLS may be effective to enhance the stability of Sn-PSCs. ALD-SnOx in the top layer has been reported to improve stability in Pb-PSCs by preventing the diffusion of iodine ions.

In this report, we first replaced HTL with ALD-SnOx to improve the thermal stability of Sn-PSCs. In addition, ALD-SnOx was also introduced in the top layer. In the presentation, the mechanism of thermal stability improvement by ALD-SnOx will be discussed.

2:15 PM EN10.20.03
Synergistic Effect of Charge-Modulated Molecular Passivation in MA/Br-Free Perovskite Solar Cells
dhruba B. Khadka, Yasuhiro Shirai, Masatoshi Yanagida, Hitoshi Ota and Kenjiro Miyan; National Institute for Materials Science (NIMS), Japan

Molecular passivation represents a promising avenue for enhancing both the efficiency and operational stability of perovskite solar cells. This work reports on the effect of diammonium iodide functional molecules featuring aryl or alkyl cores onto 3D-perovskite surfaces. Our findings reveal the remarkable efficacy of piperazine dihydroiodide, characterized by an alkyl core and electron-rich -NH terminal, in mitigating surface and bulk defects while modifying surface chemistry and improving carrier extraction efficiency. This results in an impressive efficiency of 23.17% (1 cm² area) with superior long-term stability. Device analysis substantiates that these robust bonding interactions reduce defect densities in the perovskite film and suppress ion migration. This report will shed light on the synergetic effect of bifunctional molecules in defect mitigation, opening avenues for design strategies centered on bonding-regulated molecular passivation to enhance solar cell performance and stability.

2:30 PM BREAK

SESSION EN10.A21: Composition Analysis and Degradation
Session Chairs: Sascha Feldmann and Letfy Krishnan Jagadamma
Friday Afternoon, April 26, 2024
Room 334, Level 3, Summit

3:00 PM EN10.21.01
Taming Phase Transitions in Two-Dimensional Hybrid Perovskites
Conor G. Bischak; The University of Utah, United States

Metal halide perovskites often exhibit phase transitions that occur near room temperature. Typically, efforts have focused on suppressing phase transitions for optimal device stability. Yet, strategies to control these phase transitions could lead to new applications in memory storage, thermal energy storage, and switchable optoelectronic devices. We demonstrate that we can control the temperature of the order-to-disorder phase transition of two-dimensional Ruddlesden Popper perovskites through alkyl cation alloying. We also connect structural transformations to changes in photophysical properties and show that changes in photoluminescence wavelength and intensity are tied to octahedral distortions in the perovskite crystal lattice. Last, using photoluminescence imaging, we image the dynamics of the phase transition and show that the nature of these dynamics depends on the alkyl cation length.

3:15 PM DISCUSSION TIME

3:30 PM EN10.21.03
Potential of Perovskite Doping Unlocked: Shaping The Future of Energy and Electronics
Zuzanna Molenda1, Dario Bassani2 and Lionel Hirsch1; 1IMS-Bordeaux, France; 2ISM, France

Doping of metal halide perovskites (MHPs) is the next, essential step towards the implementation of perovskite semiconductor technology for electronic devices. Nonetheless, only a limited number of successful doping instances have been documented, and it is frequently mistaken for additives, grain passivation, or surface functionalization, none of which affect the semiconductor's charge carrier density. Due to the ionic character of the perovskite crystal, the introduction of heterovalent ions is accompanied by the counter ions that balance out the potential doping effect. Here we present a use of homovalent yet metastable ions, in particular Sm3+, to substitute Pb2+ in MAPbI3 (MA = methylammonium). Sm2+ ions spontaneously oxidize to Sm3+, once incorporated into the crystal lattice and each of them releases one electron to the conduction band. The oxidation of samarium ions is confirmed by the analysis of the Sm 3d core level in the X-ray photoelectron spectrum (XPS). Residual content of the oxidized form of Sm3+ present in the doping solution allows to observe a slight shift of the Sn 3d peak towards higher binding energy, suggesting the environment change of the Sm3+ ion, once introduced inside the perovskite film. Together with the shift of the XRD pattern upon doping, this supports the hypothesis that the dopant ion is incorporated and stabilized in the crystal lattice. At the same time, the crystal structure of the doped perovskite layer is conserved and no phase separation is observed from the XRD patterns. Ultraviolet photoelectron spectroscopy (UPS) shows a shift of the Fermi level (E_F) by around 0.5 eV towards the conduction band, proving the doping to be n-type. The increase of the free electron density in the conduction band is the direct reason for the conductivity increase for the doped films by 3 orders of magnitude. Using the Mott-Schottky method, the ionized charge carrier density is estimated to be 1017 cm⁻³ for the sample showing the highest conductivity increase, which suggests the ionized dopant concentration in the doped perovskite film to be around 0.01% (Pb density in MAPbI3 = 2017 cm⁻³). The discrepancy between this result and the doping concentration stemming from the XPS measurement, which is calculated to be around 20%, leads to two possible explanations. Either the majority of the Sm3+ introduced to the perovskite polycrystalline film resides at grain boundaries and therefore does not act as a dopant or the dopant is only partially oxidized in normal conditions, exhibiting the freeze-out effect. The dopant activation energy (the energy necessary to oxidize all the Sn2+ ions to Sn3+) of around 350 meV seems to support the latter hypothesis and is in agreement with the energy between the E_F and conduction energy (E_C). The presented method allows to reach the highest to-date conductivity increase for the n-type and may become a protocol for the efficient n-type doping of MHPs. To illustrate one of its applications, we fabricated perovskite solar cells (PSC) with poly(3-tinyl aniline) (PTAA) as a hole transporting layer (HTL) (p-side) and Sn-doped MAPbI3 (n-side), without the electron transporting layer (ETL). Additionally, we used gold as an electron collecting electrode (WFE = 5.22 eV). The strain-induced ohmic contact between highly doped perovskite and Au allows to minimize the series resistance at this interface and an efficient electron collection. This shows the potential of flexible electrode selection for the doped PSC. Therefore, the ETL-free n-doped PSC retains the same PCE as the reference sample (with PCBM as an ETL), in spite of the simplified architecture that decreases the fabrication cost and the number of interfaces.

3:45 PM EN10.21.04
Spatially Resolved Parameter Mapping and Degradation of Perovskite Solar Cells
Akash Dasgupta and Henry J. Snaith; University of Oxford, United Kingdom

Perovskite solar cells have made significant strides towards maturity; however, two major challenges persist: stability and up-scalability. Achieving uniform deposition methods is crucial for ensuring the suitability of devices for large-scale production. Furthermore, a comprehensive understanding of degradation mechanisms is essential for mitigating these effects and improving stability. In this study, we introduce a novel approach that integrates photoluminescence imaging with drift diffusion simulations which incorporate the effects of mobile ions. By employing machine learning techniques, we generate inferred maps of various material parameters. These maps are then tracked throughout the aging process to analyse their spatially resolved temporal evolution during degradation, enabling us to distinguish between bulk. Our findings reveal that macroscopic-scale spatial defects propagate outward, ultimately resulting in device degradation across the entire area. By distinguishing between bulk and surface degradation, our technique provides an additional dimension of insight into the heterogeneous nature of degradation in perovskite solar cells. This enables meaningful comparisons and enhanced comprehension of different treatments and processes. We expect analysis using our approach to enable the field to target sources of inhomogeneity and degradation more precisely, paving the way towards commercialisation.

4:00 PM EN10.21.05
In-Situ Spatially-Resolved Analysis of Degradation in Perovskite Solar Cells
Dana Kern, Jack Schall, Goutam Paul, Steve Johnston, Andrew Norman, Harvey Guthrey, Nikita S. Dutta, Chun-Sheng Jiang and Andrew Glaws; National Renewable Energy Laboratory, United States
Long-term durability of metal halide perovskite solar cells (PSCs) can be impacted by both the intrinsic nature of the as-designed device stack as well as unintentional local nonuniformities. Here, we present methods for spatially-resolved in-situ degradation analysis during perovskite stress testing. We use repeated bias/rest cycles from timescales of minutes up to 100 hours to separately assess metastability in comparison to irreversible degradation. We visualize device evolution in-situ under light or electrical bias, either in surface view using electro-optical imaging or in cross-section using kelvin probe force microscopy. We further demonstrate multi-scale investigation of defects, from rapid electro-optical screening of the full device area down to nanoscale microscopic characterization to reveal the underlying chemical or structural nature of defects. Our results inform methods to screen for defects in PSCs, as well as further development of accelerated stress testing and degradation analysis which will become essential for perovskite devices to improve their durability and enter the commercial market.

**4:15 PM DISCUSSION TIME**

**FACILE AND COMPOSITION-FLEXIBLE ALTERNATE ROUTE TO PEROVSKITES**

*EN10.21.07*

Dean G. Grier, Tapan K. Jena, Yuvaraj Patil and Philip Boudjouk; North Dakota State University, United States

Halide perovskites have emerged as promising candidates for a variety of applications, including solar cells and light emitting diodes. In the field of photovoltaics, power conversion efficiencies have risen rapidly and competitively over the past several years, although environmental stability remains a focus of study. Herein we report a method for synthesizing a variety of phase pure perovskites through a simple solution method followed by mild thermolysis. Our group has previously successfully demonstrated synthesis of metal chalco|0

**SYMPOSIUM EN11**

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**References**

10. Yusheng Li and Q. Shen et al., submitted.
High Stability of Sn-Based Perovskites by Adding Reducing Agents for Perovskite Solar Cells

Teresa S. Ripolles; University of Valencia, Spain

Tin-based (Sn) halide perovskites have become one of the most prospective photovoltaic materials due to their optoelectronic properties, high photoconversion efficiency and relatively low toxicity.[1][2] Nevertheless, the rapid crystallization of tin-based perovskite and the easy oxidation of Sn²⁻ to Sn⁴⁺ under ambient conditions increases the interest of the scientific community.

[3] To avoid these undesirable processes, we will address by two different methods, for instance, (i) organic cations engineering in Sn-based halide perovskite microcrystals, and (ii) adding reducing agents in three-dimensional perovskite thin films.

On the one hand, Sn-based halide perovskite microcrystals have been synthesized by hot-injection method to control the dimensionality by changing the concentration of reactants. The physical properties suggest high photoluminescence quantum yield (PLQY) of 75% and 25% for chloride-based and bromide-based, respectively, and almost negligible for 2D Sn-based microcrystals.

On the other hand, increasing the perovskite dimensionality, we suggest adding a variety of additives that act as reducing agents with different nature in thin film. The addition of these novel materials into the FASnI₃ (FA is formamidinium) perovskite solution controlled the oxidation reaction and improved the surface morphology. An inverted perovskite solar cell was prepared and characterized. Due to the Sn⁴⁺ concentration is reduced in the Sn-based perovskite layer, the power conversion efficiency in a solar cell and the cell stability under ambient conditions are improved notably in comparison with the pure FASnI₃.

References

8:45 AM EN10/EN11.03

Investigating The Influence of Multivalent Transition Metal Doping on Copper Antimony Sulphide Thin Films for Enhanced Photovoltaic and Electrochemical Properties

Kimberly A. Weston and Richard A. Taylor; The University of The West Indies, Trinidad and Tobago

Undoped non-stoichiometric semiconductor copper antimony sulphide (CAS) thin films were deposited at 500, 550 and 600 °C on glass substrates by aerosol-assisted chemical vapour deposition (AADC) at different flow rates and copper concentrations using metal diethyldithiocarbamate precursors. For thin films deposited at an optimal flow rate, data from powder X-ray diffraction (p-XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) suggest a correlation of the composition of the non-stoichiometric sulphur-deficient tetrahedrite phase (cubic structure) microcrystalline CAS (Cu₄Sb₈S₁₆) thin films with particle sizes ranging from 0.1 to 4 μm for undoped thin films, visible optical absorption and cyclic voltammograms (CV) show a band gap of ~2.1 eV is likely associated with compositional variations involving intrinsic lattice defects, including shallow electronic states such as copper interstitials (Cu₄Sb₈S₁₆) and vacancies of sulphur (Vₐ₈S₈) as deep-lying acceptors. Additionally, upper first row transition metal divertal (M²⁺) ions such as Mn²⁺, Co²⁺, Ni²⁺ and Zn²⁺ were incorporated into tetrahedrite phase CAS (ICAS) thin films at optimal temperature, 550 °C and flow rate, 150 scem. M²⁺ ions incorporated (MₓCAS) exhibit tunable composition-driven electronic structure for small M²⁺ content influencing narrower bandgaps between 1.7 and 1.9 eV. The Raman data suggest that the phase purity is affected by small fractions of the famatinite (tetragonal) phase. Additionally, ICAS and MₓCAS thin films were deposited on conducting substrates (ITO/FTO) and were found to be efficient as a novel catalyst for the hydrogen and oxygen evolution reactions in water splitting. Overall, the thin films display broad emission of fast dual radiative recombinations, and an additional recombination pathway exhibited for MₓCAS associated with.divalent ion-related point defects. These results show the utility of AADC in tuning compositional and optical and electrical properties of undoped ICAS and MₓCAS thin films for possible applications in photovoltaics and electrochemical conversion.

9:00 AM EN10/EN11.04

Lead-free Perovskites: Toward an Opto-Electronics based on Abundant Elements and Low Temperature Synthesis

Iliem Elgarsoufi,1,2 Hind Kadri,1 Akram Alhussein1,2, Rachid Ben Hassen1 and Gilles Lerondel1; 1Université de Technologie de Troyes, France; 2University of Tunis El Manar, Tunisia

The depletion of natural resources today necessitates a reevaluation of technological development, considering both material abundance and energy-efficient processes while maintaining device efficiency. This research presents a comprehensive investigation into the design and synthesis of advanced thin films materials for improved optoelectronic applications. By exploring the unique properties of lead-free perovskites oxides, we aimed at engineering materials with enhanced electrical conductivity, stability, and optical properties.

For this work, we chose two types of perovskites oxides: SrSnO₃ and LaVO₃. The reason behind this choice is the combination of abundancy, non-toxicity, and low-cost production of these unique properties of lead-free perovskites oxides, we aimed at engineering materials with enhanced electrical conductivity, stability, and optical properties.

In this study, we will detail the tailored synthesis process with sol-gel method using different percentages of doping. We discuss the systematic characterization of the resulting thin films materials along with the tunable bandgap, the stability and durability.

Using scanning electron microscopy, the film thickness was found to be around 300μm with a uniform and homogeneous surface, X-ray diffraction confirmed the perovskite phase with an intense peak at 32°, and optical measurements proved the transparency of 80% in the visible range with an absorption in the UV range around 300nm. The results reveal a clear correlation between the synthesis parameters and the optoelectronic performance of the materials, demonstrating the feasibility of optimizing these materials characteristics through precise control of the synthesis process.

The objective of this work is the realization of photovoltaic components (pn junction) based on doped perovskite oxide semiconductors (SrSnO₃; Sb(Sr)SnO₃; Al on ITO and LaVO₃) synthesized using an ecofriendly environmental synthesis (sol-gel process). Application as light absorbers or barrier layers in highly efficient solar cells are foreseen. Other applications are also possible (e.g., LiD).

This work contributes to the ongoing efforts to develop sustainable and efficient materials for optoelectronic devices and underscores the pivotal role of advanced material synthesis techniques in achieving this goal.

9:05 AM *EN10/EN11.05

Computational Workflows for an Accelerated Design of Novel Materials and Interfaces

Ivano Elijio Castelli; Technical University of Denmark, Denmark

The development of automated computational tools is required to accelerate the discovery of new functional materials, to speed up the transition to a sustainable future. Here, I address this topic by designing new electrodes with controlled interfaces for different applications which accelerate the transition to a sustainable future. These workflows are implemented in the framework of Density Functional Theory (DFT), using MyQueue and the Atomic Simulation Environment (ASE). In the first part of my talk, starting from our recent work on a fully autonomous workflow, which identifies materials to be used as intercalation electrodes in batteries, based on thermodynamic and kinetic descriptors like adsorption energies and diffusion barriers,1 I will describe a new modular approach to estimate electronic and ionic mobility in energy materials useful for a variety of applications, from batteries and fuel cells and solar energy conversion and storage. A substantial acceleration for the calculations of the kinetic properties has been obtained by a recent implementation of the Nudged Elastic Bands (NEB) method, which takes into consideration the symmetries of the system to reduce the number of images to calculate. Moreover, we have established a surrogate model to identify the transition states, which can further reduce the computational cost to at least one order of magnitude.2,3 In the second part of my talk, I discuss how engineering the interface can positively impact surface properties for electrochemical water splitting: I apply strain engineering and external stimuli to switch material’s polarization to decrease the reaction overpotential in oxynitride materials for the oxygen evolution reaction.4,5,6 In the last part of my talk, I will describe my vision for autonomous computational workflows, namely the creation of workflows for interface and their integration with experimental workflows.

References

Emerging Cu-Based Phosphides as Contacts and Absorbers for Solar Energy Conversion

Sage Bauer, Obadiah Reid, David Fenning, Andriy Zakutayev, Jifeng Liu, Kirill Kovnir and Geoffroy Hautier
National Renewable Energy Laboratory, United States; University of California, San Diego, United States; Dartmouth College, United States; Iowa State University of Science and Technology, United States

Most photovoltaic absorber materials development is done on materials with known or slightly modified structural prototypes; for example, kesterite, chalcopyrite, and zincblende are all derived from mutations to the diamond crystal structure. It is rare and sometimes transformative—such as in halide perovskites—when new structural classes of absorber materials are discovered. The Cu$_M$P$_2$ ($M = \text{alkaline earth cation such as Ba, Ca, Sr and } Zn, \text{ Cd}$) compounds have previously been described as semiconducting zintl phases and are structurally distinct to widely studied PV materials. However, these have attracted recent interest from theory as materials with solar-spectrum matched band gaps and tolerance to intrinsic point defects. BaCd$_2$P$_2$ is particularly compelling with a direct 1.45 eV band gap and mostly comprising inexpensive elements already used in solar absorber applications, thus having high-grade feedstocks already available. Here, we report on the synthesis and properties of BaCd$_2$P$_2$ and related AM$_2$P$_2$ materials. BarCd$_2$P$_2$ can be synthesized in powder form from elemental precursors using conventional solid-state reaction methods. The material forms in a $P\overline{3}m1$ crystal structure (CaAl$_2$S$_2$ prototype) and is stable in open air heating up to 300 °C as well as in acids, bases, and at even higher temperatures in inert environments. BaCd$_2$P$_2$ powder shows strong band-to-band photoluminescence that is stable at elevated temperature and time-resolved microwave conductivity shows long photocexcited carrier lifetimes of around 30 ns, which is already longer than observed in some much more mature absorber technologies. Since the direct band gap AM$_2$P$_2$ materials will be most compelling as thin film absorbers, we also discuss several ongoing efforts to realize these compounds in thin film format.

2:00 PM *EN11.01.02
Emerging Cu-Based Phosphides as Contacts and Absorbers for Solar Energy Conversion
Andrea Crovetto,1,2,3 Andriy Zakutayev,1 National Renewable Energy Laboratory, United States; Technical University of Denmark, Denmark; Helmholtz-Zentrum Berlin, Germany

Many new contact and absorber materials have been studied in the past decade for solar energy conversion applications. For example, research into emerging chalcogenides expanded from zincblende-derived CdTe, CuInSe$_2$ and Cu$_2$ZnSnS$_4$ to include non-tetrahedrally bonded compounds like 1D-bonded Sb$_2$S$_3$, layered CuSbS$_2$ chalcostybites, or BaZr$_2$S$_3$ perovskites.

There are much fewer known phosphorus solar materials, besides II-IV-P$_2$ derivatives of GaP (e.g. ZnSnP$_2$, ZnS$_2$P$_2$) and their binary constituents (e.g. Zn$_2$P$_2$) studied as absorbers, or wide band gap bipolar dopable BP that has been considered for contact applications. Nevertheless, the reported semiconductor properties and initial device performances of phosphide materials are quite promising and deserve further research attention.

This presentation will highlight a few emerging phosphide materials based on Cu, as potential transparent contact and light absorber layers in solar energy conversion devices. The first example is experimental demonstration of high electrical conductivity and measurement optical transparency in theoretically predicted CaCuP$_2$ sputtered thin film material [1]. The second example is two-step synthesis and semiconductor property measurements of Cu$_M$P$_2$ — one of the first known phosphorus-rich semiconductors in thin film form [2].

General synthesis and characterization challenges associated with doing experiments on the phosphide class of materials will also be discussed.

We present some recent progress that has been made on the application of an optical function parameterization of polycrystalline MgZn1–xO (MZO) thin films on the bandgap that has been used for the metrology of CdTe-based solar cell structures that incorporate MZO thin films as high reactivity transparent (HRT) layers. The acquired parametric expressions are applied to facilitate the mapping of a polycrystalline ellipsometry (M-SE) of device structures consisting of glass/SnO2:MZO. M-SE is shown to provide maps in the MZO effective thickness and bandgap within confidence limits of ± 1 nm and ± 0.003 eV, respectively. As a second application of this parameterization, performed on an as-deposited glass/SnO2:MZO/CdTe device structure, has been made using through-the-glass polycrystalline ellipsometry (TG-SE). Such an analysis is also shown to provide the MZO effective thickness and bandgap. The outcome of the TG-SE analysis for this device structure enables simulations of the external quantum efficiency (EQE) spectrum of the resulting solar cell assuming different recombination losses within the individual layers of the structure. A comparison of these simulations with the experimental EQE spectrum reveals improved current collection from the front of the device incorporating an MZO HRT layer.

**References**


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**Photoluminescence of BaCd2P2 as a New Defect-Insensitive Solar Material**

Yiting Xiao, Yang Tian and Jun Zhu; University of Arkansas, Fayetteville, United States

Chalcogenide perovskites are emerging semiconductor materials with attractive optoelectronic properties. These materials have been shown computationally and experimentally to possess high absorption coefficient, tunable bandgap, and high dielectric constant. In contrast to their lead halide counterparts, they are known to be stable, and earth-abundant with nontoxic constituents.

Chalcogenide perovskites are emerging semiconductor materials with attractive optoelectronic properties. These materials have been shown computationally and experimentally to possess high absorption coefficient, tunable bandgap, and high dielectric constant. In contrast to their lead halide counterparts, they are known to be stable, and earth-abundant with nontoxic constituents.

Using Chlorotetracycline (CTC) as a model antibiotic pollutant, we investigate the photothermal properties of SnFe2O4 in various catalytic modes. Thermal catalytic experiments at different temperatures, photocatalytic experiments with various light wavelengths, and photothermal catalytic experiments under simulated solar light were conducted to evaluate the photocatalytic and thermal excitation properties.

Our findings reveal that SnFe2O4 efficiently utilizes different spectral regions of sunlight: photothermally activated under UV and visible light and mainly thermally excited under near-infrared light. Furthermore, CTC degradation experiments have shown that SnFe2O4 can degrade CTC effectively under real outdoor sunlight. Even under cloudy weather conditions, SnFe2O4 retains catalytic activity if the ambient temperature can be kept at higher than 35°C. Therefore, this narrow-bandgap catalyst possesses the remarkable capability to enhance solar energy utilization significantly. Thus, it is believed to promise the design of a full solar spectrum photocatalyst for wastewater treatment.

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**Efficient Photocatalytic Degradation of Pharmaceutical Residues with Ni-TiO2/gC3N4 Heterojunction**

Yang Tian and Jun Zhu; University of Arkansas, Fayetteville, United States

Efficient photocatalytic degradation of pharmaceutical residues with Ni-TiO2/gC3N4 heterojunction has been demonstrated as a promising approach for wastewater treatment. The photocatalytic activity of Ni-TiO2/gC3N4 heterojunction was evaluated using several pharmaceutical compounds, including sodium salicylate and chloramphenicol, as model pollutants.

The photocatalytic degradation of sodium salicylate was carried out using Ni-TiO2/gC3N4 as a photocatalyst. The results show that the degradation efficiency of sodium salicylate can reach up to 82.3% within 4.5 hours. The optimization of the Ni to TiO2 ratio, the gC3N4 to Ni-TiO2 proportion, and catalyst dosage was performed using the Central Composite Design and Response Surface Methodology (CCD/RSM). The experimental results showed that the degradation efficiency of sodium salicylate can be further improved by optimizing these parameters.

The degradation of chloramphenicol was also studied using Ni-TiO2/gC3N4 as a photocatalyst. The results demonstrate that the photocatalytic degradation efficiency of chloramphenicol can reach up to 78.2% within 6 hours. The optimization of the Ni to TiO2 ratio, the gC3N4 to Ni-TiO2 proportion, and catalyst dosage was performed using the CCD/RSM. The experimental results showed that the degradation efficiency of chloramphenicol can be further improved by optimizing these parameters.

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**Search for earth-abundant, defect-insensitive solar materials can play a significant role in future photovoltaics. Here we experimentally verify BaCd2P2 as a promising candidate for low-cost, high-efficiency photovoltaic materials, as predicted by high-throughput screening of nearly 40,000 semiconductors. Its optimal band gap of 1.45 eV and properties such as temperature stability and long carrier lifetime make BaCd2P2 a strong photocatalytic candidate. We were able to experimentally demonstrate the optical performance of BaCd2P2 by comparing its photocurrent density (PL) intensity with that of GaAs. The relatively low-purity (99.9%) BaCd2P2 powder had direct gap PL intensity in the same order as GaAs powder obtained from a prime single crystalline wafer, suggesting that it is insensitive to impurities and defects. We further present an in-depth investigation of the PL spectrum of this promising material by studying the impact of temperature, excitation laser power, and composition variations. Nearly all our experimental data have agreed with our theoretically calculated properties of BaCd2P2. The calculated band structure suggested a direct gap of 1.45 eV and an indirect gap of 1.46 eV. The PL spectrum of BaCd2P2 at 298 K, had a peak at 847 nm (1.46 eV), aligning well with the predicted band structure, and another, broader, peak at 980 nm. At 78 K we observed a separate peak on the lower wavelength side of the 847 nm peak resulting from the indirect gap transition, further validating our computed band structure. This material also showed great temperature stability, increasing the temperature to 368 K had only a slight decrease in the PL emission by ~5%, which fully recovered when going back to 298 K. Our work on excitation power dependence of PL intensity has enabled us to confirm the nature of the 847 nm peak and gain a better understanding of the 980 nm peak. We did this by modifying the well-known equation $I_{PL} = C \cdot (P_{exc})^e$ (meant to model the change in PL intensity with power) to account for competing nonradiative processes such as Auger recombination at higher excitation powers and consider the potential saturation of available states. We developed a more generalized equation that treats PL intensity as a function of thermal excitation, laser excitation, and radiative recombination. For the 847 nm peak, we repeatedly got a value of the $e$ parameter that was strongly indicative of a band-to-band transition. We saw that the 980 nm peak does not blueshift with decreasing temperature and that it had a strikingly similar response to PL laser excitation power variations as the radiative defect of Si-doped GaAs, appearing at 950 nm, leading us to hypothesize that the 980 nm peak of BaCd2P2 is due to a shallow radiative defect. We conducted an evaluation of the change in the 950 nm defect PL peak when using off-stoichiometric BaCd2P2 samples. We observed that the peak intensities and is slightly redshifted in Ba-poor samples. We further used the data from our studies of PL intensity change with temperature to calculate the activation energy of the prominent nonradiative defects.
Z-scheme photocatalysts have emerged as a promising solution to address the efficiency challenges in solar-assisted water splitting, thanks to their capability to efficiently absorb visible light and maintain the essential charge potential required for overall water splitting. To ensure the successful operation of Z-scheme photocatalysts, it is crucial that the two constituent photocatalysts and the charge recombinant layer are precisely arranged in a specific sequential order. However, previous research has predominantly utilized Z-scheme photocatalysts in a randomly mixed configuration, thereby preventing the full exploitation of the unique attributes inherent to Z-scheme photocatalysts.

This study demonstrates the fabrication of a nanocone-structured BiVO4/SrTiO3 Z-scheme photocatalytic thin film, enabling effective Z-scheme charge transfer. The fabrication process involves the preparation of a nanocone BiVO4 structure on a glass substrate, the formation of a BiVO4/reduced graphene oxide (RGO) composite nanocone structure, and the deposition of SrTiO3 nanoparticles to form BiVO4-RGO-SrTiO3 Z-scheme photocatalyst. The resulting structure comprises BiVO4, RGO, and SrTiO3 arranged sequentially. A comparative analysis between randomly mixed Z-scheme photocatalysts and the arranged Z-scheme photocatalyst demonstrates a significant enhancement in hydrogen production efficiency for the latter, underscoring the pivotal role of precise arrangement in Z-scheme photocatalysis.

Additionally, the study investigates how the superhydrophobic surface properties of the nanocone structure influence the capture of hydrogen and oxygen gas bubbles generated during the water splitting reaction in photocatalyst module. The nanocone-structured Z-scheme thin film efficiently captures gas bubbles due to its superhydrophobic surface characteristics, while the randomly mixed Z-scheme photocatalyst experiences reduced gas bubble detachment, resulting in decreased photocatalyst production efficiency.

This study underscores the importance of meticulous Z-scheme photocatalyst arrangement and highlights the advantages of the nanocone structure in improving gas bubble capture during the water splitting process, thus contributing to the advancement of photocatalytic hydrogen production.

Semiconductor nanocrystal-based photocatalysts have garnered significant attention for their potential applications in diverse fields, including hydrogen production, CO2 conversion, and pollutant removal. However, a major hurdle to improving their efficiency arises from the fact that the radiative recombination rate of semiconductor nanoparticles (~hundreds of nanoseconds) is much faster than the rates of photocatalytic reactions (~microseconds to ~milliseconds). This leads to the loss of the majority of charges before they can actively participate in the desired photocatalytic reactions, resulting in low efficiency. Therefore, it is crucial to develop structures that facilitate efficient charge separation to address this efficiency issue in photocatalysts. The most common approach to tackle this challenge involves utilizing core/shell structures to create a type-II band alignment structure. However, this approach has a drawback: while it enhances charge separation, it tends to trap electrons or holes within the core, limiting their participation in photocatalytic reactions.

In this research, we explore the influence of type-II core/crown nanoplatelets (NPLs) on photocatalytic reactions. These NPLs possess a type-II band alignment structure while exposing both the core and crown regions externally, enabling active participation of both electrons and holes in photocatalytic reactions. To maximize the efficiency of charge separation in this open structure, we prepared core/crown nanoplatelets with various compositions, including CdS, CdSe, and CdTe, while carefully controlling the surface area of both the core and crown regions.

We conducted femtosecond laser-based time-resolved photoluminescence measurements and transient absorption measurements to analyze the carrier dynamics of the prepared NPLs. Then, we performed water-splitting experiments under light irradiation to clarify the relationship between charge separation and photocatalytic activity. The results revealed that as the carrier lifetime of the photocatalyst increased, the hydrogen generation rate also significantly increased. This highlights the significance of the charge carrier lifetime as a pivotal parameter impacting photocatalytic activity.

Moreover, to validate the significance of an open structure, such as the core/crown configuration, we prepared type-II core/shell quantum dots with the equivalent composition and similar lifetimes to the core/crown nanoplatelets. Surprisingly, despite the efficient charge separation structure of the type-II core/shell quantum dots, their photocatalytic efficiency decreased. These findings underscore the importance of an open structure that facilitates the active participation of both electrons and holes in photocatalytic reactions while concurrently prolonging the carrier lifetime, ultimately resulting in enhanced photocatalyst efficiency.

The BaZrS3 chalcogenide perovskite shows strong light absorption, high chemical stability, is nontoxic, and is made from earth-abundant elements. These properties make it a promising candidate material for application in optoelectronic technologies, including next-generation photovoltaic absorber materials [1]. It has been proposed as a more chemically stable alternative to the widely studied lead-based metal halide perovskite family [2]. Although the chemical and physical properties of this perovskite are favorable, a scalable synthesis technique remains an open challenge. Standard solid-state synthesis requires temperatures that are not suitable for device integration (~900°C).

Several studies have now established that the perovskite forms at moderate temperatures (500-600°C) through liquid-flux assisted synthesis [3]. This method is based on the formation of BaSx in a sulfur-rich environment. Other methods based on molecular precursors or nanoparticles have also been proposed, but no good quality crystalline thin films have been formed to date [4,5]. Progress is hindered by our limited understanding of the underlying reaction thermodynamics.

In our work, we use density functional theory and lattice dynamics to calculate the thermodynamic and vibrational properties of BaZrS3 and its competing ternary, binary, and elemental phases. We consider the experimentally reported BaSx, ZrSx (x = 1, 2, 3) and BaZrS3 phases. Using our open-source code ThermoPot [6] we calculate the temperature and pressure-dependent Gibbs free energy of formation with reference to competing ternary, binary, and elemental phases.

We find that to promote the formation of BaZrS3 through liquid-flux there is a “goldilocks” zone for temperature and sulfur partial pressure. This is driven by the high sensitivity of Gibbs formation energy to the sulfur gas allotrope. At intermediate temperatures (500°C) and higher pressures (>10 Pa) the Sx allotrope dominates and suppresses the formation of BaSx. At lower pressures (<10 Pa) the S allotrope dominates and forms BaSx. We find good agreement between our results and those reported in the experimental literature [5]. Our work provides insights into the reaction thermodynamics of this promising material and suggests the experimental regimes to target for future synthesis.

References:

5:00 PM EN11.03.13
First Principles Thermodynamic Model of BaZrS3 Synthesis Prakriti Kayastha, Giulia Longo and Lucy Whalley; Northumbria University, United Kingdom

Kesterite solar cells have recently achieved a significant efficiency milestone, now at the edge of the 15% threshold, thanks to the innovative solution-based approach developed by Gong et al [1]. While thin-film chalcogenides are renowned for their stability in comparison to organic or perovskite counterparts, the phenomenon of light soaking has persisted as a recurring characteristic in solar cell devices. Light soaking refers to the alteration of a solar cell's characteristics after being exposed to illumination for a specific duration. Importantly, this property,
The Defect Chemistry of Emerging, Wide-Bandgap Absorber BiOI
Adair Nicolson

From the family of bismuth-based absorbers, BiOI has emerged as a leading candidate due to its improved air stability and lack of ultrafast charge-carrier localization, which can pose a defect tolerance observed in lead halide perovskites. Beyond the implications for solar cells, these instabilities offer promising possibilities for applications extending beyond the energy sector. One such application is the potential for creating optically controlled memristors, a novel development with significant ramifications in the field of neuromorphic computing and beyond. This research offers a new perspective on light-induced metastabilities in Kesterite solar cells, shedding light on their potential for controlled applications in emerging technologies.

8:30 AM EN11.04.01
The Defect Chemistry of Emerging, Wide-Bandgap Absorber BiOI
Adair Nicolson1, Sein R. Kavanagh2, Alex M. Ganose2 and David O. Scanlon3; 1University College London, United Kingdom; 2Imperial College London, United Kingdom; 3University of Birmingham, United Kingdom

Wide-bandgap solar absorbers are seeing significant interest for a variety emerging photovoltaic technologies, from top-layers in tandem cells to single junction devices for indoor applications. V-VI-VII materials have been studied for photocatalysis, but have recently gained interest as “perovskite-inspired” materials (PIMs) for solar absorber applications. These are materials which stray from the perovskite structure, but share an elementary space, thus keeping the strong antibonding character at the band edges and large dielectric constant, which are associated with the defect tolerance observed in lead halide perovskites.

From the family of bismuth-based absorbers, BiO1 has emerged as a leading candidate due to its improved air stability and lack of ultrafast charge-carrier localization, which can pose a challenge for many Bi containing PIMs originating from the reduction in dimensionality. However, large concentrations of electron traps have been measured in BiO1 thin films, the potential source of poor device performance.

Therefore, in this project we perform the first, complete investigation into all intrinsic point defect in BiO1 at the hybrid DFT level, using the shaken-break method to thoroughly search the complex defect potential energy surface. This will allow the identification of harmful defects and guide the development of fabrication processes to reduce their impact.


8:45 AM EN11.04.02
Air-Stable Bismuth Sulfobromide (BiSBr) Visible-Light Absorbers: Optoelectronic Properties and Potential for Energy Harvesting
Xiaowu Guo1, Yi-Teng Huang1, Hugh Lohan1,2, Junzhi Ye1, Yuanbao Lin1, Huimin Zhu4,1, Akshay Rao3, Iain McCulloch1 and Robert L. Hoye1; 1University of Oxford, United Kingdom; 2Imperial College London, United Kingdom; 3University of Cambridge, United Kingdom; 4University of Strathclyde, United Kingdom

Bismuth sulfobromide (BiSBr) is a quasi-one-dimensional semiconductor, but very little is known about its optoelectronic properties or how it can be processed as thin films. We develop a solution processing route to achieve phase-pure, stoichiometric BiSBr films (ca. 240 nm thick), which we show to be stable in ambient air for over two weeks without encapsulation. The bandgap (1.91 ± 0.06 eV) is ideal for harvesting visible light from common indoor light sources, and we calculate the optical limit in efficiency (i.e., spectroscopic limited maximum efficiency, SLME) to be 43.6% under 1000 lux white light emitting diode illumination. The photoluminescence lifetime is also found to exceed the 1 ns threshold for photovoltaic absorber materials worth further development. Through X-ray photoelectron spectroscopy and Kelvin probe measurements, we find the BiSBr films grown to be n-type, with an electron affinity of 4.1±0.1 eV and ionization potential of 6.0±0.1 eV, which are compatible with a wide range of established charge transport layer materials. This work shows BiSBr to hold promise for indoor photovoltaics, as well as other visible-light harvesting applications, such as photoelectrochemical cells, or top-cells for tandem photovoltaics.


9:00 AM EN11.04.03
Photoanodes and Thin-Film Solar Cells Based on SbSBr, SbSe and BiS Absorbers
Eduardo Magari1,2, Ivan Caño Prades1, Alejandro Navarro1, Cibrán López Álvarez1, Oriol Segura Blanch1, Hao Zhe Chun2, Joaquim Puigdollers1, Jordi Llorca Pique1, Lluis Soler Turu1, Lydia H. Wong2 and Edgardo Saucedo2; 1Universitat Politècnica de Catalunya, Spain; 2Nanyang Technological University, Singapore

Emerging quasi-1D (Q-1D) van der Waals materials, (Sb,Bi)(S,Se,Sb)I, hold the potential to be a breakthrough in photovoltaic (PV), photocatalytic (PC), and photoelectrochemical (PEC) applications, aiming to address some of the main issues affecting even the more mature PV, PC, and PEC technologies. Although this materials family has rarely been explored for these applications, mixed chalcogen-halides fulfill the urgent need for innovative and renewable energy sources based on earth-abundant, low-toxicity, thermally stable, and defect-tolerant compounds. This materials class has the peculiarity of possessing a crystallographic structure in which the atoms are held together by strong covalent bonds along one of their crystallographic directions and weak van der Waals bonds along the other two directions. When properly oriented, it results in a highly anisotropic material composed of nano/micro-ribbons with unique conductive properties. The high tunability of these materials and the results obtained in the present work place these semiconductors in the spotlight for a wide range of applications, including next-generation PV tandem and transparent applications, photocatalytic hydrogen production, and oxygen and hydrogen evolution reactions (OER, HER) among others.
The nano/micro-ribbon structure, coupled with the extremely uniform single-crystal phases, leads to an increased number of photons that reach the space charge region, and the light-trapping effect reduces reflection. This morphology enhances the optoelectronic properties of SbSBr and BiSeI-based solar cells, the OER of Q1-D van der Waals-based photoanodes, and the photocatalytic activity of such photocatalysts. The dense coverage of properly oriented nano/micro-ribbons increases the surface area, a key parameter for improving photons and reactant absorption, enabling the synthesis of efficient, phototoxic, photostable, and nontoxic photoanodes and photocatalysts. Furthermore, the band gaps of the obtained materials range between 1.25 and 2 eV, making them active to visible light and allowing an optimal usage of the solar spectrum.

The above-mentioned reasons are indicative of what can be achieved with this relatively unexplored technology. To date, no mixed chalcogen-halide compounds have been synthesized using physical vapor deposition (PVD) techniques, primarily due to the complexity of the material and the varying vapor pressures involved. This work marks the very first successful attempt to synthesize and investigate Q1-D van der Waals-based semiconductors using an innovative methodology that involves the co-evaporation of chalcogenides followed by high-pressure annealing under the appropriate atmosphere. Various characterization techniques (XRD, XRF, SEM, EDX, PDS, UV-Vis, Raman spectroscopy, and DFT calculations) have demonstrated the high tunability of the morphology of this compound family by modifying the annealing conditions, confirming the possibility of synthesizing high-quality single-phase material with PVD techniques for the first time.

The versatility of the system allows for the optimal distribution of nano/micro-ribbons in terms of height, thickness, density, and orientation, according to the final device's use. An array of operational Q1-D van der Waals-based solar cells and photoanodes, each derived from distinct stack combinations, will be showcased and thoroughly examined, together with some preliminary results on photocatalytic hydrogen production under visible light. Notably, solar cells with open-circuit voltages reaching up to 600 mV, and photoanodes, even when utilizing non-protected absorbers, have achieved a photoanode current of nearly 2 mA/cm². This study demonstrates how these novel compounds represent a promising development in advanced energy conversion applications.

9:30 AM EN11.04.05
Theoretical and Experimental Characterization of Highly Anharmonic Chalcohalide Anti-Perovskites for Energy Applications
Pol Benitez Colmínas, Ivan Caño Prades, Cong Liu, Cibran López Alvarez, Jonathan Turnley, Rakesh Agrawal, Edgardo Saucedo, Claudio Cazorla, Universitat Politècnica de Catalunya, Spain; Purdue University, United States
Silver chalcohalide antiperovskites (AH) are a family of materials with chemical formula Ag₃BrₓClₓS₃₋ₓ, where 0 ≤ x ≤ 1. These materials have shown promising properties for use in photovoltaic devices, particularly due to their band gap tunability and high optical transparency.

Inorganic phosphosulfides – materials containing phosphorus, sulfur, and at least one metal – are a vast and chemically versatile family of materials. Since metal phosphides and metal sulfides are among the highest-performing optoelectronic semiconductors, it seems reasonable to consider the phosphosulfide family as a potential material for photovoltaic applications. Solar cells, photovoltaic devices, and solar cookers are all examples of energy conversion systems that can benefit from the use of these materials.

9:45 AM EN11.04.06
Photoactive CuₓP₅S₁₀ Films via a Combinatorial Synthesis Platform Dedicated to Multi-Anion Semiconductors
Lena A. Mittmann, Javier Sanz Rodrigo and Andrea Crovetto; Technical University of Denmark, Denmark
Inorganic phosphosulfides – materials containing phosphorus, sulfur, and at least one metal – are a vast and chemically versatile family of materials. Since metal phosphides and metal sulfides are among the highest-performing optoelectronic semiconductors, it seems reasonable to consider the phosphosulfide family as a potential material for photovoltaic applications. Solar cells, photovoltaic devices, and solar cookers are all examples of energy conversion systems that can benefit from the use of these materials.
incorporating volatile metals. The whole system is glove-box integrated.

In the second part of this contribution, we will show the first experimental results on Cu$_2$PS$_4$ films, the first directly deposited phosphosulfide film specifically intended as a PV or PEC absorber.[1–4] The experimental results are complemented by computational studies carried out within our group. The computational task has been of crucial importance for obtaining properties that are difficult to measure experimentally, and for interpreting experimental results. Importantly, we show that the photoluminescence decay time of unoptimized Cu$_3$PS$_4$ films is already above 100 ns, demonstrating that phosphosulfides deserve close attention by the PV and PEC research community.


10:00 AM BREAK

SESSION EN11.05: Computational PEC/PV I

Thursday Morning, April 25, 2024
Room 335, Level 3, Summit

10:30 AM – EN11.05.01
Computational Approaches for Clean Energy Materials: Defect Graph Neural Networks, Equilibria with Interacting Defects and Interface Structure Prediction

Stephan Lany,
National Renewable Energy Laboratory, United States

Currently, 80% of the global final energy consumption occurs in form of fuels and only 20% as electricity. On the other hand, renewable energy additions come almost exclusively in the form of electricity (dominantly photovoltaics and wind). Thus, a successful energy transition will require enormous growth in renewables, sufficient to convert excess electricity into fuels, as well as the development of non-electricity based solar fuel technologies. As much as photovoltaic capacities have grown over the past 20 years, it is far from clear that current technologies and materials are up to the task to grow from here by yet another factor 100 until 2050. Therefore, sustained research efforts on emerging inorganic semiconductors for solar electricity and fuels are essential for facing the double challenge of climate change and energy security. Computational materials science can make important contributions, guiding and supporting research activities through both materials search and discovery and through detailed studies that help to develop a mechanistic understanding of materials performance and bottlenecks. This presentation will highlight three recent computational projects with relevance for photovoltaics and solar fuels (1) Defect graph neural networks (dGNN) for materials discovery in solar thermochemical hydrogen (STCH) [1]. The dGNN approach facilitates broad and fast materials screening for defect properties. (2) Modeling highly off-stoichiometric systems by evaluating the free energy of defect interaction [2]. This approach allows quantitative prediction of H$_2$ production in complex STCH oxides. (3) First-principles atomic structure prediction for interfaces [3]. This work showed how an atomically thin CdCl$_2$ interlayer phase enables in principle ideal electron transport across the incommensurate SnO$_2$/CdTe interface.


DOI: https://doi.org/10.1038/s43588-023-00495-2


DOI: https://doi.org/10.1063/5.0104008

11:00 AM – EN11.05.02
Statistics of Crystal Defects from Dilute Limit to Alloys, Excluded Volume Exchange Interaction and Effective Energies of Defect Ensembles

Mike Scarpulla, University of Utah, United States

Point defects determine the properties of otherwise-perfect semiconductors and insulators, thus computing their concentrations accurately is of prime importance. Typically, the dilute limit is assumed leading to Boltzmann statistics, however it is obvious that multiple defects or defect complexes cannot occupy the same site at the same time. Herein, we present closed-form expressions for point defect statistics applicable for all concentrations; thus refining defect and alloy theories. These expressions prevent unphysical prediction of more defects than available sites when either a) any defect of type $j$ in chargestate $q$ has zero or negative formation energy $\Delta E_q^j$ (e.g. charged defects at certain Fermi energies) or more interestingly b) when multiple defects and/or chargestates have small $\Delta E_q^j$ compared to the thermal energy $kBT$. An important insight is that different statistics arise if 1) host atom or 2) site conservation is assumed: Case 1 corresponds to a finite crystal with $N_q$ sites and moving displaced host-crystal atoms to extra unit cells on the surface, while Case 2 corresponds to an infinite crystal with $N_q$ sites per volume and moving displaced host-crystal atoms into external reservoirs (e.g. the case corresponding to modern DFT supercell calculations). Anomalously to quantum Fermions but classical in origin, the mutual exclusion between defects of any type can be conceptualized as an exchange interaction energy. Additionally, we demonstrate that multiple configurations of a defect, multiple configurations of a chargestate, or other arbitrary subgroups of defects and complexes can be gathered together into objects having effective formation energy. This allows, for example, plotting the finite-temperature formation enthalpy of a defect having multiple chargestates as a continuous function of Fermi level or using an effective chemical potential to enforce constraints on subgroups of defects, amongst other applications. These fundamental tools add flexibility and accuracy to quantitative defect calculations and join smoothly to thermodinamics of solutions and alloys while adding only minor computational costs.

11:15 AM – EN11.05.03
Doped: A Python Package for Solid-State Defect and Dopant Calculations

Seán R. Kavanagh¹, David O. Scanlon² and Aron Walsh³; ¹Harvard University, United States; ²University of Birmingham, United Kingdom; ³Imperial College London, United Kingdom

Defect-induced non-radiative recombination typically represents the dominant limiting factor in the efficiencies of emerging inorganic solar cells / photocatalysts.¹ Computational methods are showed how an atomically thin CdCl$_2$ interlayer phase enables in principle ideal electron transport across the incommensurate SnO$_2$/CdTe interface.

Doped-induced non-radiative recombination typically represents the dominant limiting factor in the efficiencies of emerging inorganic solar cells / photocatalysts.¹² Computational methods are widely used to predict defect behavior in solar materials, before combining and comparing theoretical predictions with experimental measurements. However, there are many critical stages in the computational workflow for defects, which, when performed manually, not only leave room for human error but also consume significant researcher time and effort. Moreover, there are growing efforts to perform high-throughput defect investigations,³⁴ necessitating robust, user-friendly and efficient software implementing this calculation workflow. Here we report doped, our python package for the full generation, calculation setup, post-processing and analysis of defect supercell calculations.³⁴ The generation and thermodynamic analysis (i.e. defect formation energy diagrams, chemical potentials, doping analysis etc.) are agnostic to the underlying first-principles software, while input file generation is supported for several of the most widely-used DFT codes, including VASP, PHI-aims, CP2K, Quantum Espresso and CASTEP. A defect charge state prediction algorithm is implemented, which is shown to significantly outperform previous oxidation-state approaches in terms of both consistency and completeness. Moreover, doped is built to be compatible with other computational toolkits for advanced defect characterisation, including ShakeNBreak¹⁰ for defect structure-searching, py-sc-fermi¹³ for in-depth concentration, doping and Fermi level analysis, and CarrierCapture²¹ for non-radiative recombination calculations. Its object-oriented python framework make it readily usable in high-throughput architectures such as atomate(2) or AiiDA, with examples included in the documentation.

We will discuss the key features of doped for computational defect workflows, exemplified with relevant solar cell materials (CdTe, Sb$_2$Se$_3$, r-Se). We anticipate that doped will serve as a highly useful tool for computational defect researchers, being an efficient platform for conducting reproducible calculations of solid-state defect properties.

5 DOI: https://doi.org/10.1063/5.0104008
10 ShakeNBreak, https://github.com/ahällstom/ShakeNBreak
In order to improve the efficiency of solar cells, stable materials with suitable optoelectronic properties must be found. For this purpose, phosphosulfides offer a large and varied range of semiconductors with very diverse compositions, structures, and therefore, optoelectronic properties. This is mainly due to the wide range of oxidations states that phosphorus can take in this class of materials (from -3 to +5). We are currently studying phosphosulfides for solar energy by a multi-faceted approach, including first-principles calculations, high-throughput experiments, and machine learning.

It is estimated that the number of chemically-plausible ternary phosphosulfides is close to 1800, yet just around 100 have been synthesized, and only a handful have been investigated for PV or PEC applications. A high-throughput screening process is performed here for over 800 of these materials, obtained from metal substitution in 67 structural prototypes reported in the Materials Project, resulting in some completely unknown potential candidates as wide-gap solar cell absorbers in tandem solar cells. On top of these simple elemental substitutions, we have also explored some previously unreported phosphosulfide stoichiometries, based on analogy with other puiocgenous (N, As, Sb) and chalcogens (Se, Te). Unlike the case of most of the already-known phosphosulfides, these structures have phosphorus-rich stoichiometries, which appears to be correlated with favorable optoelectronic properties. The initial criteria for the screening process are thermodynamic stability, intermediate band gaps and low effective masses. As a result, around 100 new phosphosulfide materials potentially suitable for solar cell applications are obtained from this virtual screening. Most of these compounds are not present in computational materials databases and have never been synthesized. More detailed calculations on a selected subset of these new materials suggest that a few of them deserve experimental investigation as PV absorbers.

The large volume of materials screened gives us a unique opportunity to identify composition-structure-property trends in phosphosulfides with special emphasis on optoelectronic energy conversion applications. We will show how these trends can be used to design new optoelectro phosphosulfides beyond ternary systems.

**References**

Discovering efficient and scalable photocatalysts for water splitting is a major challenge for the sustainable production of carbon-free hydrogen. In this presentation, we tackle that challenge and expand the list of known water-splitting photocatalysts using data-intensive screening based on accurate first-principles calculations of band gaps, band edges, and free energies of electrochemical decomposition. Building on previous studies [1,2] which show that inserting pre-transition (s-block) metals in binary metal oxides can improve redox activity while preserving solar absorption, we specifically target the family of post-transition (p-block) metal oxides. We analyze the influence of adding s-block cations on the band gaps and band edges of these materials and on their photocatalytic efficiency. Based on this analysis, we screen 109 ternary metal oxides and identify nine candidates, among which two appear to not have been previously proposed as water-splitting photocatalysts [3]. We then extend these results to the family of ternary s- and p-block metal sulfides, leading to the discovery of additional photocatalytic compounds, which warrants further studies [4].


2:30 PM *EN11.06.04
Navigating The Vast Materials Landscape for Photovoltaics with NOMAD
Jose Marquez Prieto; Humboldt University of Berlin, Germany

Accelerating the development of innovative solar materials demands a fundamental transformation in lab methods, particularly in enhancing efficiency in production, characterization, and device integration. Numerous research labs are beginning to adopt more efficient methods to achieve the necessary acceleration, including high throughput computation and experimentation, and the emergence of some autonomous labs. All these efforts generate a massive volume of data that needs to be organized, automated and made ready for AI analyses and programmatic access.

This talk offers insight into how NOMAD (https://nomad-lab.eu), an open-source platform developed by the NFDI (Germany’s National Research Data Infrastructure) consortium FAIRmat (https://fairmat-nfdi.eu), can help individuals and labs in this task. NOMAD is designed to tackle these challenges by enhancing the accessibility and usefulness of materials science data following the FAIR principles - making data Findable, Accessible, Interoperable, and Reusable. I will overview the dramatic improvements within the NOMAD infrastructure beyond computational materials science, specifically tailored for experimental solar cell research, and highlight an application created for detailed visualization and investigation of a broad, AI-ready solar cell dataset. As an illustration, I will examine the historical advancement of charge transport layers for perovskite solar cells using network analysis, demonstrating how it is possible to navigate effectively this extensive materials space.

To provide a digitization platform for experimental developments, the NOMAD platform incorporates a flexible electronic lab notebook (ELN), configured for customization to meet the specific needs of individual research laboratories, thereby facilitating the efficient capture, transfer, and processing of AI-ready data and metadata within a well-organized FAIR database framework.

Ultimately, this presentation aims to illuminate the path forward in the realm of semiconductor materials for solar applications, guided by data-centric methodologies and collaborative infrastructures like NOMAD, which are indispensable in accelerating the journey toward efficient and sustainable solar energy solutions.

3:00 PM BREAK

SESSION EN11.07: Nitride PEC
Session Chairs: Jose Marquez Prieto and Vladan Stevanovic
Thursday Afternoon, April 25, 2024
Room 335, Level 3, Summit

3:30 PM *EN11.07.01
Accelerating The Development of Semiconductor Thin Films through Advanced Automated Characterization. Sebastian Siodl; Empa-Swiss Federal Institute of Materials Science and Technology, Switzerland

The discovery of new functional materials remains a key challenge in the development of next-generation sustainable technologies. Fueled by advances in high-throughput computation, new exciting materials are being predicted at an ever-increasing rate. Combinatorial high-throughput materials science techniques hold the promise to match this rate by facilitating the rapid exploration of complex phase spaces. Today, combinatorial materials science workflows are employed in many laboratories around the world. While gradient deposition of combinatorial thin-film libraries can be implemented in most standard deposition equipment, a comprehensive tool box for rapid materials characterization which is just as crucial is often harder to realize. In this presentation, it will be shown how accelerated thin-film materials development is performed in the Coating Technologies group at Empa. We employ a workflow consisting of reactive combinatorial physical vapor deposition, automated characterization and semi-automated data analysis which covers most common thin-film characterization techniques as well as functional property mapping. In recent years, we extended this infrastructure to include high-throughput surface analysis, but also optical measurement setups for accelerated aging studies. This extension not only complements the existing workflows, but provides additional insights that were previously much harder to obtain. It will be shown how surface analysis mapping can facilitate the discovery of new semiconductor materials in complex phase spaces, such as the wide band gap nitride semiconductors Zn$_2$VN$_2$[1,2] or Zn$_2$TaN$_2$[3]. In addition, it will be shown how accelerated optical aging studies combined with machine-learning assisted data analysis can generate insights into the operational stability and degradation kinetics of more volatile materials.


4:00 PM EN11.07.02
Co-Design of Zinc Titanium Nitride Semiconductor towards Durable Photoelectrochemical Applications
John Mangum$^1$, Sijia Ke$^{2,3}$, Andriy Zukateyev$^1$, Jeffrey B. Neaton$^{2,3}$ and Annie Greenaway$^1$1 National Renewable Energy Laboratory, United States; 2 University of California, Berkeley, United States; 3 Lawrence Berkeley National Laboratory, United States

Development of photoelectrochemical (PEC) systems requires, among other advances, photoelectrode materials that are both photocatalytically active and stable in harsh electrochemical environments.

We have intentionally searched for a candidate photoabsorber based on co-design principles, wherein design for photoactivity is based on the ability to integrate the new material with established semiconductors and design for stability is based on the propensity for the photoabsorber to self-passivate during operation. This has led to the first synthesis and substantial development of wurtzite ZnTiN$_2$ as a photoabsorber. Initially, high-throughput combinatorial synthesis was used to identify the radio-frequency co-sputtering parameter space for ZnTiN$_2$. Cation disorder in this film reduced the bandgap to $-2.0$ eV, appropriate for solar fuel generation, and the ZnTiN$_2$ surface was found to transform to stable oxides under CO$_2$-relevant electrochemical conditions. Together, these characteristics indicate that ZnTiN$_2$ could be used as a photoelectrode, but the optoelectronic and crystalline properties of the material would require substantial improvement before operation in PEC applications. Next, experimental integration of ZnTiN$_2$ with established semiconductor systems allowed us to rapidly improve the crystalline and optoelectronic properties of the sputtered ZnTiN$_2$ films, paving the way for high photocatalytic activity for PEC to be demonstrated using this semiconductor. We will report on materials quality advances in ZnTiN$_2$ thin films as well as progress toward demonstration of this material as a photoelectrode. Future work will focus on developing PEC device structures based on the improved ZnTiN$_2$ photoelectrode films by optimizing semiconductor properties (e.g. doping) and interfaces with surrounding device layers.


4:15 PM EN11.07.03
Defect Engineering of Ta N Photanoanes: Enhancing Charge Transport and Photoconversion Efficiencies via Ti Doping
Laura I. Wagner$^{1,2}$, Elise I. Sirotti$^{1,2}$, Oliver Brune$^{1,2}$, Gabriel
In recent development, efficiency of flexible Cu(In,Ga)Se2 (CIGS) solar cells has exceeded 22%, marking a significant step towards commercial viability. [1] In particular, the deliberate alkali treatment boosted their efficiency, yielding a comparable effect to diffused alkali from soda-lime glass substrate. Besides alkali treatment, understanding stress-induced properties is crucial to how to enhance solar conversion efficiency remains a persistent challenge. In line with this, we present a novel constructive strategy for a ternary-material-system photoanode, aimed at enhancing solar conversion efficiency. We report a transformative approach to create a ternary-material-system photoanode, with a high degree of tunability. This approach is based on a ternary compound, Ti-doped Ta3N5, which has shown promising optoelectronic characteristics.

Bismuth vanadate (BiVO4) is an outstanding photoanode material for photoelectrochemical water splitting. In this work, a series of single crystalline BiVO4 photoanodes are synthesized by pulsed laser deposition (PLD). Once coated with a thin layer of cobalt oxides (CoOx) co-catalyst, also by PLD, the photoanodes support efficient photoelectrochemical generation of chlorine (Cl2) from brine under simulated solar light. Activation of the chlorine generation reaction (CIER) is optimized when the thickness of CoOx is about 3 nm, with the faradic efficiency of CIER exceeding 60%. Detailed studies show that the CoOx co-catalyst layer is amorphous, uniform in thickness, and chemically robust. As such, the co-catalyst also effectively protects the underlying BiVO4 photoanodes against photodegradation. The other metal oxides co-catalysts are also compared, detailed mechanism on how the cocatalyst layers influence the performance of BiVO4 photoanode is revealed. This work provides insights on using artificial photosynthesis for by-products that carry significant economic value while avoiding the energetically expensive oxygen evolution reaction.

Heterostructured Hematite Photoanodes featuring C3N4 with In-Situ Grown Ni-CoP2 for Boosted Photoelectrochemical Water Oxidation

The high demand for renewable and clean energy resources has led to the rapid development of cutting-edge materials for photoelectrochemical (PEC) water splitting. However, the question of how to enhance solar conversion efficiency remains a persistent challenge. In this study, we present a novel constructive strategy for a ternary-material-system photoanode, aimed at simultaneously improving charge separation and transfer, as well as water oxidation efficiency. Specifically, we demonstrate the PEC efficiency of composite Ti-Fe2O3/CN/NCP photoanodes obtained by loading hierarchical C3N4 (CN) nanosheets anchored in-situ grown Ni-doped CoP2 (NCP) onto porous Ti-doped hematite (Ti-Fe2O3) photoanodes. The resulting Ti-Fe2O3/CN/NCP photoanodes exhibit a remarkable enhancement of photocurrent density (2.01 mA cm−2 at +1.23 V_RHE) compared to Ti-Fe2O3 photoanodes (0.28 mA cm−2 at +1.23 V_RHE). It is noteworthy that CN and NCP serve to deplete photogenerated electrons and remove photogenerated holes directionally from the surface of Ti-Fe2O3. This leads to the facile transfer and separation of electron-hole pairs necessary for exceptional catalytic performance. Moreover, we undertake a systematic analysis of the role of CN and NCP to gain deeper insights into the underlying mechanisms for the superior PEC water oxidation process.
Synthesis of Complex Pnictide Semiconductors
Kirill Konnin; Iowa State University, United States

Bismuth vanadate (BiVO₄, BVO) is an outstanding photoanode material for photoelectrochemical water splitting. In our recent work, single crystalline BVO photoanodes were synthesized by pulsed laser deposition (PLD) method on YSZ(110) substrates. Through tuning different characters of BVO films deposited, they were found to be effective and influential in photoelectrochemical water splitting. Generally, the various characters of BVO were realized by tuning the deposition conditions of PLD, the growth mechanism of BVO thin films between YSZ(110) and conventional substrate orientation YSZ(100) was also compared. Furthermore, all the differences will have a direct influence on photoelectrochemical water splitting. Detailed surface characterizations and mechanistic research were performed to understand the inherent correlation between BVO growth conditions and performance, which will have a heuristic effect towards future photoanode design for solar water splitting.

Enhancing Photoelectrochemical Water Splitting Performance via Controllable Deposition of BiVO₄ on YSZ(110)
Zhaoyi Xi, Chenyu Zhou and Mingzhao Liu; Brookhaven National Laboratory, United States; Stony Brook University, The State University of New York, United States

Here we report on the growth of single crystals of BaZrS₃ and their crystal structure and optoelectronic properties compared to thin films. The BaZrS₃ crystals were grown by chemical vapor deposition (CVD) using iodine as a transport agent. The resulting material and grown crystals were characterized by powder X-ray diffraction (XRD) and LeBail analysis of the diffraction pattern, as well as by single-crystal X-ray diffraction. The chemical composition of the crystals was determined by X-ray fluorescence. The band gap energy was determined from the diffuse reflectance measured by UV-VIS spectroscopy.

Reference:

Solution-Based Synthesis of Low Dimensional Pnictogen Chalcogeno-Halides based on (Sh,Bi)(S,Se)(Br,I) for Sustainable Energy Applications
David Rovira Ferrer, Ivan Caño Prades, Joaquim Puigdollers and Edgardo Saucedo; Universitat Politècnica de Catalunya, Spain

Quasi one-dimensional (Q1-D) structures based on van der Waals materials are gaining increasing interest in the search for novel energy applications such as photocatalysis, energy storage or photoelectrochemical reactors. This attention is driven by the high stability and low environmental impact of chalcogenides and chalcogeno-halides in contrast to third generation solar cells, especially Pb-based perovskites. The optoelectrical properties of these materials can be easily tuned through compositional engineering. A wide bandgap range (from 1 to 3.5 eV) can be achieved with available candidates for single-junction solar cells. The ShBi chalcogeno-halides compounds, generally formulated as MCHₓ (M = Sb, Bi; Ch = S, Se; X = I, Br), crystallize in an orthorhombic Pnma space group consisting of covalently bonded ribbons along one crystallographic direction, while they are stacked together by van der Waals interactions in the other directions. This feature gives rise to unique optoelectronic properties when the material is properly oriented, such as enhanced carrier transport and increased mobility. In addition, it has been suggested that these compounds might possess a defect-tolerant electronic structure due to the trivalent metal cation, which is encouraging their development. Despite these encouraging properties, the correct synthesis of these materials containing a halogen and a chalcogen in the structure is still a big challenge. Binary materials such as (Sh,Bi)(S,Se)₂ can occur as secondary phases, as well as sub-optimal morphologies. Uneven and uncompact films with uncontrollable ribbon orientation can form. This presentation will introduce a new methodology to synthesize mixed chalcogeno-halides developed by the authors of this work. Thin films of the complete set of ternary van der Waals (Sh,Bi)(S,Se)(Br,I) chalcogeno-halide semiconductors have been synthesized by dissolving MX₃ and selenourea/thiourea in N,N-dimethylformamide (DMF), followed by multiple spin-coating and hot-plate annealings at low
temperatures (< 400 °C). Additionally, antisolvent incorporation during spin-coating, followed by a drying step at a temperature below the solvent’s boiling point, have been applied to ensure that all organic residues are removed. This one step methodology provides less complexity compared to previous sequential procedures relying on diffusion of one precursor in a previously deposited film, which can lead to a gradient in the composition. Different surface treatments over the molybdenum substrate are explored to selectively orient texture in the (001) direction by improving the solution adhesion and increasing the nucleation sites. In the second part of the presentation, the fundamental properties of these compounds obtained by electrical and optical characterization will be discussed. The measurement of the bandgaps, band structures, optical and transport properties will be shown. The last part of the presentation will be dedicated to the challenges and possible technological solutions for the fabrication of solar cell devices using this innovative absorber synthesis route. The use of different electronics and holes transport layers, and architectures inspired in bulk-heterojunction devices using blended ribbons of BSI and Bi4Sb3/Sb3I7 as donor and acceptor, respectively, will be discussed. These solar cell prototypes will be shown, with very encouraging open circuit voltages around 500 mV, and conversion efficiencies exceeding 1%. Finally, the perspective of these materials and the possible advantages with respect to current chalcogenide and halide technologies, will be presented and discussed.

5:00 PM EN11.08.11
An ALD-Grown Al-Doped Zinc Oxide/n-Si Isotype Heterojunction for Solar Water Splitting C. S. Wang 1, P. H. Tsen 2, Y. S. Lai 3 and Kusn Y. Hsu 1; 1National Tsing Hua University, Taiwan; 2National Yang Ming Chiao Tung University, Taiwan; 3Taiwan Semiconductor Research Institute, Taiwan
It is well known that zinc oxide (ZnO) films are good passivation layers to semiconductor solar cells. Doped ZnO also serves as an excellent transparent electrode material. The efficiency of many solar cells has been enhanced by adopting this oxide material in the device structures. Besides, ZnO can be prepared by several large-area growth methods such as sputtering, evaporation, CVD, sol-gel, spray, ALD, etc. This benefit the use of ZnO in solar applications. In addition to being a transparent passivation layer or conducting electrode, n-type doped ZnO thin film can directly form an anisotype heterojunction with p-type silicon (p-Si) or an isotype heterojunction with n-type silicon (n-Si). These heterojunctions function simply as solar cells. When converting light into electrical energy, compared with conventional semiconductor p-n junctions, the ZnO/n-Si heterojunctions show no power loss at the near-surface region in the devices if the incident light comes from the ZnO side, because the ZnO films are transparent to visible light. This advantage further extends the application of ZnO to the active region of devices. In particular, the current flow in the n-ZnO/n-Si heterojunction should be easier since it involves only majority carriers. While numerous studies on the n-ZnO/p-Si anisotype heterojunction were conducted, much fewer works on the n-ZnO/n-Si isotype heterojunction can be found in the literature. In this work, an aluminium-doped ZnO (AZO) thin film was grown on an n-Si substrate by atomic layer deposition (ALD) with in-situ doping technique to form an isotype heterojunction. And a self-powered solar water splitter formed by serially connecting several of such heterojunctions was demonstrated. The device was fabricated by first using the ALD system to grow a 53 nm thick AZO film on a 0.685 mm thick n-Si (2-7 Ω-cm resistivity) substrate. The growth temperature was low and set at 280 °C for best (002) crystalinity of the AZO film. The AZO film thickness was designed for minimum visible light reflection. The aluminum doping was performed by using an in-situ doping technique which involves the introduction of the Al2O3(CH3)3 (TMA) precursor during the deposition process, which helps precise film thickness control. The resultant AZO film was characterized by Hall measurement to have a high resistivity of 2.48 x 107 Ω-cm and a high electron concentration of 1.3 x 1020 cm-3. Therefore, the fabricated AZO/n-Si junction behaves like a Schottky junction, and the AZO itself can be the anode contact. TiN was coated at the backside of the Si substrate as the cathode. When serially connecting several devices, copper tape was used as the interposer. The rectifying dark I-V curve of the AZO/n-Si junction was measured, from which the Schottky barrier height was extracted as 0.632 eV. When illuminated by the light from a tungsten-halogen lamp with an irradiance of 100 mW/cm2, the open-circuit photovoltage was measured to be 0.38 V and the short-circuit current density was about 1 mA/cm2. To demonstrate the usefulness of the AZO/n-Si isotype heterojunction device, we tried to use it to split DI water under illumination. By using the linear sweep voltammetry (LSV), it was found that the threshold voltage of DI water splitting for the fabricated AZO and TiN electrodes is 1.6 V. This indicates that at least 5 fabricated AZO/n-Si junctions must be connected in series to initiate splitting DI water under illumination. Such experiment has been carried out and the production of hydrogen gas was successfully observed.

5:00 PM EN11.08.12
Electron Transport Layers for CO2 Reduction: Conductivity, Selectivity and Stability Rajiv Ramanujam Prabhakar and Joel W. Ager; Lawrence Berkeley National Laboratory, United States
Electron transport layers (ETLs) used as components of photocathodes for light-driven CO2 reduction (CO2R) in aqueous media should have good electronic transport, be stable under CO2R conditions, and, ideally, be catalytically inert for the competing hydrogen evolution reaction (HER). Here, using planar p-Si (100) as the absorbing material, we show that TaOx satisfies all three of the above criteria. TaOx films were synthesized by both pulsed laser deposition (PLD) and radio-frequency (RF) sputtering. In both cases, careful control of the oxygen partial pressure during growth was required to produce ETLs with acceptable electronic conductivity. p-Si/TaOx photocathodes were interfaced with ca. 10 nm of a CO2R catalyst: Cu or Au. Under front illumination with simulated AM 1.5G in CO2-saturated bicarbonate buffer, we observed, for both metals, faradaic efficiencies for CO2R products of ~50% and ~30% for PLD TaOx and RF sputtered TaOx, respectively, at photocurrent densities up to 8 mA cm⁻². p-Si/TiO2/Cu photocathodes were also evaluated but produced mostly H2 (~97%) due to reduction of the TiO2 to Ti metal under CO2R conditions. In contrast, a dual ETL photocathode (p-Si/TiO2/TaOx/Cu) was selective for CO2R, which suggests a strategy for separately optimizing selective charge collection and the stability of the ETL/water interface. The maximum photovoltage obtained with p-Si/TiO2/Cu devices was 300 mV which was increased to 430-460 mV by employing ion implantation to make p+-Si/TaOx Cu structures. Photocathodes with RF sputtered TaOx ETLs are stable for CO2R for at least 300 min. Techno-economic analysis shows that the reported system, if scaled, could allow for an economically viable production of feedstocks for chemical synthesis under the adoption of specific CO2 credit schemes, thus becoming a significant component to carbon-neutral manufacturing.
Further to understand the why PLD TaOx electron transport layer exhibits higher product selectivity over RF sputtered TaOx, we investigated using ambient pressure x-ray photoelectron spectroscopy (APXPS) how the Cu catalyst oxidation state changes with different CO2 partial pressures. There was evidence on favorable change in the oxidation state of Cu towards Cu2+. The last part of the presentation will be dedicated to the challenges and possible technological solutions for the fabrication of solar cell devices using this innovative absorber synthesis route. The perspective of these materials and the possible advantages with respect to current chalcogenide and halide technologies, will be presented and discussed.

5:00 PM EN11.08.13
Photolithography Technologies for Metallic Meshes and Local Contacts on CIGS Thin Film Solar Cells with NIR-Transparent TCO Layers SeongYeon Kim, Si-Nae Park, Dong-Heon Jeon, Van-Quy Hoang, Jaebaek Lee, Ali Amanat, Shi-Joon Sung and Dae-Hwan Kim; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)
Recent breakthroughs in efficiencies of up to 14.9% 1 for Cu2ZnSn(S,Se)4 (CZTSSe) solar devices have reignited interest in CZTSSe as an inorganic thin-film solar absorber. Traditionally, Mo-coated soda lime glass (SLG) substrates have been the standard for chalcogenide thin-film photovoltaics (PVs). Such substrates, however, can hinder the applications of thin-film PV, namely, semi-transparent and bifacial irradiation for building integrated PV applications. In this study, we explore the deposition of CZTSSe directly onto fluorine-doped tin oxide (FTO) by solution-based methods. The precursor solutions containing copper(II) chloride dihydrate, tin(II) chloride, zinc chloride and thiourea were formulated by employing mixtures of dimethyl formamide (DMF) and isopropanol (IPA).2-3 We also investigate the effect of adopting an one- or two-step heat treatment process at each layer during spin coating, prior to the reactive annealing step in the development of multilayer metal organic chemical vapor deposition (MOCVD) and solution deposition (SD) processes. We also studied the effects of using co-source precursors rather than separate precursors for each layer, and investigated the use of a buffer layer to improve film morphology, adhesion and optical properties. The Cu2ZnSn(S,Se)4 films exhibited high photovoltaic performance with a short-circuit current density of 18 mA cm⁻², an open-circuit voltage of 0.75 V, a fill factor of 0.65, and an overall efficiency of 13.3%. This work was supported by the Korea Energy Management Corporation (KEMCO) and the Daegu Gyeongbuk Institute of Science and Technology (DGIST).
A transparent conducting oxides (TCO) for CIGS thin film solar cells, Al-doped ZnO (AZO) is widely used because of their wide band gap energy (\(E_g = 3.37 \text{ eV}\)), high optical transparency, conductivity and based on earth-abundant materials. However, for the application of TCO layer for modules fabrication, AZO has an issue about optical loss in the visible and near-infrared spectrum. This causes electrical, optical and fill factor (FF) losses in the integration of solar cells in a module, which is known as cell to module (CTM) losses. To solve those issues, we have fabricated CIGS solar cells with hybrid electrodes of metallic grids / TCO layers.

Photolithography is versatile technology to make the patterns as we desired and demanded for semiconductor devices. We have patterned metallic meshes on AZO layer of CIGS solar cells using by photo lithography technique with negative photoresists. We fabricated photore sist template by exposure and development processes and deposited aluminum or silver metallic layers on the template about 1 \(\mu\)m of thickness and lifted off the photore sist to complete metallic meshes with attempting to minimize the linewidth by 2–3 \(\mu\)m and also minimize transmittance loss controlling by grid distance about 100 to 200 \(\mu\)m. As a result, Al meshes occupying from 2.20 to 2.84% in a cells whereas reference devices have 3.94 to 4.66 % of grid area. In both case of Al and Ag meshes devices, Jsc has been improved to 27.98 mA/cm² than 27.73 mA/cm² of the reference devices. In the case Ag meshes devices, Voc has been improved to 0.65 V which is closer to 0.66 V of the reference cell. By these results, we will discuss how to fabricate the solar cells with composite transparent electrode better way.

On the other hand, we have fabricated Hydrogen-doped Indium Oxide (In\(_2\)O\(_3\)-H) by sputtering process with H\(_2\) and O\(_2\) reactive gases with various mass flow controlling to improve NIR transmittance and high mobility. We have fabricated CIGS solar cells with dot-shaped local contacts instead of AZO layer and compare the parameters to clarify how NIR transparency and mobility improves the power conversion efficiencies.

Also, we fabricated local contacts with MgF\(_2\) passivation layer with dot-shaped local contacts with various diameters and spacings on Mo back contact before CIGS deposition. We will discuss how those diameter and distance affecting on solar cells power conversion efficiency improvements.

**SESSION EN11.09: Chalogenides PV/PEC I**

**Session Chairs: Sage Baurers and Andriy Zakutayev**

**Friday Morning, April 26, 2024**

**Room 335, Level 3, Summit**

8:00 AM *EN11.09.01*

**CdsSe Solar Cells with V\(_{OC}\) > 1V** Sachit Grover, Mohammad Taheri, Taylor Hill, Elline Hettrachthy, Xiaoping Li, Dmitriy Krasikov, Gang Xiong, Darius Kuciauskas, Craig Perkins and Angus Rockett; First Solar, United States; 2Colorado State University, United States; 3National Renewable Energy Laboratory, United States; 4Colorado School of Mines, United States

An efficient, low-cost, scalable, and stable top-cell photovoltaic absorber is needed to make thin-film based tandem solar cells. Using cadmium selenide (CdSe) as an example, we highlight our methodology for rapid assessment of novel photovoltaic absorber materials and identify challenges towards making high efficiency devices.

With a bandgap of 1.72eV, CdSe is well suited as a top-cell absorber in a two-junction tandem solar cell. We assess the potential of CdsSe as an absorber through several measurements including external radiative efficiency (ERE), carrier density, polycrystalline grain-size and orientation. Well formulated films of CdsSe are found to be n-type, hexagonal, and exhibit high ERE (>0.2%). Photoluminescence and sub-band external quantum efficiency confirm that this absorber is capable of implied open-circuit voltage above 1 V. A transparent conducting oxide coated on glass forms the electron-contact to the CdSe thin-film grown on top of it. The hole-contact is formed by organic hole-transport layers used in conjunction with a bilayer of transition metal oxide and thin-gold. Solar cells with measured V\(_{OC}\) > 1V have been demonstrated with this device structure. Despite good V\(_{OC}\), the devices made so far exhibit a limited fill factor and short-circuit current that cannot be completely accounted for by resistive or optical losses. By connecting a multitude of metrology techniques to device modeling results we conclude that the minority carrier collection is limited as the mobility and lifetime product (\(\mu\)\(\tau\)) product is about \(10^3\) cm²/V. This is attributed primarily to low hole mobility. Another key challenge is the unusually large ionization potential of CdsSe at ~6.5 eV. SCAPS simulations indicate that improving the \(\mu\)\(\tau\) and reducing the band-offset at the hole contact should lead to improved carrier collection. Defect signatures identified through sub-band photoluminescence measurements suggest selenium vacancies could be the primary origin.

In conclusion, well researched p-type transparent contact layers with a deep valence-band alignment are needed as hole contacts for CdSe solar cells. Options for designing a CdSe device that can be used in a thin-film based tandem are limited by the n-type absorber and require improved minority-carrier diffusion length.

8:30 AM *EN11.09.02*

**Cation Mutation in Cu\(_2\)Zn(Ge\(_{1-x}\)Si\(_x\))Se\(_4\) Solid Solution as a Path Towards CRM-Free Top Absorber Layer for Tandem Solar Cells** Galina Gurieva, Sara Niedenzu, Alicia Manjon-Sanz, David C. Matzdorf, Melanie Kirkham and Susan Schor; 1Helmholtz-Zentrum Berlin, Germany; 2Oak Ridge National Laboratory, United States; 3FU, Germany

The search for sustainable, efficient, and cost-effective photovoltaic materials continues to be a challenge in the field of solar energy production. In particular, the development of critical raw material free top absorber layers for tandem solar cells is crucial in the effort to transition away from fossil fuels and towards a greener energy future. The emergence of compound semiconductors has provided an opening into low-cost fabrication of thin-film solar cells, made possible a reduction in absorber layer thickness, and therefore lead to a decrease in production costs.

In this work, we explore the potential of tetrahedral cation mutation in Cu-based quaternary chalogenide semiconductors (Cu\(_2\)ZnSi\(_x\)Ge\(_{1-x}\)Se\(_4\)) with the aim of finding a material with increased bandgap (ideally around 1.7 eV) and reduced structural disorder. Cu\(_2\)ZnSi\(_x\)Ge\(_{1-x}\)Se\(_4\) is known to be the main culprit of the low \(V_{OC}\) in the only CRM-free material used in PV technology at the moment (Cu\(_2\)ZnSn\(_x\)Se\(_{2-x}\)). One of the ways, previously shown to completely block structural disorder, especially the Cu\(_2\)ZnSn\(_x\)Se\(_{2-x}\) phase, is to replace Zn with Si. This approach adds an additional challenge of coordinating tetragonal kesterite structure in Cu\(_2\)ZnGeSe\(_4\) to the monoclinic wurtzite-kesterite type structure in Cu\(_2\)ZnSnSe\(_4\) with a significant increase in the bandgap as well [3].

We studied crystal structure, cation distribution and intrinsic point defect scenario in Cu\(_2\)ZnSn\(_x\)Ge\(_{1-x}\)Se\(_4\) mixed crystals (powder samples) by neutron diffraction. This method enables us to differentiate the isoelectronic cations Cu\(^{+}\), Zn\(^{+}\), and Ge\(^{4+}\) in the crystal structure analysis. These investigations enabled us to deduce the structural transition scenario of the Cu\(_2\)ZnGe\(_x\)Sn\(_{2-x}\) in the vicinity of the phase boundary.

To solve those issues, we have developed a new methodology to design and fabricate high-quality thin-film solar cells. We introduced a new approach to improve the performance of CIGS solar cells by using a high-quality AZO layer as the transparent conducting oxide. This approach not only improves the efficiency of the solar cells but also reduces the cost of production.

Sachit Grover, Mohammad Taheri, Taylor Hill, Elline Hettrachthy, Xiaoping Li, Dmitriy Krasikov, Gang Xiong, Darius Kuciauskas, Craig Perkins and Angus Rockett; First Solar, United States; 2Colorado State University, United States; 3National Renewable Energy Laboratory, United States; 4Colorado School of Mines, United States

With a bandgap of 1.72 eV, CdSe is well suited as a top-cell absorber in a two-junction tandem solar cell. We assess the potential of CdSe as an absorber through several measurements including external radiative efficiency (ERE), carrier density, polycrystalline grain-size and orientation. Well formulated films of CdSe are found to be n-type, hexagonal, and exhibit high ERE (>0.2%). Photoluminescence and sub-band external quantum efficiency confirm that this absorber is capable of implied open-circuit voltage above 1 V. A transparent conducting oxide coated on glass forms the electron-contact to the CdSe thin-film grown on top of it. The hole-contact is formed by organic hole-transport layers used in conjunction with a bilayer of transition metal oxide and thin-gold. Solar cells with measured V\(_{OC}\) > 1V have been demonstrated with this device structure. Despite good V\(_{OC}\), the devices made so far exhibit a limited fill factor and short-circuit current that cannot be completely accounted for by resistive or optical losses. By connecting a multitude of metrology techniques to device modeling results we conclude that the minority carrier collection is limited as the mobility and lifetime product (\(\mu\)\(\tau\)) product is about \(10^3\) cm²/V. This is attributed primarily to low hole mobility. Another key challenge is the unusually large ionization potential of CdSe at ~6.5 eV. SCAPS simulations indicate that improving the \(\mu\)\(\tau\) and reducing the band-offset at the hole contact should lead to improved carrier collection. Defect signatures identified through sub-band photoluminescence measurements suggest selenium vacancies could be the primary origin.

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Kesterite Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe), an earth-abundant and non-toxic material, is widely regarded as a promising light absorber for photovoltaic devices. Extensive research has focused on understanding recombination mechanism at the grain boundaries (GBs) which detrimentally impacts device performance, while their behavior within the material's bulk remains relatively unexplored. In this study, in-depth carrier recombination mechanism was investigated using atomic force microscopy-based characterization. A flexible CZTSSe thin film solar cell with an efficiency of 12.2% was prepared using a sputtering method on a Mo foil substrate. In particular, the sample was subjected to mechanical etching using a focused-ion beam to expose a plane at the specific depth. After that, electrostatic potential at the revealed surface was obtained by Kelvin probe force microscopy. At the surface and subsurface, formation of both conduction and valence bands was observed due to the widening band gap and increased charge accumulation at the GBs than in intragrain. The type of band bending is efficient for carrier separation as it repels electrons from the GBs while collects holes. [1] Additionally, a significantly high work function difference between bulk and interface reduced as the sample was subjected to grinding condition confirmed through Raman spectroscopy. Kelvin probe force microscopy reveals that the work function difference between bulk and interface reduced as the sample was subjected to LiF PDT process achieving a 10.4% efficiency with significant enhancement of carrier selectivity.

In-depth carrier recombination mechanism at grain boundaries in flexible kesterite thin film solar cells with 12.2% efficiency

Hwang2, Jaebaek Lee2, Dong-Hwan Jeon2, Yunae Cho1,1, Dae-Hwan Kim2, Jin-Kyu Kang2, Kee-Jeong Yang2 and William Jo1,1; 1Ewha Womens University, Korea (the Republic of); 2Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

H.K. Park et al., npj Flexible Electronics, 6 (2022) 91.
high efficiency kesterite absorbers. In particular, the distribution of secondary phases, grain quality, defect concentration, sulfur content and carbon residues will be assessed by micro-Raman spectroscopy. Also, the in-depth compositional homogeneity as well as Sn and Cu oxidation states will be characterized by XPS, revealing insights on the deep-defect density (Sn, lifetime related) and the shallow defect density (Cu, doping related). Moreover, the combination of XPS, UPS and PL will allow reconstructing the in-depth band structure, revealing key insights on the charge carrier transport of high quality kesterite materials.

Overall, the present study will reveal the most relevant factors induced by the Ag and Cd incorporation in the lattice of high efficiency kesterite absorbers, paving the way for further improvements without requiring the use of expensive, scarce and toxic elements.

9:45 AM EN11.09.07
Exploration, Prediction and Experimental Verification of Structure and Optoelectronic Properties in I$_2$-Eu-IV-X$_4$ (I = Li, Cu, Ag; IV = Si, Ge, Sn; X = S, Se) Chalcogenide Semiconductors
Max McWhorter, Tianlan Wang, Garret C. McKeown Wessler, Yi Yao, Ruiyi Song, Volker Blum and David B. Mitzi; Duke University, United States

Recent extensive research into the defect-resistant I$_2$-II-IV-X$_4$ (I = Li, Cu, Ag; II = Ba, Sr, Eu, Pb; IV = Si, Ge, Sn; X = S, Se) family of quaternary chalcogenide semiconductors suggests excellent potential for applications in photovoltaics, thermoelectrics, and nonlinear optics. Among these compounds, Eu-containing members are understudied, with only five previously synthesized members. Herein, we undertake a comprehensive study of the possible structures and electronic properties of all eighteen of the Eu-based combinations within I$_2$-Eu-IV-X$_4$ (I = Li, Ag; IV = Si, Ge, Sn; X = S, Se). To further understand the broader I$_2$-II-IV-X$_4$ family and test the geometric tolerance factor (reported in our previous work) as a tool for predicting potential stable structures, we first use hybrid density functional theory to systematically study these rare-earth-including I$_2$-Eu-IV-X$_4$ semiconductors. Lowest-energy quaternary structure candidates, band structures, and densities of states are computably predicted for all eighteen compounds. Following this screening process, the previously unknown compound CuEuSnSe$_4$ was selected and synthesized due to its predicted optoelectronic-relevant direct band gap. Optimal synthesis conditions were determined, and the experimentally derived structure, lattice parameters, and dispersion of CuEuSnSe$_4$ was found to be consistent with the predictions from both geometric tolerance factors and hybrid DFT, validating our predictive approaches and confirming a 1.55 eV band gap. Along with strong optical absorption in the visible range, this band gap suggests potential for CuEuSnSe$_4$ in photovoltaic and other optoelectronic applications.

10:00 AM BREAK

10:30 AM EN11.09.08
AgBiS$_2$ Nanocrystals: An Emerging Chalcogenide Absorber for Solution Processed Ultra-Thin Film Solar Cells
Gorsimasis Konstantatos; ICFO, Spain

In this talk I will discuss recent progress in our group on the development of a new class of thin film solar cells employing Silver Bismuth Sulphide as an emerging absorber for solution-processed eco-friendly solar cells. I will first introduce our first report on AgBiS$_2$ colloidal nanocrystal solar cells reporting power conversion efficiency of ~6% [1]. Then I will discuss on the opportunities of tuning the optical properties of this ternary compound via controlling cation disorder homogenization. We demonstrated that by homogenizing cation disorder in this compound we can drastically increase the absorption coefficient of this material as one with the high absorption amongst the semiconductors considered for photovoltaics. This takes advantage of the extended size of the device architecture led us to reach power conversion efficiencies of ~9% albeit using an absorber of only 35 nm [2]. In the last part of my talk I will describe our initial efforts on developing AgBiS$_2$ nanocrystal inks and their use with environmentally friendly solvents that led us to achieve efficiencies in excess of 7% [3]. I will conclude my talk with our most recent findings towards an improved passivation strategy of AgBiS$_2$ nanocrystal inks along with the formation of a double heterojunction in the device stack that led to power conversion efficiencies in excess of 10% with Voc of 0.5V, FF of 0.75 and Jsc of 28 mA/cm$^2$.

References:

11:00 AM EN11.09.09
Generalizing Synthesis Approaches for BaMS$_3$ Chalcogenide Perovskites and Related Materials
Shubhanshu Agarwal, Kiruba Catherine Vincent, Jonathan Turnley and Rakesh Agrawal; Purdue University, United States

Over the past decade, lead halide perovskites have witnessed a remarkable surge in solar device efficiencies. They possess a defect-tolerant crystal structure, showcasing outstanding optoelectronic and charge transport properties with tunable bandgaps. However, their progress is hindered by limited air, moisture, and thermal stability. While research on these exceptional materials should continue, there is a need to identify stable alternatives that exhibit similar appealing properties. Chalcogenide Perovskites have emerged as promising substitutes for lead halide perovskites. These materials also display defect tolerance and boast one of the highest light absorption coefficients. They demonstrate considerable stability against air, moisture, and thermal conditions, and their bandtails can be tailored for either single-junction or tandem solar cell applications.

Nevertheless, Chalcogenide Perovskites face a challenge in high-temperature synthesis. Historically, they have been synthesized at temperatures exceeding 900°C, either as powders or vacuum-deposited thin films. This high-temperature synthesis restricts the choice of substrates for material deposition. Additionally, not all the intermediary layers in a solar cell can endure such high temperatures. Therefore, it is imperative to synthesize these materials at the highest quality at low to moderate temperatures (≤600°C). In recent years, multiple research groups have successfully synthesized nanoprisms or inhomogeneous solution-processed films at low temperatures. However, a comprehensive understanding of the critical parameters enabling this achievement is still lacking.

In this work, we present a comprehensive framework for the synthesis of low-temperature BaMS$_3$ compounds (M=Zr, Hf, Ti) while discussing the interplay of precursor reactivity, availability of a transport agent, and an oxygen sink as the primary factors governing low-temperature synthesis with limited contamination. Furthermore, to validate our framework, we introduce four novel methods to synthesize BaMS$_3$ compounds at low temperatures, adhering to the guidelines outlined in the framework. Our results highlight a unique opportunity to synthesize BaMS$_3$ compounds using cost-effective precursors at low temperatures, offering guidance for future research on these materials.

11:15 AM EN11.09.10
Solution-Processed Chalcogenide Perovskite Thin Films Utilizing Amine Thiol Chemistry
Kiruba Catherine Vincent, Jonathan Turnley, Shubhanshu Agarwal and Rakesh Agrawal; Purdue University, United States

Growing technological advancements necessitate the development of versatile semiconductor materials capable of addressing diverse challenges. These materials must demonstrate robust stability, natural abundance, environmental friendliness, and tunable properties to cater to diverse applications, such as transistors, photovoltaics, thermoelectrics, LEDs, and more. Additionally, they should enable efficient and high-throughput synthesis. In the domain of photovoltaics, we can recognize two material systems competing to meet these requirements – emerging chalcogenides and lead halide perovskites. Emerging chalcogenides, such as Cu$_2$ZnSn(S,Se)$_4$, offer low toxicity and earth-abundant elements but have struggled to achieve high efficiencies. On the other hand, lead halide perovskites are breaking efficiency records, while also being highly air-stable and scalable.

In this work, we present a versatile, moderate-temperature solution-processing synthesis approach for BaZrS$_3$, a notable chalcogenide perovskite for tandem solar cell applications and for the related BaHfS$_3$ perovskite, suitable for LED and water-splitting applications. We utilized the well-known alkali thiocarbon fund system to blade coat our films. This method produced crack-free
films with minimal carbon residue and hence provided a promising step forward for the chalcogenide perovskite research. Subsequently, we conducted comprehensive material, morphological,
and optoelectronic characterizations on these films to gain valuable insights that can guide the fabrication of high-performance devices.

11:30 AM EN11.09.12
Routes Towards Improved Open Circuit Voltage in Sb2Se3 Solar Cells Thomas Shalvey and Jonathan D. Major; University of Liverpool, United Kingdom
Sb2Se3 is a defect tolerant, earth-abundant, stable semiconductor which has shown promise for low cost thin film photovoltaic power generation. It has a large absorption coefficient, suitable
band gap, simple binary composition and benign grain boundaries compared to typical 3D materials. These attributes have helped solar cell efficiencies to surpass 10% with relatively little
research effort in comparison to other absorber technologies. Despite this encouraging progress, the rate of improvement appears to have slowed recently as record devices approach the detailed
balance limit of short circuit current density. This means that further improvements are likely to originate primarily from increasing the open circuit voltage (Voc) and/or fill factor (FF).

Interfaces within a solar cell play a key role in both the Voc and FF, and therefore we have carried out a detailed study of the partner layers in the Sb2Se3 device structure either side of the
absorber layer. We have replaced the standard CdS front contact with TiO2, which has a wider band gap and is far more robust, making it more amenable to the subsequent high temperature
processing steps required for large grain, crystalline Sb2Se3 thin films. The initial solution processed TiO2 layer has been replaced with a sputter deposited film which improved device
uniformity and increased FF, however was prone to run-to-run variations in TiO2 film quality and the inconsistent appearance of ‘S’-shape JV curves. This issue has now been resolved through
careful control of the sputtering process, which has led to exceptionally high short circuit current densities and significantly improved FF, however the impact on Voc has been limited. The
back interface was then studied to determine the role of the hole transport material (HTM) in Sb2Se3 devices, and assess whether this could be an area for improvement. Several commonly
used organic HTM layers were compared against one another, and to a simple Au contact. The direct Sb2Se3-Au contact is limited by a secondary barrier causing ‘rollover’ in JV curves, despite
being seemingly favourable band positions. Each of the HTM layers demonstrated the ability to eliminate this secondary barrier, thereby lowering the series resistance and improving the fill
factor. Whilst this increases the champion efficiency, the improvement is relatively minor, especially considering the gradual oxidation of the Sb2Se3 back surface produces a similar self-
passivation effect. Instead, the HTM layers have a far more drastic effect on the average efficiency, which is attributed to a pinhole blocking effect by the solution processed organic films.
Nonetheless, Voc remains below 500mV for all devices tested.

After thoroughly investigating the partner layers, we are now turning our attention to the Sb2Se3 layer itself. We are currently exploring several routes to improve the quality of the absorber
layer. This includes a comprehensive study of dopants and defects in Sb2Se3, whereby the growth of high purity single crystals with the controlled addition of selected extrinsic dopants will
inform the most suitable compositions to target in thin films, both in terms of stoichiometry and p-type dopant incorporation. This is particularly important given the apparent chalcogen-poor
stoichiometry reported by most groups, especially for PVD processed films as well as the lack of rigorous control over doping type typically found in literature reports. The transfer of
knowledge gained from this single crystal study towards full devices will be accelerated via the use of a novel dual source close space sublimation chamber. This will allow co-deposition of
different source material with varying stoichiometry and dopant concentration, and therefore allow a wide range of material compositions to be rapidly deposited. These compositions will then
be assessed in terms of their implied Voc in order to carry out a loss analysis to identify the different contributions to the remaining deficit.

SESSION EN11.10: Chalcogenides PV/PEC II
Session Chairs: Sachit Grover and Gerasimos Konstantatos
Friday Afternoon, April 26, 2024
Room 335, Level 3, Summit

1:30 PM *EN11.10.01
Raman Spectroscopy at The Nanoscale: From Materials to Devices for Energy Conversion Mirjana Dimitrievska; Empa–Swiss Federal Laboratories for Materials Science and Technology, Switzerland
The pace at which major technological changes take place is often dictated by the rate at which new materials are discovered, and the timely arrival of new materials has always played a key
role in bringing advances to our society. Machine learning and advanced simulation and modeling techniques have recently massively accelerated the fast screening and discovery of new
materials. There is however today a bottleneck in the exploitation of these emerging materials. Indeed, after the materials’ existence and/or properties are predicted in silico, their synthesis
and integration in devices to demonstrate functionality remain major challenge. Fast and reliable characterization can significantly accelerate materials optimization and bring them to the forefront
of applications.

This talk will give an overview on the key role that Raman spectroscopy plays in accelerated semiconductor materials development for optoelectronic and energy conversion applications. I will
show how Raman spectroscopy could be effectively used for probing fundamental properties of materials, such as crystal quality, phase purity, and defects. This will follow with presenting
Raman-based methodologies for nanoscale detection of defects and impurities in materials, leading to establishing accurate phase diagrams and predictive synthesis-structure-property
relationships. I will focus on wide range of material systems, from thin films to 1D and 2D materials. Finally I will discuss Raman-based mapping of the defect structure/spatial of thin film solar
cells to optimize device structure.

2:00 PM EN11.10.02
Exploring Selenium Viability for Semi-Transparent Photovoltaics Arnau Torrens1, Ivan Caño Prades1, Alejandro Navarro1, Axel Gon Medalla2, Dionale Sylla2, Jose M. Asensi Lopez3, Sergio Girado1, Kunal Tiwari4, Edgardo Saucedo1, Zacharie Jehl Li-Kao1, Joaquim Puigdollers1, Pablo Ortega1 and Marcel Placidi1,2,3; EPFL, Switzerland; 1UPC, Spain; 2IREC, Spain; 3UB, Spain
Selenium (Se) holds historical significance as the first material used in a solar cell [1], in 1883, marking the initial exploration of materials capable of harnessing solar energy. However, it took
over a century before being seriously considered for photovoltaics, achieving at this time an efficiency of 5% [2] with the following Au/Se/TiO2/FTO architecture. In 2017, Todorov improved the
device architecture with more suitable selective contacts (Au/MoOx/Se/ZnMgO/FTO) and achieved the current worldwide efficiency record of 6.5% [3]. This breakthrough reignited interest in selenium
for photovoltaics, resulting in many recent research publications, with a particular focus on its potential as a top cell in tandem configurations, due to low temperature processing (melting point around 200 °C) and a direct bandgap of approximately 1.95 eV. However, Se appears also well suited for semi-transparent and/or indoor applications. Although its energy bandgap may initially not seem ideal for semi-transparent, recent findings suggest that very thin (less than 50 nm) amorphous silicon devices can achieve high visible transparency and impressive efficiencies, with promising light utilization efficiencies (LUE) of 0.7% [4]. Notably, the current world-wide efficiency record involved a 100 nm layer, but there is variability in the literature regarding the optimal absorber thickness, ranging from 100 nm to several micrometres, which could compromise its suitability for semi-transparent applications.

To check the viability of Se for semi-transparent PV, several amorphous layers of different thicknesses were prepared using an evaporation system. These layers were optically characterized
before and after hot plate crystallization at temperatures around 200 °C, a process widely reported in literature. This crystallization step, both on glass and FTO, resulted in the formation of
separated Se crystallized islands. In an effort to enhance the Se adhesion during crystallization, we initially avoided the use of Te, known to improve it, but potentially detrimental for device
performance. Additionally, we explored the option of performing the crystallization step on complete device architectures, incorporating various selective contact layers before Se deposition,
both in substrate and superstrate configurations, yielding valuable insights. All the results of this work will be presented at the MRS Meeting and the viability of selenium for semi-transparent
photovoltaics discussed.


2:15 PM EN11.10.03
Monolithic Selenium/Silicon Tandem Solar Cells Rasmus Nielsen; Andrea Crovetto, Alireza Assar, Ole Hansen, Ib Chorkendorff and Peter C. Veisberg; Technical University of Denmark, Denmark
Elemental selenium, the world’s oldest photovoltaic material, is reemerging as a promising inorganic thin-film PV absorber. With a direct bandgap of 1.95 eV in its trinodal phase and a high
absorption coefficient (>104 cm−1) in the visible region, it is a promising candidate for the top cell in tandem devices. Furthermore, its long-term air stability, monoatomic composition, and low
melting point of 220°C makes processing simple, low-cost, and compatible with most bottom cells.
We present the first monolithically integrated selenium/silicon tandem solar cell, demonstrating a highly encouraging open-circuit voltage of 1.68 V. Guided by device simulations, we identify critical energy barriers restricting the flow of charge carriers and investigate the potential of using other carrier-selective contact materials, resulting in a tenfold increase in the overall power conversion efficiency. In parallel with the tandem devices, we fabricate and characterize bifacial single junction selenium solar cells to gain insights into the polarity-dependent PV performance. In view of these results, we set forth strategies for further improving the device performance to realize higher efficiency selenium/silicon tandem solar cells.

2:30 PM EN11.10.04
Advancing CO2-to-Fuel Conversion: Synthesizing Tellurium-Based Semiconductors Shaham Quadir, Sage Bauers and Andriy Zakutayev; National Renewable Energy Laboratory, United States

Converting CO₂ into energy-dense liquid fuels through the use of renewable energy sources is considered as an important component of addressing ongoing and future energy crises. The most elegant method for this conversion is the photoelectrochemical (PEC) reduction of CO₂, but the key challenge in realizing this process effectively lies in the development of highly efficient photocathode materials. In particular, operationally stable p-type photocathodes that can provide electrons to facilitate the required CO₂ reduction processes are required.

In this study, we synthesized a new semiconductor thin film absorber material, Zn(GaTe₂)ₓ, via combinatorial sputtering approaches. The material was prepared using a 2-step process wherein room-temperature growth was followed with flash lamp annealing from 300 °C – 550 °C. Our X-ray diffraction study shows that Zn(GaTe₂)ₓ goes through a phase transition from cubic (F-43m) to tetragonal (I-42m) upon increasing Ga content, indicating a nearly complete ordering of atoms and vacancies on the zincblende lattice. Upon changing the cation ratio, a new peak observed in the X-ray diffraction pattern at an angle of ~35° with cubic structured Zn(GaTe₂)ₓ alloy, suggesting an intermediate amount of order can be achieved. At an optimal ratio of Zn:Ga:Te, Raman scattering reveals longitudinal optical (LO) peaks up to the third order when excited with a wavelength of 532 nm and displays superior photo luminescent properties, suggesting its potential to enhance CO₂ reduction capabilities. In the room temperature photoluminescence (PL) spectra, a defect emission is observed at 1.6 eV for all ratio of Zn(GaTe₂)ₓ.

Time-resolved photoluminescence (TRPL) data indicates a shift in lifetime during the transition from an ordered to a disordered state.

2:45 PM EN11.10.05
Photovoltaic Efficiency of Transition Metal Dichalcogenides Thin Films by Ab Initio Excited-State Methods Pedro Venezuela¹, Enesio Marinho Jr², Cesar Villegas³ and Alexandre Rocha³,¹Universidade Federal Fluminense, Brazil; ²Unesp, Brazil; ³Universidad Privada del Norte, Peru

Transition metal dichalcogenides (TMDCs) have garnered significant interest in optoelectronics, owing to their scalability and thickness flexibility. Due to their electrical and optical properties. In particular, thin films of TMDCs could be used in novel photovoltaic devices. In this work, we employ ab initio many-body perturbation theory within GwWg-BSE approach to accurately compute the optoelectronic properties of thin films of 2H-TMDCs composed of Mo, W, S, and Se. Subsequently, we evaluate their photovoltaic performance including excitation recombination effects, and show this is a key ingredient. We obtain efficiencies of up to 29% for a 100-nm thick film of WS₂, thus providing an upper limit. We also include other phenomenological recombination mechanisms that could be present in current samples. This slightly reduces efficiencies, indicating that even with current synthesis technologies, there is still potential for further enhancement of TMDCs' performance in photovoltaic applications.

3:00 PM BREAK

SESSION EN11.11: PEC, Other Materials
Session Chairs: Andrea Crovetto and Mirjana Dimitrievska
Friday Afternoon, April 26, 2024
Room 335, Level 3, Summit

3:30 PM EN11.11.01
Integrated Photoelectrochemical Systems for Scalable Water Splitting and CO₂ Reduction Virgil Andrei; University of Cambridge, United Kingdom

Photoelectrochemical (PEC) systems hold the potential to lower the costs of sustainable solar fuel production by integrating light harvesting and catalysis within one compact device.[1] However, current deposition techniques limit their scalability, while fragile and heavy bulk materials can affect their transport and deployment. Here, we first demonstrate the fabrication of lightweight artificial leaves by employing thin, flexible substrates and carbonaceous protection layers.[2] Lead halide perovskite photocathodes deposited onto indium tin oxide coated polyethylene terephthalate achieve an activity of 4266 μmol H₂ g⁻¹ h⁻¹ using a platinum catalyst, whereas photocathodes with a molecular Co catalyst for CO₂ reduction attain a high CO:H₂ selectivity of 7.2 under a lower 0.1 sun irradiation. The corresponding lightweight perovskite-BiVO₄ PEC devices display unassisted solar-to-fuel efficiencies of 0.58% (H₂) and 0.035% (CO₂), respectively. Their potential for scalability is demonstrated by 100 cm² standalone artificial leaves, which sustain a comparable performance and stability of ≈ 24 h to their 1.7 cm² counterparts. Bubbles formed under operation further enable the 30-100 mg cm⁻² devices to float, while lightweight reactors facilitate gas collection during outdoor testing on a river. The leaf-like PEC device bridges the gap in weight between traditional solar fuel approaches, showcasing activities per gram comparable to photocatalytic suspensions and plant leaves.[3] The presented lightweight, floating systems are compatible with modern fabrication techniques, and may enable open water applications, while avoiding competition with land use. The carbonaceous protection layers and rational design principles are successfully applied to an underexplored BiO light absorber, increasing the photocathode stability towards hydrogen evolution from minutes to months.[4] Similar PEC systems approaching a m² size can take advantage of the modularity of artificial leaves,[5] whereas thermoelectric generators can further bolster water splitting by utilizing waste heat to provide an additional Seebeck voltage.[6,7]


3:45 PM EN11.11.02
Photo-corrosion of CuBi₂O₄ Monitored by Operando Surface-Sensitive X-Ray Scattering Davide Derelli¹, Francesco Caddeo¹, Kilian Frank², Kilian Krötzsch², Patrick Ewerhardt³, Marco Krüger¹, Sophie Medicus¹, Lars Klemeyer¹, Marvin Skiba¹, Charlotte Ruhlmeier¹, Olof Gutowski³, Ann-Christin Dippel³, Wolfgang Parak¹ and Dorota Koziej¹; ¹University of Hamburg, Germany; ²Ludwig-Maximilians-Universität München, Germany; ³Deutsches Elektronen-Synchrotron DESY, Germany

The low stability of most semiconducting materials is one of the key factors that hinders the development of efficient and durable PEC water splitting cells. Monitoring the semiconductor-electrolyte interface during operation is crucial to understand all the underlying photo-corrosion processes and in turn establish appropriate mitigation strategies. In this work, we show a novel method to study operando the semiconductor-electrolyte interface during PEC operation. In particular, we developed a custom-built PEC cell that allows to assess operando the crystalline and morphological evolution of the semiconductor surface by grazing-incidence X-ray scattering, making use of two detectors to collect simultaneously the total scattering (Σ) and the small-angle X-ray scattering (SAXS) signals. We applied the technique to monitor the evolution of CuBi₂O₄ films, a promising p-type semiconductor to be used as a light harvesting material in the cathodic compartment of a PEC cell. Our operando approach, together with complementary X-ray absorption near edge spectroscopy (XANES) and inductively coupled plasma mass spectroscopy (ICP-MS) measurements, allows...
us to uncover the multiple degradation pathways affecting CuBi$_2$O$_4$ films performance during PEC operation. We find that CuBi$_2$O$_4$ reduces to metallic Bi and Cu, with the first one being the fastest process. We also find that Cu ions are released in the electrolyte during long-term stability tests, while at the same time BiPO$_4$ is formed at the surface of the CuBi$_2$O$_4$ film, due to the presence of PO$_4^{3-}$ ions in the electrolyte. Our work provides a detailed picture of the degradation mechanisms occurring at the surface of CuBi$_2$O$_4$ electrodes under operation and poses the methodological basis to study the photocorrosion processes of a wide range of PEC materials.

4:00 PM EN11.11.03 Spectroscopical Study on Electron Storage in Nano-Sized Tungsten Oxide Irene Martin$^{1,2}$, Luca Rebecchi$^{1,3}$, Andrea Rubino$^{1}$ and Ilka Kriegel$^{1}$; $^{1}$Istituto Italiano di Tecnologia, Italy; $^{2}$Politecnico di Torino, Italy; $^{3}$Università degli Studi di Genova, Italy

Dark photocatalysis is a promising technology for fuel production, which combines light harvesting properties with energy storing materials. The system involved would both work as a photocatalyst and rechargeable solar battery under illumination, so that electrons released during the discharge could be exploited for ‘dark’ reactions, e.g. CO$_2$ reduction reaction (CO$_2$RR) and hydrogen evolution reaction (HER). Thus, it also implies the investigation of materials capable of storing electrons for hours [1]. Tungsten(III) oxide (WO$_3$) has drawn interest owing to its ability of trapping electrons through intercalation of positive ions, accommodating negative charges at W centres [2], and being utilised for prolonged anti-corrosion activity in the dark (i.e. photocathodic protection) [3].

In the work herein presented we investigated the potential use of WO$_3$ nanoparticles for dark photocatalytic CO$_2$RR by means of photo-doping process. We analyzed the charge storing properties of the WO$_3$ colloidal nanoparticles via UV-VIS-NIR spectroscopy, by monitoring absorption changes under illumination. The increase of the LSPR peak and the blue shift of the band gap due to the Moss-Burstein effect indicate that WO$_3$ undergoes electron accumulation, similar to what has already been reported for indium tin oxide (ITO) and other metal oxide nanocrystals (MO NCs) [4]. The results obtained in our study suggest that these materials can be valid candidates for next generation of photocatalytic systems.


4:15 PM EN11.11.04 Layered Intergrowths with SrBi$_2$O$_4$Cl$_3$ and Bi$_2$GdO$_4$Cl as Building Blocks Towards Stable Visible Light Mediated Photocatalysis. Nayana Christudas Beena and Sara Skrabalak; Indiana University, United States

Photocatalysts capable of visible light absorption that are also durable against photocorrosion are crucial to achieving overall water splitting. A unique layered intergrowth comprised of SrBi$_2$O$_4$Cl$_3$ and Bi$_2$GdO$_4$Cl building blocks is achieved by a flux-based approach. The feasibility of tuning the intergrowth’s optoelectronic properties was investigated by varying the stoichiometry of the intergrowths. Intergrowth formation resulted in the destabilization of the O-2p and Cl-3p orbitals, elevating the valence band maximum position. In addition, local symmetry changes around the Bi sites due to the presence of Sr$^{2+}$ and Gd$^{3+}$ cations play an important role in lowering the conduction band minimum position. Furthermore, the minimal recombination of photogenerated charge carriers can be attributed to the charge separation due to the presence of an internal static electric field between the layers. The systematic study of these materials conducted using X-ray diffraction and electron microscopy provides insights into how intergrowth stoichiometry serves as a lever to optoelectronic properties and photocatalytic performance of visible-light responsive multi-metal oxyhalide intergrowths.

SYMPOSIUM ES01

Next-Generation EV Battery Materials—Bridging Academic, Government and Industry Research April 23 - May 9, 2024

Symposium Organizers
Jeffrey Cain, General Motors
Zachary Hood, Argonne National Laboratory
Matthew McDowell, Georgia Institute of Technology
Yue Qi, Brown University

Symposium Support
Bronze
Georgia Tech Advanced Battery Center
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* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION ES01.01: Research and Collaboration Across Academic, Government and Industry Sectors
Session Chairs: Jeffrey Cain and Zachary Hood
Tuesday Morning, April 23, 2024
Room 425, Level 4, Summit

11:00 AM *ES01.01.02
Advanced Battery Materials from Labs to Markets Yi Cui; Stanford University, United States
The automotive industry's transition to renewable energy relies, among others, on layered oxides, like LiNixCoyMnzO2 (NCM) and LiNixCoyAlzO2 (NCA), for high-performance applications. These materials promise enhanced capacities within a stable cycling range. While the theoretical specific capacity is above 270 mAh/g, in reality only around 240 mAh/g can be realized under conditions closely resembling real-world applications. Interestingly, specific capacities exceeding 260 mAh/g can be achieved upon very slow cycling, highlighting that capacity loss is caused by sluggish lithium diffusion. A structural characteristic strongly linked to charge transport is the presence of intercalation site defects, including Ni_Li substitutional point defects, which are inherently found in state-of-the-art Ni-rich layered oxide materials. To investigate the effect of these defects have on cycling performance, we have developed a synthesis method for perfectly layered LiNi0.5O2 (LNO) through sodium to lithium ion exchange. Our analyses, including X-ray techniques and NMR spectroscopy, confirm that this route produces a material entirely devoid of Ni_Li defects. Overall, this method serves as a foundation for re-evaluating the impact of factors that are well recognized for influencing the cyclability, such as nickel content, defect concentration and particle size.

We attribute an ambivalent role to Ni_Li defects, recognizing their negative effect on lithium diffusion, particularly limiting the discharge capacity. However, we also identify a secondary contribution of Ni_Li defects, which is not readily observable in state-of-the-art LNO materials due to the intrinsic presence of substitutional point defects. As the defect concentration approaches zero, the high-voltage regime (high SOC) becomes unstable, as evidenced by increased oxygen release and capacity loss of more than 10%. Owing to the ambivalent nature of Ni_Li defects, we propose a hypothesis that achieving an optimal balance between diffusion and stabilization is crucial to fully harness the material's capacity.

2:00 PM ES01.02.03

Unlocking The Full Capacity of Ni-Rich Layered Oxide Cathodes: The Impact of Lithium Site Defects on Diffusion and Stability

Leonhard Karger1,2, Svetlana Korneychuk1, Wessel Van den Bergh1,2, Aleksandr Kondrakov2,4, Jürgen Janek2,5 and Torsten Brezesinski1,2; 1Karlsruhe Institute of Technology, Germany; 2BELLA, Germany; 3BASF Corporation, Germany; 4Justus-Liebig-Universität Giessen, Germany

The ever-increasing demand for renewable energy and electric vehicles calls for high-energy-density rechargeable batteries. Cathode materials such as layered oxides play a crucial role in determining batteries' energy density and safety. LiNi0.5Mn1.5O4 (NMC), as the dominating cathode, has been successfully commercialized for many years. In addition, there is a consensus that integrating NMC cathodes into all-solid-state batteries (ASSBs) is an effective way to achieve high energy densities. However, NMC cathodes are still facing many challenges, particularly, during the perusing of the high Ni concentration and high cut-off voltages. In the presentation, we will discuss the interface degradation of the NMC cathode at multiple length scales. By comprehensive imaging and spectroscopic techniques, we could bridge the degradation phenomenon from the electrode scale to the atomic scale. We will present the challenges of characterizing the surface properties of the cycled layered cathode and summarize our strategies that can enhance the surface stability of NMCs. Our fundamental understanding will inform the design principles at multiple length scales in batteries. Shifting our focus to solid-state batteries (SSBs), there is a growing body of research on SSBs incorporating NMC cathodes and argyroite solid electrolytes (SEs). However, these advanced ASSBs face significant challenges in terms of low initial Coulombic efficiency and rapid capacity degradation. Therefore, we will also explore the interface degradation mechanisms in composite SSB-NMC cathodes utilizing the NMC/Li2PSi3Cl combination as a platform.

2:15 PM ES01.02.04

A Multimodal Investigation of Controlled Oxygen-Vacancy Formation to Prevent the Degradation in Ni-Rich NMC811 Cathode

Sumaiyatul Ahsan1,2, Svetlana Korneychuk1, Wessel Van den Bergh1,2, and Byron D. Gates; Simon Fraser University, Canada

Identifying high performing and cobalt-free transition metal-based energy storage solutions are a key feature for a cost-effective transition away from the fossil fuel economy. To inform the design of new materials, and the engineering of existing battery materials, a strong understanding of fundamental processes within the device is required. Lithium-ion batteries (LIB) are periodically evaluated by post-mortem (PM) autopsy, wherein a battery is disassembled and each cell component is analyzed separately, providing insights towards which areas of study are most critical to prevent device failure. When investigating cathodes in this manner, typically only whole-cathodes are studied where active material particles are encased in polymeric binders and adhered to a current collector. This provides some access to PM characterization through surface imaging, but cannot demonstrate a full understanding of the consequences of electrochemical cycling on the inner and base layers of cathode particles. Additionally, completely structural and composition characterizations are challenging due to the organics present. Seeking to develop a more detailed understanding of how cathodes particles deteriorate within an LIB, a procedure has previously been developed in the Gates Research Group to non-destructively harvest single cathode particles from their binder matrix for comprehensive post-mortem study. Building on this methodology, a systematic investigation into single cathode particles is presented.

In this work, cobalt-free LiNi0.5Mn1.5O4 cathode particles are harvested at different points in their cycle life and characterized as PM isolated single particles to identify and track trends of cathode deterioration over time. High-resolution scanning electron microscopy images of hundreds of individual particles are systematically assessed for physical features of deterioration from cycling. These assessments are supported by X-ray diffraction and standard electrochemical analyses. With use of statistical analyses applied to the detailed imaging data, a template is created to enhance failure mechanism diagnostics and contribute experimental evidence to models of cathode degradation, informing the design of future cost-effective materials.

2:30 PM ES01.02.05

Deciphering The Interfacial Chemistry and Degradation Pathway of Layered Cathode Materials

Linqin Mu; Arizona State University, United States

Seeking to develop a more detailed understanding of how cathode particles deteriorate within an LIB cell, a procedure has previously been developed in the Gates Research Group to non-destructively harvest single cathode particles from their binder matrix for comprehensive post-mortem study. Building on this methodology, a systematic investigation into single cathode particles is presented.

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temperatures has been analyzed using the in-situ X-ray diffraction (XRD) measurement. The intensity ratio of planes (003)/(104) decreases for oxygen-reduced structure, indicating a disordered cation layer with increased Oxygen loss. Oxygen occupancy reduces from 0.99 to 0.975, indicating the presence of 1.52% oxygen vacancy in the structure. Ni occupancy in the Li layer rises from 0.17 to 0.21, indicating increased Ni$^{2+}$-Li$^{+}$ mixing. Increased concentration of Ni$^{2+}$ induces more cation mixing. Hence, the oxidation state of modified NMCs has been investigated with X-ray absorption near-edge spectroscopy (XANES). The coordination structure was further examined through extended XAS fine structure (EXAFS). A first-principical calculation-based computational model was employed to calculate oxygen vacancy formation energy and a Quantum Espresso-based Xspectra package was used to reproduce the experimental metal K-edge XANES data to analyze the optimum vacancy concentration required for the higher oxidation state of Ni (3+,4+). Finally, an ex-situ transmission electron microscopy study of the modified structure reveals the crack propagation in surface layers and the effect of the dense dislocation layer in crack annihilation.

References:

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2:30 PM *ES01.02.05

Single Crystal Ni-Rich Cathodes for Advanced Li-Ion Batteries

Jie Xiong$^{1,2}$, Yang Gao$^{1}$, 1Pacific Northwest National Laboratory, United States; 2University of Washington, United States

High energy Ni-rich cathode will play a key role in advanced Li-ion batteries, but it suffers from moisture sensitivity, side reactions and gas generation. Single crystalline Ni-rich cathode has a great potential to address the challenges present in its polycrystalline counterpart by reducing phase boundaries and materials surfaces. However, synthesis of high-performance single crystalline Ni-rich cathode is very challenging. This talk will discuss a cost-effective drop-in approach to synthesize and scale up high-performance single crystal Ni-rich cathode materials enabled by nanoscale phase segregation during calcination process.

3:00 PM BREAK

3:30 PM *ES01.02.06

Ceramic Nanowires for Li-Ion Batteries with Improved Safety, Energy and Power

Gleb Yushin$^{1,2}$, 1Georgia Institute of Technology, United States; 2Sila Nanotechnologies, Inc., United States

The recently discovered low-cost and highly scalable synthesis of ceramic nanowires or nanofibers enable their applications in high-performance Li-ion batteries, solid-state batteries and supercapacitors. Highly flexible ceramic separators produced from aluminum or magnesium oxide or oxyhydroxide nanowires or tunable dimensions enhance the safety, rate capabilities and energy density of a broad range of electrochemical energy storage devices. Compared to polymer or ceramic-coated polymer separator members, ceramic nanowire separators are not flammable or combustible and offer outstanding thermal stability, thereby improving battery safety. The higher porosity, smaller thickness and excellent wetting of ceramic nanowire separators by electrolytes result in lower resistance, higher efficiency, higher power, faster charging and often improved cycle stability of Li-ion batteries. Their lower attainable thickness also contributes to higher specific and higher volumetric energy densities in Li-ion cells. This invited talk will provide an overview of our progress in synthesis and energy storage-related implementations of this promising technology.

4:00 PM *ES01.02.07

Porous Boron Nitride as Scaffold for Silicon Composite Anode Material

Michael Karl$^{1,2}$, Alena Kalyakina$^2$, Johanna Ranninger$^2$, Christoph Dräger$^2$, Stefan Haufe$^2$ and Simone Pokrant$^1$;

$^1$University of Salzburg, Austria; $^2$Wacker Chemie AG, Germany

Aiming for higher specific energies and energy densities, lithium-ion battery (LIB) research explores silicon (Si) as an alternative high-capacity negative electrode/anode material. One of the challenges associated with employing Si materials in LIBs is their strong volume expansion upon lithiation (more than 300%), leading to significant stress in the particles. In the case of micrometre-sized Si particles, they tend to crack or detach from the conductive network of the electrodes. An effective way to overcome these issues is to apply nano-structured Si. However, reducing structure dimensions to the nanoscale results in increased specific surface areas, which promote a larger amount of electrolyte decomposition and subsequent solid electrolyte interface (SEI) formation. This irreversible process consumes electrolyte and diminishes the energy density of a LIB cell by immobilizing lithium.

Composite materials address this challenge, one possible concept is combining carbon and nano-Si to micrometre-sized particles. A successful approach to synthesize such composites is infiltrating silicon in porous carbon particles (~65% porosity) by chemical vapour deposition (CVD) using silane. Due to the micrometre particle size, the resulting composite exhibits a moderate surface area (below 25 m$^2$ g$^{-1}$), significantly limiting SEI formation. The reduced volume expansion of the particles leads to promising electrochemical performance, but some drawbacks persist. Porous carbon is not temperature stable in ambient atmosphere and may ignite at temperatures above 250 °C.

Because of these drawbacks there is a growing interest in non-conducting and more safe alternatives. Hexagonal boron nitride (h-BN) fulfils the necessary requirements to replace carbon surfaces in contact with the electrolyte are not able to provide electrons for decomposition reactions. Thus, using insulating scaffolds is another factor reducing the undesired SEI formation, in addition to the generally low particle surface area of the Si composite concept.

In this work we present novel silicon-boron nitride composite materials, their fabrication, and their electrochemical performance as a negative electrode/anode material in a LIB. The synthesis of high-porous h-BN scaffold is carried out in a furnace under nitrogen flow, using boric acid and an amide as precursors. Ammonia atmosphere forms inside the furnace upon heating, allowing the formation of h-BN sheets. By adjusting the processing time and temperature, a highly defective h-BN structure forms, exhibiting porosities of over 65%. The porosity is similar to those achievable for the porous carbon particles. In the next step, pores are filled with silicon using the same CVD-process as reported in literature for carbon composite materials. Employed in a LIB electrode, the composites show competitive cycle lives of over 500 cycles with 80% capacity retention at a capacity exceeding industry standard graphite by more than a factor of two.

References:

U.S. DOE Supports Data-Driven Strategies to Accelerating Battery Commercialization

Chibueze Amanchukwu; University of Chicago, United States

Lithium metal batteries (LMBs) promise high energy densities for electrified transport. Liquid electrolytes are currently state-of-the-art, but they are highly volatile and flammable and exacerbate safety concerns. Solid state batteries promise to address the safety concerns plaguing liquids but suffer from highly resistive electrode/electrolyte interfaces. In our work, we explore the use of low melting inorganic molten salts as electrolytes for LMBs. These electrolytes do not contain organic moieties and are not susceptible to the reactions that plague organic moieties in conventional ionic liquids and small molecule electrolytes. Furthermore, they are non-volatile and nonflammable, retaining the promise of solid-state systems. We show these electrolytes have high ionic conductivities at ~80°C, enable smooth lithium deposits, support high Coulombic efficiencies, and can support battery cycling. These inorganic molten salts with accessible melting temperatures open a new class of electrolyte media for both conventional and next generation battery chemistries.

SESSION MT02.03/ES01.03: Joint Keynote Presentation
Session Chairs: Jeffrey Cain and Feng Wang
Wednesday Morning, April 24, 2024
Room 321, Level 3, Summit

8:00 AM *MT02.03/ES01.03.01
U.S. DOE Supports Data-Driven Strategies to Accelerating Battery Commercialization
Changwon Sub; U.S. Department of Energy, United States

The Department of Energy’s Advanced Materials and Manufacturing Technology Office (AMMTO) focuses on developing and deploying advanced manufacturing and materials technologies to support the DOE’s mission to ensure America’s energy security and environmental well-being. AMMTO invests in energy storage research, development, demonstration, and deployment (RD&D) to help stakeholders improve efficiency, cut costs, and make materials, devices, and systems with superior performance. It is recognized in the energy storage space that effective utilization of data-driven experiment, analysis and modeling is critical to accelerating the development and optimization of new technologies, improving manufacturing processes and reducing cost, leading to reduced time to commercialization and deployment of transformative technologies.

In this talk, AMMTO’s approach to data-driven technology development and manufacturing will be highlighted. In addition, there will be a robust discussion of a wide variety of DOE’s efforts in the context of technical and manufacturing challenges regarding scale-up and performance that still prevent the battery manufacturing community from achieving cost targets and commercial viability.

SESSION MT02.04/ES01.04: Joint Session: Materials, Manufacturing and Emerging Opportunities in Data-Driven Analysis and Modeling
Session Chairs: Jeffrey Cain and Feng Wang
Wednesday Morning, April 24, 2024
Room 321, Level 3, Summit

8:30 AM *MT02.04/ES01.04.01
Resource-Aware Materials, System and Process Design for Battery Materials
Elsa Olivetti¹, Kevin Joon-Ming Huang¹, Karan Bhuwalka¹, Mrigi Munjal¹, Richard Roth¹, Romain Guillaume Billy², Daniel Beat Müller², Thorben Preim² and Jennifer L. Rupp²; ¹Massachusetts Institute of Technology, United States; ²Norwegian University of Science and Technology, Norway; ³TU Munich, Germany

This presentation will provide a systems perspective on scaling needs in battery materials for electric vehicles ranging from our use of language model methods to source micro-challenges in the academic literature around electrode/electrolyte interfaces to materials supply chain issues including the impact on local communities for extraction of these materials. By providing a systems analysis on the extraction, beneficiation and refining complexities associated with these technologies linked to the more fundamental research activities at the bench, this talk aims to provide insight at multiple length scales of the challenge in realizing next-generation EV battery materials.

9:00 AM *MT02.04/ES01.04.02
Paradoxical Role of Structural Degradation of High-Nickel Layered Oxides and Electrode Crosstalk in Capacity Retention upon Storage of Lithium-Ion Batteries
Hyejeong Hyun¹, Hyo jung Yoon², Subin Choi¹, Juri Kim², Tom Regier³, Zachary Arthur³, Seokkoo kim² and Jongwoo Lim¹; ¹Seoul National University, Korea (the Republic of); ²LG Energy Solution, Korea; ³Canadian Light Source, Canada

Batteries undergo both active cycling and prolonged idle storage throughout their lifespan. While degradation mechanisms induced by cycling and their mitigation techniques have been deeply studied, the specific effects of storage without cycling remain largely unexplored. Notably, battery performance also sees a unique decline over time, contingent on the state-of-charge (SoC) when the batteries are at rest. Capacity decline during SoC70 storage primarily arises from electrode slippage and Li inventory loss in a full cell. This is accompanied by a minor structural breakdown of Ni-rich layered oxides cathodes. Conversely, SoC100 storage leads to a more pronounced structural impairment of Ni-rich cathodes and pronounced side reactions. Intriguingly, these severe side reactions curtail the Li inventory loss, electrode slippage, and the reduction of full-cell capacity during SoC100 storage. In addition to standard degradation processes, such as Li/Ni cation mixing, the formation of surface reconstruction layers, and the emergence of exhausted phases, cathodes stored at SoC100 displayed an unexpected contraction of interlayer spacing during post-storage cycling, highlighting the atypical effects of storage. Based on the mechanisms of capacity reduction highlighted in this study, we propose strategies to counteract the aging caused by storage. This research offers valuable perspectives for refining battery production and management to enhance their calendar lifespan.

9:15 AM *MT02.04/ES01.04.03
Improving Rate Capability in High-Energy Thick Lithium-Ion Batteries through Graded and Structured Electrodes
Chih-Hsuan Hung¹, Srikanth Allu² and Corie L. Cobb¹; ¹University of Washington, United States; ²Oak Ridge National Laboratory, United States

Next-generation electric vehicles (EVs) made with Lithium-ion batteries (LIBs) require both higher energy density and higher power density to reach $80/kWh at a 300-mile range as laid out by the US Department of Energy.¹ LIBs made with nickel-rich layered oxide cathodes and graphite anodes can maintain energy densities around 250 – 300 Wh/kg at low charge and discharge rates.²,³ However, due to slow ion transport encountering with increasingly thick electrodes, these LIBs exhibit poor rate capability, with more than 50% capacity loss experienced at 4C and higher charge/discharge rates.⁴ Graded electrodes (GEs) are one approach that have been proposed to improve the efficiency of lithiation in thick electrodes. GEs assemble two or more electrode layers with differing porosity values into a single thick electrode. In addition to GEs, structured electrodes (SEs) are another means to enhance transport in thick electrodes by redistributing electrode materials on a micron-scale into line- and grid-pattern electrode architectures. The controlled electrode architecture introduced by SEs reduces the effective electrode tortuosity and enables better electrolyte infiltration in thick battery electrodes.⁵,⁶ Our research aims to uncover new SE and GE electrode designs for EV batteries. In this study we explored the individual and combined benefits of SEs and GEs for improving the rate capability of high-energy LIBs through computational modeling in VIBE,⁷ a suite of multi-scale and multi-physics battery modeling tools developed by Oak Ridge National Laboratory. A three-dimensional physics-based continuum-scale electrochemical model was used in VIBE to model a series of electrode designs for a comparative electrode design analysis, including conventional electrodes, GEs, SEs, and combined SE and GE geometries. A LiNi0.5Mn1.5O4 with C027.5 cathode and graphite anode are used as model material systems due to their current relevance for EVs. To ensure a consistent analysis, the active material loading is held constant for all models to allow us to study the effect of mass distribution and electrode design on LIB rate capability. Our current results show that at high discharge rates of 2C, 4C, and 6C, SE LIBs demonstrate a 33 – 37 % improvement in energy density, and the combined SE and GE LIB electrode designs demonstrate a 46 – 67% improvement in energy density over conventional cells. This study demonstrates the advantage of implementing SEs and GEs for thick electrode LIBs with improved rate capability. These results affirm the need to pursue new manufacturing approaches that enable SE and GE electrode designs to enhance the performance of existing LIB materials.
References

Acknowledgement
This material is based upon work supported by the U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy (EERE) under the Advanced Materials and Manufacturing Technologies Office, Award Number DE-EE0010226. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

9:30 AM *MT02.04/ES01.04.04
Battery Informatics in Devices & Discovery Steven B. Torrisi; Toyota Research Institute, United States

The increasing accessibility of battery data, both on the device and materials level, is driving exciting new questions in battery science and engineering. These span the full materials life-span, from how fleet-level users can best leverage on-vehicle diagnostic data to how R&D scientists can identify promising new materials. In this talk, I will highlight recent work which explores both device prediction tasks related to vector databases for batteries and history-agnostic degradation prediction as well as data-driven discovery of new principles in cathode design. Attention will be paid to the ways in which industrial, governmental, and academic labs can complement each other's strengths in the collection and use of data.

10:00 AM BREAK

SESSION ES01.05: Battery Technology and EVs
Session Chairs: Jeffrey Cain and Yue Qi
Wednesday Morning, April 24, 2024
Room 425, Level 4, Summit

10:30 AM *ES01.05.01

The acceleration of electric vehicle adoption has elicited perceived and sometimes real shortages in raw materials supplies for Li-ion batteries that lead to price volatility [1] and motivate the search for alternative “post-Lithium” cell chemistries. This presentation will begin with an overview of existing Na-ion cell chemistries and showcase their strengths and limitations in a comparison of currently achievable cell-level energy densities between Na-ion cells and Li-ion cells. Then, Prussian Blue analog (PBA) materials will be discussed in depth as active materials for Na-ion cells. Natron Energy has commercialized the first Na-ion battery that is entirely based on PBA active materials in both positive and negative electrodes. In contrast to earlier concepts that rely on hexacyanoferrate redox couples, we invented a PBA negative electrode material based on hexacyanomanganate(II/I) redox chemistry. Upon charging, sodium manganese hexacyanomanganate accepts an unusually high occupancy with intercalated Na ions, while the C-coordinated Mn site attains a +1 oxidation state with low-spin configuration that is typically only encountered in organometallic Mn compounds. The combination of these two unique properties leads to a low sodiation potential near 1.9 V vs. Na/Na+. When sodium manganese hexacyanomanganate negative electrodes are paired with positive electrodes based on hexacyanoferrate PBAs, full cell voltages up to 2V can be achieved. While the open structure of PBAs and low voltage limit cell energy density, these cells are capable of extremely fast full charge (up to 20C) and deep discharge (up to 60C) with high energy retention and no risk of thermal runaway. Owing to the minimal structural changes of the PBA host lattice (less than 3% volume change during cycling), this PBA-PBA cell architecture can achieve exceptionally long service life with tens of thousands of cycles [2]. Insight into Natron’s progress in scaling up active materials production and mass manufacturing of cells will be given, and the unique high-rate deep-discharge capabilities will be discussed in the context of commercial applications where Na-ion batteries can close important gaps that are not addressed with Li-ion batteries, especially behind-the-meter applications such as uninterruptible power supplies, demand charge management, and support for electric vehicle fast charging.


11:00 AM ES01.05.02
Chemical Pre-Processing of Transition Metal Chalcogenide Electrode Materials Joseph Stiles, Brianna L. Hoff, Fang Yuan, Scott B. Lee, Craig Arnold and Leslie Schoop; Princeton University, United States

We have identified H_xCrS_2, which is produced through proton exchange of NaCrS_2, as a new sodium ion battery electrode with improved performance over its parent material. H_xCrS_2 sees a measured capacity of 728 mAh g^-1 and an improvement in diffusion constant of three orders of magnitude better than NaCrS_2. Notably, the structure of H_xCrS_2 consists of an alternating crystalline/amorphous motif as a result of Cr migration during desodiation which is seemingly responsible for the improvement in performance. The alternating structure enables access to reversible Cr redox in the material which supports the high capacities. A range of techniques is used to study the mechanism by which the presence of the amorphous phase allows for these improvements. We then apply similar synthetic conditions to a library of other materials in which removal of the alkali ion results in transition metal migration to identify candidates which may feature similar structural motifs and study their electrochemical behavior. Through the development of pre-processing techniques such as proton exchange, we can re-explore electrode chemistries which may have previously been rejected due to migration of the transition metal in the absence of capacity limiting side reactions.

11:15 AM ES01.05.03
Developing Manganese- and Iron-Rich Cathodes for Sodium-Ion Batteries Ivrenem L. Abate; Massachusetts Institute of Technology, United States

Decarburizing transportation, grid and industries require low-cost batteries made from abundant, environmentally friendly, sustainable elements in the critical minerals supply chain. To this regard, Mn- and Fe-rich sodium-ion battery cathodes are particularly interesting. However, the practical use of these materials is inhibited by their structural instability upon deep desodiation. In this talk, I will present how my group is combining insights from advanced computational (both ground and excited state) experimental (electrochemistry, x-ray scattering and electron microscopy) techniques 1) to prevent structural disorder during deep desodiation via thermodynamic and kinetic design principles and 2) to develop environmentally sustainable cathodes.

11:30 AM *ES01.05.04
Pathways to Commercially Relevant Lithium Metal Batteries for EVs and Electric Aircraft Brett A. Helms; Lawrence Berkeley National Lab, United States

Lithium metal batteries are widely regarded as essential to the greater effort to electrify transportation beyond EVs, while also providing opportunities for fast charge and extended driving range. Yet, while energy density considerations have primarily driven this perspective and R&D investments, there are ongoing challenges in managing ion fluxes across interfaces, which impacts aspects of both performance and cycle life. Here, I will discuss the design of ion-transporting materials, both solids and liquids, which enable lithium metal cell chemistries to meet demanding performance requirements in conventional and emerging uses cases, including eVTOL. I will discuss data-driven research paradigms that accelerate the identification of ion-transporting materials and those that create useful interphases capable of high areal ion fluxes relevant to high power batteries and those capable of fast charge. I will further discuss how these discoveries have been translated into larger cell formats and provide context into how to advance to packs and modules.

SESSION ES01.06: Materials and Manufacturing
Session Chairs: Zachary Hood and Justin Sadowski
Lithium-ion batteries (LiBs) have become an indispensable part of modern energy storage technologies, characterized by their high energy density, lightweight design, long lifespan, and low self-discharge rates. However, the relentless pursuit of innovation seeks to further elevate LIB capabilities. This study focuses on the development of a high-performance anode material for LiBs, introducing a composite combining nickel iron oxide (NiFe₂O₄) and nitrogen-doped reduced graphene oxide (N-doped rGO). NiFe₂O₄ is well-established for its high theoretical capacity, while N-doped rGO offers excellent conductivity and environmental sustainability. The NiFe₂O₄/N-doped rGO composite material exhibits several advantages. Firstly, it exhibits a high capacity, thanks to the synergistic combination of NiFe₂O₄ and N-doped rGO, resulting in increased energy storage capabilities. Secondly, the outstanding conductivity of N-doped rGO enhances charge transfer kinetics, enhancing the rate of lithium-ion transport and reducing energy losses during charging and discharging processes. Moreover, the NiFe₂O₄/N-doped rGO composite material demonstrates effective cycling stability, minimizing capacity degradation over extensive cycles. Its superior rate performance ensures efficiency even at high current rates, making it particularly suitable for high-power applications or scenarios requiring fast charging. Finally, the use of N-doped rGO and nickel iron oxide reduces reliance on finite natural resources and minimizes adverse environmental impacts, aligning with the vision for sustainable energy storage solutions. In conclusion, the NiFe₂O₄/N-doped rGO composite material developed in this work presents a promising solution to meet the present energy storage demands and provides a route for the development of environmentally friendly and sustainable energy technologies.

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**Anticorrosive Electrolyte Designs for Lithium Metal Batteries**

Electrolyte is a critical component in lithium metal batteries (LMBs). It is recognized that the solvation structure near the Li ion plays a crucial role in determining the solid-electrolyte-interphase (SEI) properties and thus the reversibility of Li plating and stripping. The concepts of highly concentrated electrolyte (HCE) and locally highly concentrated electrolyte (LHCE) have received much attention these days because of their ability to induce inorganic-rich SEI that is beneficial in improving the cycle life. Nonetheless, most of fluorinated solvents used as diluents in LHCEs have low LUMO levels such that Li metal can easily corrode upon contact with the electrolytes. We will introduce my group’s recent approach of adding an inert solvent in the electrolyte to serve as a kinetic barrier for fluorinated diluents in the so-called swollen SEI layer. The given approach can be expanded to a variety of electrolyte combinations with which both the cycle life and calendar life of LMBs can be improved simultaneously.

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**Challenges and Solutions to Lithium Metal Battery Design for High Performance Applications**

Cuberg designs and manufactures high energy density, liquid electrolyte-based, lithium metal battery systems for an array of electric aviation and high performance automotive applications. The challenges and phenomena associated with reversibly cycling a lithium metal anode are numerous: the consumption electrolyte in side-reactions, the formation of thick and resistive solid-electrolyte interfaces, and the formation of mossy, high surface area lithium deposits. The emergence of these phenomena and their role in limiting cycle life performance are also well-established in literature, but mostly limited to simple constant current charge and discharge profiles. However, when evaluating the cycle life performance of lithium metal pouch cells during realistic aviation flight missions or high-performance automotive drive profiles, these degradation phenomena can be considerably more subtle and complex. In this talk, we will discuss some of the challenges we observe, considerations we have, and design approaches we take when constructing lithium metal batteries for these realistic and high-performance applications.
small amount of bismuth doping can have a profound impact on the cycling stability of this cathode material, both in half cells and also in hard carbon anode full cells. Furthermore, ambient environment storage of the Bi-doped materials (even in humid environments) does not reduce performance and in some cases seems to improve it. This finding holds promise for enhanced feasibility and reliability in sodium-ion batteries and could be beneficial for advancing the application of sodium-ion batteries in large-scale applications.

5:00 PM ES01.07.03
Low-Cost Silicon from Natural Sand for Lithium-Ion Batteries and Its Electrochemical Response to Oxygen Content
Zhigang Z. Fang, Zehua Lin, Pei Sun and Chengsheng Zhou; University of Utah, United States

The cost-effectiveness is an essential factor to be considered for the commercial viability of Silicon (Si) anode for lithium-ion batteries, alongside factors such as electrochemical performance and safety considerations. Here, we utilized low-cost natural sand as raw material and employed the magnetothermic reduction method to produce battery-grade silicon with an impressive ~98% yield rate. Additionally, Si with varying oxygen content was produced by adjusting the stoichiometry of magnesium and reduction temperature. We also explored the effect of oxygen content on the electrochemical performance as an anode. Our findings indicated a linear decrease in both the initial discharge capacity and initial coulombic efficiency with increasing oxygen content. In contrast, the capacity retention at the 20th cycle and the lithium-ion diffusion coefficient exhibited an opposing trend. By comparing the electrochemical impedance spectroscopy and lithium-ion diffusion coefficient of those samples, we observed that the sample with high-oxygen content samples displayed less change in charge transfer impedance after cycling, while their lithium-ion diffusion coefficient exhibited a more pronounced increase.

5:00 PM ES01.07.05
High-Performance CuO as an Anode Material via Facile Synthesis for Lithium-Ion Batteries
Nischal Ojha1, Sunny Choudhary1, Brad Weiner2, Gerardo Morelli3 and Ramatiyar1;
1University of Puerto Rico, Rio Piedras, United States; 2University of Puerto Rico at Rio Piedras, United States

While carbon matrices have demonstrated effectiveness in enhancing the electrical conductivity and accommodating the volume expansion of CuO-based anode materials in lithium-ion batteries (LIBs), achieving an optimized utilization ratio of the active CuO component remains a challenging obstacle. In this investigation, we have devised a straightforward synthesis approach to fabricate ultrafine CuO nanoparticles integrated within a high surface area carbon matrix denoted as CuO@C. We discovered that with the use of sodium carboxymethyl cellulose binder and fluoroethylene carbonate additives, this anode exhibits enhanced performance compared to previous reports. This material, owing to its distinctive architecture, reveals a notable reversible capacity of 800 mA h g\(^{-1}\) at 100 mA h g\(^{-1}\) following 100 cycles and exhibits prolonged cycling stability, recording a reversible capacity of 450 mA h g\(^{-1}\) at 400 mA h g\(^{-1}\) over 500 cycles. The exceptional lithium-storage performance of CuO@C is attributed to its high surface area carbon matrix and the presence of ultrafine CuO nanoparticles, which afford a greater abundance of exposed active sites favorable to electrochemical reactions.

Keywords: CuO, high surface area, carbon matrix, lithium-ion batteries, electrochemical reactions

5:00 PM ES01.07.06
Investigation of 3-Dimensional Structured Anodes for Fast Charging in Lithium-Ion Batteries
Michelle E. Katz1, Vinh Q. Nguyen1, Daniel Abraham2 and Corie L. Cobb1; 1University of Washington, United States; 2Argonne National Laboratory, United States

Lithium-ion batteries (LIBs) with fast charging capabilities are a critical component in electric vehicle (EVs) to reduce charging times to 15 minutes or less.1 Current research and development efforts are focused on optimizing fast charging behavior with graphite and silicon-based anodes. However, these anode materials face challenges which include irreversible side reactions, lithium plating, and cracking caused by volumetric strain, all of which limit their fast charge behavior. As an alternative to graphite and silicon, the use of Li\(_4\)Ti\(_5\)O\(_{12}\) (LTO) anodes in LIB cells has been discussed.2,3 LTO is considered a zero-strain material and, furthermore, does not develop a solid-electrolyte-interphase (SEI) during electrochemical cycling. These properties help improve cycling stability and safety at high discharge rates. Although the higher nominal voltage of LTO (\(\sim1.5\) V vs. Li/\(Li^+\)) leads to lower energy density, recent research into material modification and discharge strategies that improve LTO energy density make it more attractive for fast charging.4 Additionally, 3-dimensional (3D) electrodes have been investigated by researchers over the last few decades to improve power density of battery cells.5,6 In this work, we take this concept a step further and investigate the impact of 3D structural design on the fast charge performance of LTO anodes. Our objective is to determine if a re-design of electrode architecture can enable better fast charging behavior for rates up to 10C and make these LTO anodes competitive with graphite-based anodes.

Acknowledgement
This work was funded in part by a Defense Advanced Research Projects Agency (DARPA) Young Faculty Award and Director's Fellowship under grant number D19AP00038. The views, opinions, and findings expressed in this work are those of the authors and should not be interpreted as representing the official views or policies of the Department of Defense or the U.S. Government, and no official endorsement should be inferred. This is approved for public release and distribution is unlimited.


5:00 PM ES01.07.07
Novel Design and Scalable Synthesis of Silicon Anodes for High-Energy Lithium-Ion Batteries
Mushtaq Ahmad Dar1, Hany Sayed Abdo1, Mohammad Rezaul Karim1, Nabeel H. Alharthi1 and Dong-Wan Kim2; 1King Saud University, Saudi Arabia; 2Korea University, Korea (the Republic of)

As the world races toward achieving net-zero emissions by 2050, there will inevitably be a surge in demand for high-energy batteries. Silicon is one of the most promising anode materials for next-generation lithium-ion batteries because it possesses a theoretical specific capacity that is almost ten times higher than that of the current graphite anode. However, silicon-based anodes usually suffer from a short cycle life due to the particle pulverization caused by the substantial volume change of Si (~300%) during the lithiation and delithiation process. To improve the cyclability of silicon anodes, we developed a novel scalable process for synthesizing bulk-core, porous-shell silicon that can alleviate the detrimental effects caused by volume expansion. By precisely controlling the processing parameters, both the size of the bulk core and the thickness of the porous shell can be tailored. The silicon with novel structure exhibits excellent electrochemical performances, much greater than 3D porous and bulk silicon counterparts. To further enhance the cycling performance of silicon, carbon coating was implemented via polyolamine precursor. The resulting Si-C composites showed good cycling performance up to 500 cycles. Our research offers a novel, scalable, low-cost production route for silicon anodes for high-energy lithium-ion battery applications.

5:00 PM ES01.07.08
Single-Point Hydrothermal Synthesis, Characterization and Electrochemical Properties of SnO\(_2\) Nanostructures
Mushtaq Ahmad Dar1, Hany Sayed Abdo1, Mohammad Rezaul Karim1, Nabeel H. Alharthi1 and Dong-Wan Kim2; 1King Saud University, Saudi Arabia; 2Korea University, Korea (the Republic of)

Nanostructured materials have gained significant interest in the field of science owing to their exceptional characteristics and efficacy in numerous fields. Tin oxide (SnO\(_2\)) shows potential as a material for energy storage purposes, namely in lithium-ion batteries. The electrochemical properties of this material make it a promising candidate for anode materials, allowing for effective storage and release of lithium ions during charging and discharging processes. Tin oxide's effective electrical conductivity enhances battery performance, making it a crucial constituent in the development of advanced and efficient energy storage technologies. This investigation into the electrochemical characteristics of tin oxide represents a significant advancement in the effort to enhance the efficacy and reliability of battery technology across several fields. In this research, we successfully produced tin dioxide (SnO\(_2\)) nanostructures inspired by sea-urchins by using a hydrothermal process strategy. The hydrothermal approach, known for its low
investigating the electronic and lattice structures of LFSO is of great importance, as Fe-based redox systems exhibit simultaneous anionic redox and O2 release, and as a result, always display highly hysteretic charge-discharge behavior. Consequently, the pursuit of novel cathode materials from economically viable and earth-abundant elements gains increasing attention, holding potential for enhanced thermal stability and cycle performance of SIBs. For this purpose, we have designed and synthesized a TPDA-NiCOF via post-synthetic linker exchange for high-performance cathodes in sodium-ion batteries. Our results show that the 4.2 V plateau is accompanied by a classical two-phase transition, and the electronic charge compensation stems from a novel high-valent Fe-based redox couple. While the presence of Sb in the system limits its commercial interest, LFSO serves as the ideal model system in which to characterize high-valent Fe redox. Some preliminary work carried out into substitution/doping strategies opens the door to achieving low-hysteresis, high voltage Fe redox in layered oxides using earth-abundant elements, which could serve to reduce our dependence on Co/Ni-based positive electrodes.

We also perform X-ray diffraction (XRD) experiments to study the structural transformations during the (dis)charge. We use FeL-edge Resonant Inelastic X-ray scattering (RIXS) in conjunction with O-edge RIXS (both of which are known to be sensitive to TM 3d orbitals) to accurately characterize the changes in Fe and O valence orbital occupancies during (dis)charge. Coupled with DFT calculations, we present a complete picture of the electronic structure changes that accompany electrochemical (de)lithiation and identify the redox-active species in the reaction. We also perform X-ray diffraction (XRD) experiments to study the structural transformations during the (dis)charge. We use FeL-edge Resonant Inelastic X-ray scattering (RIXS) in conjunction with O-edge RIXS (both of which are known to be sensitive to TM 3d orbitals) to accurately characterize the changes in Fe and O valence orbital occupancies during (dis)charge.

Recently, researchers have been looking into alternate cathode materials to get around these limitations and enhance the energy density and cycle performance of SIBs. Therefore, we have done this study, which focuses on the synthesis of highly crystalline and porous bipolar redox-active polyimide-linked covalent organic framework (COF), and deployed it as a cathode material for SIBs. For this purpose, we have designed and synthesized a TPDA-NiCOF by incorporating n-type carbonyl-based reversible redox centers into the p-type triphenylamine-based structure via a post-synthetic linker exchange technique. This approach was successful and led to the formation of a highly crystalline and purposeful polyimide, which was not achievable via direct synthesis. The TPDA-NiCOF exhibits a wide potential window of 1.0 to 3.6 V vs. Na+/Na, making it a good candidate as a cathode for SIBs. An advantageous specific capacity of 120 mAh/g at 0.02 A/g can be achieved by doping 50% CNT into the COF. This allows the capacity to be maintained at 92 mAh/g at 1.0 A/g, and even after 5000 cycles, COFs demonstrate the cathode's extraordinarily extended longevity. Our synthetic TPDA-NiCOF shows an average discharge voltage of 2.1 V, outperforming most recently published COF hosts. We believe this approach will pave the way for boosting the synthesis and design of COFs with more desired properties for energy storage and other various applications.

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The growth of radially arranged rutile-SnO2 nanostructures with a size range of 1.5-2 µm was confirmed by conducting an in-depth analysis using a variety of methods, such as x-ray diffraction (XRD), thermogravimetric analysis (TGA), fourier-transform infrared spectroscopy (FTIR), field-emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). The combined results from these investigations have verified the formation of nanostructures with a high level of purity, that have a unique radial pattern. The nanostructures had a unique morphology consisting of separate nanorods, each measuring roughly 300 nm in length and with widths varying from 30 to 50 nm. The building of rutile-SnO2 nanostructures exhibited a high degree of homogeneity and accuracy, as evidenced by the extensive characterization techniques. Interestingly, electrochemical experiments used to evaluate these nanostructures features revealed their remarkable reversible lithium storing ability. The nanostructures demonstrated a consistent and reversible lithium storage capacity of 590 mAh.g\(^{-1}\), even after undergoing 30 cycles of charging and discharging. This demonstrates their potential as exceptional materials for lithium-ion battery applications. The controlled synthesis of radially ordered rutile-SnO2 nanostructures with excellent electrochemical characteristics is demonstrated in this work, which offers significant insights into the process.
Thus, this study focuses on varying LMNO synthesis temperatures to probe the phase transition and its implications. Results indicate a parabolic relationship between the electrochemical performance of LMNO materials and synthesis temperature. This trend primarily stems from the dynamic transformation of Li-ion diffusion channels. This study not only enhances our understanding of LMNO materials but also lays the groundwork for the future development of cutting-edge cathode materials relying on the LSx structure.

(4) Shi, B.; Gii, J.; Li, L.; Wang, C.; Vu, A.; Croy, J. R.; Thackeray, M. M.; Lee, E. LT-LiMn 0.5 Ni 0.5 O 2: a unique co-free cathode for high energy Li-ion cells. Chemical Communications 2021, 57 (84), 11099-11012.

5:00 PM ES01.07.14
Unveiling The Correlation between Synthetic Parameter and Structural Stability of O-Redox Cathodes via Time-Resolved XRD Analysis on The Solid-State Synthesis Seungmin Lee1, Sang Hyuk Gong1, Kyungwo Choi2, You Seung Rim3, Teakjib Choi1 and Hyunsouk Kim1; 1Korea Institute of Science and Technology, Korea (the Republic of); 2Sungkyunkwan University, Korea (the Republic of); 3Sejong University, Korea (the Republic of)
The demand for high-energy-density sodium-based batteries has led to the investigation of the oxygen-redox (O-redox) reaction to increase the theoretical capacities of conventional cathodes. This O-redox reaction is triggered by introducing substitutes or vacancies in the transition metal (TM) layer, which generate the non-bonding electrons of lattice oxygens, thus providing additional capacity [1]. In terms of O-redox stability, the atomic arrangement of substitutes or vacancies in TM layer, which affects the distance between redox-active oxygens and TM migration barrier, is critical for determining the O-redox stability [1-2]. However, the construction mechanism of O-redox cathodes during synthesis and its correlation with O-redox stability has not been fully understood.

Herein, we aim to investigate the construction mechanism of O-redox cathodes during solid-state synthesis and evaluate their O-redox stability. Specifically, we monitor the evolving structure of cathode precursors using time-resolved X-ray diffraction (TR-XRD) analysis by controlling the synthetic parameter. Subsequently, in-depth structural studies on the cathodes are conducted using advanced characterization tools such as high-resolution electron microscopy (HR-TEM) and X-ray absorption spectroscopy (XAS). Our structural analyses reveal how the synthetic parameter influence the final cathode structure, and we further correlate these findings with the O-redox stability using the electrochemical tests.

5:00 PM ES01.07.15
Thermo-Electrochemical Characterization of LiNi0.8Co0.15Al0.05O2/Graphite-Si Full Cells Across Commercial and Academic Form Factors Patrick J. Weist1,2, Nicolas Leport3, Rachel Carter1, Corey T. Love1, Laurent Pilon1,3,3, and Gordon Waller1; 1US Naval Research Laboratory, United States; 2American Association for Engineering Education, United States; 3University of California, Los Angeles, United States
As electrochemical systems increase in size from academic coin cells to commercial 18650’s and beyond, so too do concerns about how excess heat generation can compromise the cell’s safety and performance. Heat generation in lithium ion battery systems can be attributed to a number of factors, including (1) reversible heat from desired electrochemical reactions (2) joule heating from polarization effects (3) heat of mixing from concentration effects and (4) unwanted side reactions, all of which are influenced by the system’s state of charge (SoC) and operating c-rate. Coupling galvanostatic cycling with isothermal calorimetry enables the observation of heat flow during cell operation and the quantification of the system’s thermodynamic parameters, like enthalpy and entropy. Enthalpy calculations (kJ/mol of Li+), found experimentally by the monitoring of heat flow during cell operation, must carefully correlate observed heat signatures and electrochemical processes. This requires low c-rates where overpotentials are suppressed and the observed heat flow is dominated by reversible heat. On the other hand, systematically recording the relationship between temperature and equilibrium voltage at various SoCs provides entropic information and informs the thermodynamics of the system at rest [1]. Theoretically, these thermodynamic measurements should be material specific that rely on the electrochemical redox pair’s SoC, but experimental measurements are also influenced by form factor. When thermo-electrochemical characterization is performed on commercial 18650’s, slow c-rates (~C/10) can be used to ensure that the observed heat is dominated by reversible heat from electrochemical reactions, but thermodynamic conclusions are limited to the cell level because both the cathode’s and anode’s active material exhibit changing entropic behavior with respect to their lithiation state. To be attributed to the working electrode’s active material through Li metal half-cell experimentation, but are not as robust as commercial cells.

In this work, entropic and enthalpic experiments were performed on a commercial Li0.8Co0.15Al0.05O2 (NCA)/Graphite-Si Li-ion 18650 cell using isothermal calorimetry coupled electrochemical testing. Then, in order to observe contributions from the anode and the cathode separately, the commercial 18650 was disassembled and the recovered electrodes were used to create coin cell half-cell with Li metal anodes and coin cell full cells. Coin cell level calorimetry found that the majority of heat generation during (dis)charge originated from the electrode undergoing delithiation. Additionally, full coin enthalpic potential measurements were reconstructed from coin cell half-cell data, elucidating which electrode-specific processes dictate the system’s thermodynamics at different SoCs. Together, heat signature collected across commercial and academic form factors and cell configurations compile an index of thermodynamic and kinetic behaviors of the NCA/Graphite-Si system. These findings will be discussed through a lens meant to inform decisions around commercial cell operation conditions while also serving as an experimental template for thermo-electrochemical comparisons of Li-ion battery systems across commercial and academic form factors.


5:00 PM ES01.07.17
Enhancing Interfacial Reaction Rates in Extremely Fast Charging Li-Ion Batteries Using Linear Carbonate-Based, High-Concentration LiPF6 Electrolytes Hyuntae Lee1, Hyeonguk An1, Hongjun Chang2, Janghyuk Moon2, Sujong Chae3 and Hongkyung Lee1; 1Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of); 2Chung Ang University, Korea (the Republic of); 3Pukyong National University, Korea (the Republic of)

With the growing reliance on battery-operated vehicles, addressing the safety concerns associated with lithium plating, exacerbated by high cell polarization during extremely fast charging (XFC) of Li-ion batteries, becomes imperative. This research probes into the effects of Li+ desolvation and the solid-electrolyte interphase (SEI) chemistry on cell polarizations through the use of linear carbonate (LC)-based, high-concentration LiPF6 electrolytes (LPCes). Within the LC group, dimethyl carbonate (DMC) is identified as the most thermodynamically favorable for electrochemical reactions, but thermodynamic conclusions are limited to the cell level because both the cathode’s and anode’s active material exhibit changing entropic behavior with respect to their lithiation state. To be attributed to the working electrode’s active material through Li metal half-cell experimentation, but are not as robust as commercial cells.

In this work, entropic and enthalpic experiments were performed on a commercial Li0.8Co0.15Al0.05O2 (NCA)/Graphite-Si Li-ion 18650 cell using isothermal calorimetry coupled electrochemical testing. Then, in order to observe contributions from the anode and the cathode separately, the commercial 18650 was disassembled and the recovered electrodes were used to create coin cell half-cell with Li metal anodes and coin cell full cells. Coin cell level calorimetry found that the majority of heat generation during (dis)charge originated from the electrode undergoing delithiation. Additionally, full coin enthalpic potential measurements were reconstructed from coin cell half-cell data, elucidating which electrode-specific processes dictate the system’s thermodynamics at different SoCs. Together, heat signature collected across commercial and academic form factors and cell configurations compile an index of thermodynamic and kinetic behaviors of the NCA/Graphite-Si system. These findings will be discussed through a lens meant to inform decisions around commercial cell operation conditions while also serving as an experimental template for thermo-electrochemical comparisons of Li-ion battery systems across commercial and academic form factors.


5:00 PM ES01.07.19
Fabrication of High-Performance Organic Electodes through Field-Induced Charge Transfer for Li-Ion Batteries Jihye Park1, Jun Hyung Gyu2, Dong Hwa Lee2, Hoon Shin3, Jung-Yong Lee2 and Jae Yong Song2; 1Korea Research Institute of Standards and Science, Korea (the Republic of); 2Pohang University of Science and Technology, Korea (the Republic of); 3Pohang Advanced Institute of Science and Technology, Korea (the Republic of)

Despite promising theoretical predictions, the practical performance of organic-based electrodes often falls short of expectations due to a low density of active sites, limited ion diffusivity, and high solubility in the electrolyte. In this study, we present an organic nanocomposite cathode with exceptional electrochemical stability achieved through an electric field-induced charge-transfer reaction in the nanocomposite, comprising 5,10-dihydro-5,10-dimethylphenazine (DMPZ) and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA). Cryogenic milling was adopted to form a porous nanocomposite structure. The charge-transfer reaction effectively suppresses elution, and the porous structure increases the density of active sites. As a result, the porous nanocomposite showed a remarkable improvement in organic cathode performance, including an unprecedented high capacity retention of 90% over 600 cycles, a high initial capacity of 209 mAh g\(^{-1}\), and excellent rate capability at high current densities. The performance enhancement mechanism of the organic nanocomposite cathode is elucidated through experimental analyses, including ex-situ XPS, PIFM, FTIR, and DFT calculations on the energy levels of organic components.
Development of computational resources and methods have taken a lead in current times to reliably predict promising electrode materials for the rechargeable batteries in a cost and time effective manner. This may provide an efficient route to guide experimentalists in improving the battery performance and realizing the next-generation energy efficient batteries for grid storage and electrical vehicles in terms of capacity and energy density. In view of that, using various approaches like the first-principles density functional theory and evolutionary algorithms, we comprehensively study a variety of materials to develop an understanding at the atomistic level and predict efficient anode materials for the Li-ion batteries.

8:00 AM ES01.08.01
In-Silico Investigation of Promising Anode Materials for Li-Ion Batteries Privy Johari; Shiv Nadar University, India

Boron nitride (BN) has gained attention in the field of electrochemistry due to its controllable surface chemistry and adjustable bandgap, along with mechanical robustness, thermal stability, and chemical inertness. In this work, we examine Li-ion migration behavior in defective hexagonal BN (hBN) using first-principles methods, towards applications as a separator or protected membrane in Li batteries. By comparing the activation energies of Li-ion diffusion along in-plane (between the BN layers) and out-of-plane (across the BN layers) pathways, we find that pristine hBN permits in-plane Li-ion diffusion with a relatively low energy barrier of 0.34 eV, while prohibiting out-of-plane Li-ion diffusion due to a high energy barrier (6.68 eV). Introducing defects is found effective to unlock the out-of-plane diffusion pathway despite the fact that local vacancies can trap Li and influence its consequent in-plane diffusion near the vacancy sites. In addition to the investigation of Li-ion transport behavior in hBN, we evaluate its phase stability by directly extracting its phase evolution kinetics from large-scale molecular dynamics simulations enabled by a machine-learning interatomic potential. We further investigate the impact of microstructure on the BN phase evolution kinetics and link it to various experimentally relevant conditions, which can ultimately allow us to establish strategies to fabricate BN membranes with desired properties.

9:00 AM ES01.08.02
Multiscale Modeling of Phase Evolution and Li-Ion Transport Kinetics in Boron Nitride Membranes Yilong Zhou, Marcos Calegari Andrade, Bo Wang, Tae Wook Heo, Tuan Anh Pham, Sergei O. Kucheyev and Liwen Wan; Lawrence Livermore National Laboratory, United States

Boron nitride (BN) has gained attention in the field of electrochemistry due to its controllable surface chemistry and adjustable bandgap, along with mechanical robustness, thermal stability, and chemical inertness. In this work, we examine Li-ion migration behavior in defective hexagonal BN (hBN) using first-principles methods, towards applications as a separator or protected membrane in Li batteries. By comparing the activation energies of Li-ion diffusion along in-plane (between the BN layers) and out-of-plane (across the BN layers) pathways, we find that pristine hBN permits in-plane Li-ion diffusion with a relatively low energy barrier of 0.34 eV, while prohibiting out-of-plane Li-ion diffusion due to a high energy barrier (6.68 eV). Introducing defects is found effective to unlock the out-of-plane diffusion pathway despite the fact that local vacancies can trap Li and influence its consequent in-plane diffusion near the vacancy sites. In addition to the investigation of Li-ion transport behavior in hBN, we evaluate its phase stability by directly extracting its phase evolution kinetics from large-scale molecular dynamics simulations enabled by a machine-learning interatomic potential. We further investigate the impact of microstructure on the BN phase evolution kinetics and link it to various experimentally relevant conditions, which can ultimately allow us to establish strategies to fabricate BN membranes with desired properties.

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

10:00 AM *ES01.08.06
On-Demand Capacity Extraction of Cu Current Collector for Li Batteries Jun Ho Lee, Wenbo Zhang, Sanzeeda B. Shuchi, Sarah Holmes, Sang Cheol Kim and Yi Cui; Stanford University, United States

Irreversible loss of lithium due to its high reactivity lead to decrease in the energy density of lithium batteries. The decomposition of electrolyte forms electrochemically inactive solid electrolyte interface (SEI) layer on the surface of anodes, and lithium used to form SEI cannot be retrieved. Especially, large portion of Li⁺ from cathodes are consumed during the initial cycle of LIB, and the energy density of full cells are significantly decreased afterwards. In order to supplement this loss, various pre-treatment strategies such as introducing additional lithium compounds on either anodes or cathodes have been reported. However, Cu current collector, has not been considered as a source of extra lithium and considered as dead weight, mainly due to its electrochemical inactivity with lithium. Here, we introduce a novel concept that involves utilizing Cu current collector as a lithium reservoir and extracting lithium on-demand during cycling to enhance the capacity of lithium batteries. By annealing Li and Cu, we show that Li-Cu alloy, a two-phase alloy, is formed with controllable capacity of lithium at an extraction potential of 1.2 V vs Li/Li⁺. Electrochemical and structural analyses revealed the irreversible extraction of Li during the phase transformation of the alloy. Based on electrochemical analyses, we demonstrated that Li-Cu alloy can serve as a pre-lithiated current collector in LIB, resulting in substantial increase of initial coulombic efficiency of anodes of half cells. Furthermore, relatively high extraction potential of Li-Cu alloy enabled on-demand extraction of lithium during discharging in full cells. In addition, pre-lithiated current collectors can also be employed to anode-free Li metal batteries, and capacity retention and cycle life of were observed to be improved. We anticipate that using current collector for lithium storage could enhance energy density of batteries while reducing reactivity of Li.

11:00 AM ES01.08.09
Manufacturing Structured Lithium-Ion Battery Electrodes Using Acoustophoresis Emilie Armstrong, Keith E. Johnson, Ozgenur Kavcicglu, Matthew R. Begley and Corie L. Cobb; 1University of Washington, United States; 2University of California, Santa Barbara, United States; 3Argonne National Laboratory, United States

Scalable manufacturing of high-energy and high-power Lithium-ion batteries (LIBs) with fast charge behavior is crucial for lowering the cost and enhancing the performance of LIBs for electric vehicles (EVs) to meet DOE’s current target of $80/kWh by 2030. Commercial LIBs are composed of planar electrode cell stacks that can be optimized for energy or power, but not both simultaneously. Structured electrodes (SEs) mitigate these performance trade-offs by using three-dimensional nanostructures in the anode or cathode to engineer porosity and tortuosity to

Argyrodyte Solid-State Electrolytes: Overcoming Barriers to Interfacial Stability for Advanced Manufacturing of Solid-State Batteries

1. Department of Energy,

References


Acknowledgement

This material is based upon work supported by the U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy (EERE) under the Advanced Manufacturing Office (AMO) Award Number DE-EE0009112. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government. This work was partially carried out at the Materials Engineering Research Facility (MERF) at Argonne National Laboratory, which is supported by the DOE, Office of Energy Efficiency and Renewable Energy, and the Vehicle Technologies Office, under the Contract No. DE-AC02-06CH11357. The MERF synthesized size-specific NMC-622 for the project.

11:15 AM *ES01.08.10
On Advancements toward Sustainable and Environmentally Friendly Battery Technologies Rana Mohtadi1,2; 1Toyota Research Institute of North America, United States; 2Tohoku University, Japan

Current Li-ion batteries are considered the key driver toward societal electrification, however, limitations in the performances of these batteries coupled with their reliance on critical elements call for the consideration of alternative energy storage systems. A variety of batteries are poised in theory to offer improved performances, such as those utilizing metallic anodes and cathode incorporating earth abundant elements. Herein, we will discuss these technologies and share important advancements made in our laboratories.

SESSION ES01.09: Solid-State Batteries
Session Chairs: Matthew McDowell and Thomas Yersak
Thursday Afternoon, April 25, 2024
Room 425, Level 4, Summit

1:30 PM ES01.09.01
Argyrodyte Solid-State Electrolytes: Overcoming Barriers to Interfacial Stability for Advanced Manufacturing of Solid-State Batteries Idochukwu Ezeh1,2 and Zachary D. Hood1; 1Argonne National Laboratory, United States; 2Georgia Institute of Technology, United States

Lithium argyrodyte solid-state electrolytes (SSEs) exhibit many desirable properties such as high ionic conductivity (>1 mS/cm) at room temperature1,2,3 and greater ductility than most oxide SSEs,2 enabling roll-to-roll cell fabrication relevant for EV battery packs. However, their instability in ambient air and at the Li||SSE and cathode||SSE interfaces presents challenges for scaled production and limits their cell performance.4,5 In this presentation, we present two interfacial strategies – those that involve dopants as well as pseudocapacitive interlayers – to overcome interfacial stability issues associated with argyrodyte-type SSEs (Li6PS5Cl) in solid-state batteries. By using zinc, oxygen, and chlorine as dopants, we show that members within the Li6-2x2yZnxPS5-x-yOxCl1+y system enable fast ion transport in thick battery electrodes. However, a scalable manufacturing process for creating SSEs over the large areas at the time scales required for cost-effective LIB manufacturing is still needed. To address this, we have developed a manufacturing process based on principles of acoustophoresis. Using acoustic forces, acoustophoresis rapidly assembles particles in a fluid on a micron scale, generating SE patterns over large, cm-scale areas.6 To date, we have used acoustophoretic principles to pattern SE cathodes made from size specific Lithium Nickel Manganese Cobalt Oxide (NMC-622). NMC-622 was selected as our electrode patterning material due to its relevance for EV applications. We have investigated how processing conditions can be used to tune the thickness and features of NMC-622 SEs and have conducted initial electrochemical testing.

References


1:45 PM ES01.09.02
Low-Temperature, Scalable Synthesis of Electrolyte Films: Spray Deposition of Sulfides and Oxides Colton Ginter1,2 and Zachary D. Hood1; 1Argonne National Laboratory, United States; 2University of Chicago, United States

Given the projected tenfold increase in global battery demand over the coming decade,1 it is imperative to prioritize the advancement of cost-effective, secure, and high-energy-density energy storage solutions for electric vehicles. Solid-state synthesis methods, those that are traditionally used for inorganic solid-state electrolytes (SSEs), generally require higher process temperatures, are incompatible with roll-to-roll processing, and produce millimeter-thick pellets, barring integration in energy-dense solid-state batteries (SSBs).2 New, scalable methods for low-temperature manufacturing of SSEs at thicknesses comparable to polymer separators (~20 μm) are required for widespread adoption of SSBs.2,3 Here, we describe a spray deposition process to form dense Li12+2xZnxPS5-x-yOxCl1+y films with room-temperature ionic conductivities greater than or equal to 10-4 S/cm and 10-8 S/cm, respectively, as determined by electrochemical impedance spectroscopy (EIS). Through precise control of spray parameters (including total mass, concentration, deposition rate, and substrate temperature), we successfully crafted dense, crack-free amorphous films, reaching thicknesses of 14.2 ± 0.3 μm for LPSCI and 0.188 ± 0.054 μm for LBO, all at remarkably low temperatures, below 200 °C. We augmented our findings with concurrent in situ Raman spectroscopy and EIS during the film annealing process, which revealed the presence of polyamorphism in the deposited films and a crystalization process occurring at temperatures lower than conventional solid-state methods. Our research also delves into the diverse applications of these materials in SSBs and other next-generation electrochemical devices.
Control of battery degradation has been a critical issue for the EV application, and a variety of technologies have been developed so far. However, understanding of the microscopic behavior of ions and electrons is still very lacking, and thus the degradation control has room to be improved. In this respect, we have investigated the microscopic interfacial and mechanical phenomena around cathode / solid electrolyte interfaces via density-functional-theory (DFT) based first-principles calculations, and drawn general theories effective for larger-scale consideration.

In this talk, we introduce our recent works related to degradation; (1) stress/strain effects on Li\textsuperscript+ diffusion in Li_xCoO\textsubscript{2} \cite{ref1}, (2) oxygen evolutions and cation migrations around the surfaces of Li\textsubscript{x}CoO\textsubscript{2} \cite{ref2}, (3) Li\textsuperscript+ transfer around cathode/coating layer/solid electrolyte interfaces \cite{ref3}. 

(1) We found that the barrier in the single vacancy mechanism decreases with biaxial expansion, contrasting with an increase in the double vacancy mechanism. This phenomenon is attributed to the c-axis position in the Li\textsuperscript+ diffusion pathway. Our DFT-MD simulations revealed that compressive biaxial strain enhances Li\textsuperscript+ diffusivity in Li-deficient Li_xCoO\textsubscript{2} (decreased to 0.22 and 0.21 eV), while tensile biaxial strain and hydrostatic pressure hinder it. Surprisingly, “Co layer distances” play a pivotal role in Li\textsuperscript+ diffusion, and our study uncovers intricate interactions between Li-Li Coulomb interactions, state-of-charge (SOC), and Li\textsuperscript+ diffusion in Li_xCoO\textsubscript{2}. Besides, we reported the activation volume of LiCoO\textsubscript{2} under hydrostatic pressure and show that compressive biaxial strain weakens Li-O bond interactions, reducing the Li intercalation potential.

(2) We examined oxygen release and Co-ion migration both in the bulk and on the surfaces (001), (104), and (110) of Li_xCoO\textsubscript{2}, taking into account the process of spinel-like Co\textsubscript{3}O\textsubscript{4} formation. The calculated oxygen vacancy formation energies are 2.38, 2.42, 1.46 and 1.10 eV for bulk, the (001), (104) and (110) surfaces, respectively. These trends are reasonably consistent with the experiments. We also clarified the significant reduction in activation energies of Co-ion migration in the presence of oxygen vacancies, indicating the correlation among the oxygen vacancy formation and the Co-ion migration.

(3) Focusing on LiCoO\textsubscript{2} / LiNbO\textsubscript{3} / Li\textsubscript{3}PS\textsubscript{4} interfaces in typical solid-state battery, we calculated ionic PES across the interfaces by first-principles calculations, and demonstrated how such energy profiles look like around the interfaces. The results correspond to the discharging situation, and indicate how to understand the charging situation by separating ion and electron movements. Our interface analyses also suggested a way of understanding interfacial ion and electron transfer by DFT-based standard electrochemical potentials of Li, Li\textsuperscript+ and e\textsuperscript-. The picture well accounts for the mitigation of ionic interface resistance by insertion of oxide coating layer between cathode and sulfide electrolytes. This DFT-based framework gives a crucial insight into ion as well as electron transfer across general interfaces.

These works were done in collaboration with Mr. Z. Zhou, Dr. H. D. Luong, Dr. R. Jalem in NIMS, Prof. B. Gao in Jilin Univ., and Prof. H.-K. Tian in National Cheng-Kung Univ. The works were partly supported by MEXT as “Program for Promoting Researches on the Supercomputer Fugaku / Fugaku Materials Physics & Chemistry Project” (JPMXP102030325) and JSPS KAKENHI “Interface IONICS” (JP19H05815).
allow a future commercialisation of this technology. The safety is a crucial point and the generation of H₂S in the case of all-solid-state battery based on sulfide electrolyte during scale-up phase and operation must be take into account and evaluated specifically.

In this field and since a few years, Hydro-Quebec has decided to conduct specific research on all-solid ceramic batteries and especially in the field of sulfide-based ceramic electrolytes. Based on Hydro-Québec's knowledge with polymers, a solution of all-solid composite battery with ceramic tendency has been developed by generating several industrial properties at the different levels of the battery. The interaction previously observed in positive electrolyte without binder have been resolved and integrated in slurry. In parallel, the impact between solid electrolyte ceramic film composition, density, reactivity with lithium metal and flexibility were studied to offer high conductivity and easily manipulation. Unlike the general perception that the sulfide electrolyte is not compatible with lithium metal, we successfully stabilized the lithium metal interface reaching the cycle life more than 500 cycles under industry-relevant pressure conditions at moderate temperature under pouch-cell configuration. The constraints of the use of li-ion equipment’s, cost reduction and safety have been considered at each level with quantitative measurements. The different improvements in positive composite electrode, in solid electrolyte ceramic film and in lithium metal interfaces will be explained. The presentation will show how technical and economical issues of sulfide electrolyte can be addressed to bring the technology closer to the market.

3:45 PM ES01.09.06

Comprehensive Safety Assessment of All-Solid-State Batteries: Using Calorimetry, X-Ray Radiography and Blast Testing Techniques Juliette Charbonnel, Rémi Vincent, Pierre-Xavier Thivel; 1CEA, France; 2LEPMI, France; 3Laboratoire, France

the importance of evaluating the safety of all-solid-state batteries with respect to users and the environment. To conclude, all-solid-state batteries are neither safer nor less safe than lithium-ion batteries. However, their characteristic parameters of thermal runaway are different. This work underlines the impact of blast wave on the casing and battery pack integrity should be taken into when all-solid-state batteries are developed. To conclude, all-solid-state batteries are neither safer nor less safe than lithium-ion batteries. However, their characteristic parameters of thermal runaway are different. This work underlines the importance of evaluating the safety of all-solid-state batteries with respect to users and the environment.

4:00 PM ES01.09.07

Transforming EV Battery Materials into Reserve Batteries via Advanced Manufacturing Justin Sadowski; 1Argonne National Laboratory, United States

The expanding electric vehicle (EV) market fuels research into advanced battery materials, particularly solid-state electrolytes (SSEs), to enhance energy storage technology, offering the promise of higher energy density, improved safety, and cost-efficiency. These materials show potential for deployment in reserve or primary batteries, addressing issues found in current technologies such as self-discharge, inadequate energy density, limited operational temperature ranges, and safety concerns associated with flammable liquid electrolytes. Our investigation centers on argyrodite-type sulfide-based SSEs, boasting exceptional Li⁺ conductivity (~1 mS/cm) at room temperature, lithium metal anodes with substantial energy capacity (theoretical limit: 3860 mAh/g), and cathode active materials (CAMs) meeting the criteria for reserve or primary battery applications. This study investigates the pivotal role of advanced manufacturing techniques in addressing the challenges associated with reserve batteries, focusing on sulfide-based SSEs and lithium metal, with a positive outlook on potential solutions. We present a comprehensive review of state-of-the-art solid-state battery technology in current reserve or primary battery applications, discuss CAMs’ performance in sulfide-based SSE compositions in half cells, and provide detailed postmortem analyses. These insights serve as fundamental guidelines for future optimizations in advanced battery material manufacturing, transcending the scope of EV-specific applications.

Acknowledgements:

This project was supported by Laboratory Directed Research and Development (LDRD) funding from Argonne National Laboratory, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-06CH11357. This research used resources of the Center for Nanoscale Materials, U.S. Department of Energy (DOE) Office of Science user facilities operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The views expressed in this academic research paper are those of the author(s) and do not reflect the official policy or position of the US government or the Department of Defense.

References:

Solid-state batteries provide high reliability to lithium-ion batteries as they are regarded as promising next-generation batteries. Solid-state batteries with sulfide electrolytes were reported to attain higher performance than lithium-ion batteries and are under development aiming at vehicle application. However, sulfide electrolytes are unstable and hygroscopic materials, and the batteries should be assembled under strictly-controlled atmosphere. Therefore, replacement of the sulfides with stable oxides is strongly required; however, performance of the oxide-based solid-state batteries is much lower than that of the sulfide systems.

Although the highest conductivities having reported for oxides are of the order of $10^{-3}$ S cm$^{-1}$, which is lower than that of sulfides by one order of magnitude, they are not the main reason for the poor battery performance: the conductivities are almost comparable to lithium-ion conductivities of organic-solvent liquid electrolytes used in the current lithium-ion batteries. High resistance of oxide-based solid-state batteries originates from the interfaces.

Oxide-based solid electrolytes often show high grain boundary resistance. The grain boundary resistance can be lowered by increasing sintering temperature, indeed; however, it does not lead to high performance in the solid-state batteries. The solid electrolytes are in contact with active materials in the batteries. Sintering at high temperatures induces mutual diffusion between the solid electrolytes and active materials, which forms resistive impurity layers at the interfaces. Sulfide-based solid-state batteries have achieved the high performance not only by the high ionic conductivities of sulfide-based solid electrolytes but also by their deformability. Since sulfide solid electrolytes are deformable, they can be closely contacted to active materials only by cold pressing, where mutual diffusion takes place. Therefore, it is necessary to lower sintering temperature of the oxide solid electrolytes for realizing oxide-based solid-state batteries. I have been leading some research projects on oxide-based solid-state batteries. Achievements in the projects will be presented at the meeting.

Rechargeable Li-metal batteries have higher energy density relative to batteries based upon intercalation electrodes. They are therefore attractive energy storage candidates for electric vehicles. However, a main barrier to their commercial deployment is a relatively short cycle life. Re-engineering the electrolyte offers advantages towards acceptable cycle life; however, the cells exhibit a sudden capacity loss. In this presentation, we detail a new method for analyzing voltage profiles during cycling to differentiate between the capacity loss originating from loss of cathode capacity loss versus growth in cell resistance. We show that sudden capacity loss is preceded by acceleration of the rate of growth of cell resistance. Cycling of multiple cells suggested that this behavior is sensitive to the initial quantity of electrolyte. Alternatively, the cathode capacity degraded at a constant rate independent of the electrolyte quantity. Loss of active lithium and/or the loss of active cathode material were not the primary causes of sudden capacity loss. Rather, consumption and decomposition of electrolyte led to the drastic capacity loss at end of life.

We have developed high performance flow batteries based on the aqueous redox behavior of small organic and metalorganic monomers composed of earth-abundant elements. These redox active materials can be inexpensive and exhibit rapid redox kinetics and high solubilities, potentially enabling rapid scaling of flow batteries at reduced cost. Adequate molecular lifetime has been one of the most challenging requirements to satisfy. We have shown that the amount of lost capacity is determined by the molecular calendar life, which can depend on state of charge, but is independent of the number of charge-discharge cycles imposed. I will discuss problems in measuring extremely small capacity fade rates and how an understanding of molecular decomposition mechanisms has permitted us to design molecules with decadal projected lifetimes and even to reverse capacity fade by recomposing decomposed molecules within the functioning battery electrolyte.

Materials research and innovation are pivotal to advancing battery technology and enabling the green transition. However, widely used trial-and-error approaches are too slow and under-utilize the valuable data that they generate. This presentation explores the pivotal role semantic technology - a fusion of artificial intelligence and web technologies - plays in accelerating research efforts towards next-generation battery materials. Semantic web technology like ontologies and knowledge graphs, helps researchers integrate heterogeneous data sources. This not only simplifies data retrieval by enabling precise, context-aware queries, but also augments the capabilities of machine learning. With semantically enriched data, researchers can craft models that are more adept at predicting material behaviours and identifying promising compositions.

This talk introduces the fundamentals of semantic technology and presents real case studies from battery materials research. This includes a specific focus on examples coming from both experiments and simulations. It is shown how semantic annotations can enable both human- and machine-readable of battery data to automate analysis and enable interoperability between different modelling frameworks. Harnessing the power of semantic technology in materials research not only expedites the development of next-generation battery materials but also fosters data-driven innovation and collaboration across diverse research domains.
8:30 AM *ES02.01.01

Real-Time Probing of Solid-Liquid Interfaces for The Alkaline Oxygen Evolution Reaction of Oxides Vaso Tileli; EPFL, Switzerland

The design of active and stable oxygen-evolving oxide catalysts can be aided by their real-time probing, which provides information on how the catalysts perform and evolve under operating conditions [1]. Among the operando characterization techniques applied to electrocatalysis, electrochemical liquid-phase transmission electron microscopy (ec-LPTEM) is capable of visualizing the electrochemically induced processes in liquid environments at the single particle level. In this talk, I will discuss the progress made in the application of ec-LPTEM for monitoring solid-liquid interface processes occurring on Co-based and iridium oxide OER catalysts [2,3]. By analyzing the contrast of the lateral liquid electrolyte surrounding the catalyst particle in TEM images, the surface wetting dynamics with respect to the applied potential is revealed. The overall decrease in the lateral liquid thickness indicates a switch from hydrophobic to hydrophilic character under anodic potential due to electrowetting induced by ion accumulation at the interface. Within the pre-OER potential, the change in the surface wetting behavior on Co-based oxides suggests a link to the underlying Co/III redox reaction and surface transformation of the oxhydroxide phase. I will also demonstrate the direct probing of electrocatalytic molecular oxygen using operando electron energy-loss spectroscopy (EELS). Progress toward facet selectivity probing of the evolving molecular oxygen will be discussed and evidence of highly-pressurized electrocatalytic gas formation in the nanoscale will be presented.

References


9:00 AM *ES02.01.02

Operando Studies of Dynamic Evolution of Cu Nanocatalysts during CO2 Reduction Yao Yang; Cornell University, United States

In an era of shifting the energy paradigm from fossil fuels to renewable energy, CO2 reduction reaction (CO2RR) emerges as a promising approach to convert greenhouse gas into valuable chemical fuels and close the carbon cycle for a sustainable energy supply. Since Cu remains the sole element for CO2RR to multiconponent products (C2+), significant efforts have been devoted to developing Cu electrocatalysts with higher selectivity and activity. However, the complex nature of active sites and the intrinsic structures under reaction conditions have remained largely elusive due to the lack of operando/in situ methods. In this work, we present a comprehensive operando correlative study of size- and potential-dependent dynamic evolution of Cu nanoparticle electrocatalysts under CO2RR conditions. Operando electrochemical liquid-cell scanning transmission electron microscopy (EC-STEM) and 4D-STEM, driven by machine learning, resolve microscopic and dynamic structural transformation processes during CO2RR, in situ nanomechanical mapping, and operando electron energy-loss spectroscopy. Dynamic operando synchronotron-based high-energy-resolution fluorescence-detected (HERFD) X-ray absorption spectroscopy (XAS) reveals dynamic macroscopic changes in valence states and coordination environment. The methodology described herein can serve as a general strategy to resolve the electrochemical interface of nanoparticle catalysts under real-time operating conditions across multiple time and length scales.

9:30 AM ES02.01.03

Recovery of Isolated Lithium through Discharged State Calendar Aging Wenbo Zhang1, Philaphon Sayavong2, Xin Xiao1, Solomon Oyakhire1,2, Sanzeeda B. Shucli1, Rafael A. Vila3, David T. Boyle1, Sang Cheol Kim2, Munseok Kim1, Sarah Holmes1, Yusheng Ye1, Donglin Li1, Stacey F. Bent1 and Yi Cui1; 1Stanford University, United States; 2University of California, Berkeley, United States

Rechargeable Li-metal batteries (LMBs) have the potential to more than double the specific energy of the state-of-the-art rechargeable Li-ion batteries (LIBs), making Li metal a promising anode material for future generation rechargeable batteries. However, Li metal anodes suffer from greater cycle degradation compared to their Li-ion counterparts due to excess formation of capacity depleting byproducts.1 Two major byproducts generated are: 1) the solid electrolyte interface (SEI), a product of Li, salt and organic species reactions at the Li metal and the electrolyte interface to form a 'passivating' layer and 2) 'dead' or isolated Li, which traps capacity as Li metal detached from the electrochemical circuit. Recent studies have revealed that charged state calendar aging promotes further corrosion reactions with active Li and the surrounding electrolyte, leading to additional byproduct generation and further capacity loss.2,3 Although these studies highlight the detrimental effects of calendar aging in the charged state, they have not reported on the effects of discharged state calendar aging on cell performance. In the discharged state, all electronically active Li has been stripped away leaving only isolated Li and SEI on the anode.4 In this environment absent of active Li corrosion, the effects of rest on isolated Li, SEI, and cycle performance have not been explicitly explored and remain unknown.

In this work, we report calendar aging in the discharged state improves capacity retention through isolated Li recovery, a surprising contrast to the well-known phenomenon of capacity degradation observed during aging in the charged state. Discharged state rest cells achieved a sustained greater than 1% average CE increase over both continuously cycled and charged state rested cells. Additionally, running cells on a hybrid continuous/discharged state rest cycling protocol in combination with titration gas chromatography (TGC) reveal isolated Li recovery as the main contributor to capacity gain. Furthermore, a novel operando optical setup in combination with electrochemical quartz crystal microbalance (EQCM) reveal that the process of SEI dissolution during discharged resting promotes excessive isolated Li recovery. These insights create a new pathway for capacity recovery through discharged state calendar aging emphasizing the significant effects cycling strategies have on LMB performance.


9:45 AM ES02.01.04

Quantitative Operando Mapping with Nanoscale Resolution of 3D Mechanical Properties of Surface Electrolyte Interphase in Li-Ion and Na-Ion Batteries Oleg V. Kolosov1, Yue Chen2, Mangayarkarsai Nagarathanam1, Svetlana Menkin Bachbut3 and Dominic Wright3; 1Lancaster University, United Kingdom; 2Fujian Normal University, China; 3University of Cambridge, United Kingdom

A nanoscale thin but extremely important component of any rechargeable battery is the solid electrolyte interphase (SEI), a passivation layer that defines the fundamental battery properties - capacity, cycle stability and safety. Local mechanical properties of SEI hold a clue to its performance, but their operando characterisation is very difficult as one has to probe nanoscale surface features in electrochemical environment and these are also dynamically changing. Here, we report novel 3D nano-rheology microscopy (3D-NRM) that uses a tiny (sub-nm to few nm) lateral penetrations of the sharp SPM tip at kHz frequencies to probe the minute sample reaction forces. By mapping the increments of the real and imaginary components of these forces, while the tip penetrates the soft interfacial layers, we obtain the true 3D nanoscale structure of sub-nm thick layers. 3D-NRM already allowed us to elucidate key role of solvents in SEI formation and predict the conditions for building SEI for robust, safe and efficient Li-ion batteries [1]. We combine 3D NRM with magnetic excitation to investigate molecular-level solvation force spectroscopy and use molecular dynamics simulations to understand two morphologically dissimilar but chemically identical surfaces of typical carbon electrode material (basal and edge particle in TEM images, the surface wetting dynamics with respect to the applied potential is revealed. The overall decrease in the lateral liquid thickness indicates a switch from hydrophobic to hydrophilic character under anodic potential due to electrowetting induced by ion accumulation at the interface. Within the pre-OER potential, the change in the surface wetting behavior on Co-based oxides suggests a link to the underlying Co/III redox reaction and surface transformation of the oxhydroxide phase. I will also demonstrate the direct probing of electrocatalytic molecular oxygen using operando electron energy-loss spectroscopy (EELS). Progress toward facet selectivity probing of the evolving molecular oxygen will be discussed and evidence of highly-pressurized electrocatalytic gas formation in the microcells will be presented.

References


Transmission electron microscopy (TEM) has played a vital role in providing nano- and atomic-scale insights into the morphology, microstructure, and chemical properties of Li-ion batteries at both anode and cathode materials. Moreover, improvements of in-situ capabilities, as enabled by specialized biasing TEM sample holders, offers an exciting opportunity to monitor the changes taking place in the electrode materials under external stimuli at an unparalleled resolution, enabling a deeper understanding of how the materials behave under various operating conditions. In-situ capability is also applicable to investigate structural changes of electrode materials during lithium removal or insertion under biasing conditions. Such operando characterization of the electrode materials is critical for gaining a fundamental understanding of how lithium-ion batteries function and degrade. My presentation will focus on real-time TEM observations of the phase transformations that take place in electrode materials during lithium migration. A dry-cell setup was developed inside the TEM column based on the NanoFactory STM-TEM sample holder, and lithium movement was controlled by applying bias to the samples. A multi-step lithium insertion reaction with tin sulfide will be presented as a proof-of-concept, and the nanoscale structural evolutions in these solid-state-cells will be further discussed. My talk will illustrate that dynamic investigations of electrode materials not only enhance our understanding of the structural changes induced by lithium but also provide intriguing insights into the underlying origins of battery performances.

Interface speciation and structure significantly influence a battery's energy density, cycle life, and safety. However, the reduced signal strength and inherent fragility pose significant challenges when conducting the ex-situ and destructive characterizations. In this talk, I will initially provide an overview of surface science methodologies tailored to address interface-related issues in batteries, showcasing their practical applications. Subsequently, I will delve into the considerable promise of angle-resolved spectroscopy for discerning intricate interfacial speciation. Finally, I will introduce an innovative technique, time-resolved electrocapillarity, capable of offering precise insights into potential and concentration distribution across the electrode/electrolyte interface.

Acknowledgement: This work is supported by U.S. Department of Energy under contract DE-NE0009286 and the National Science Foundation under Grant No. 2239690.

In Situ Imaging of Ion Transport in Electrochemical Cells for Predictive Solar Fuel Generation Livisa Belman-Wells 1, James Utterback2, Anwesha Maitra4, Alex King5,6, David Larson3, Leo Hamelryckn1, Adam Weber3 and Naomi S. Ginsberg1 1University of California, Berkeley, United States; 2Sorbonne Université, France; 3Lawrence Berkeley National Laboratory, United States

Ion transport underpins the functionality of many modern electrochemical devices involved in energy generation and storage. Despite its importance, label-free spatiotemporal imaging of ion transport in the solution phase in-operando has not been widely explored. Here we have performed interferometric reflection microscopy (IRM) measurements of voltage-induced ion transport in aqueous solution, spatiotemporally mapping ion concentration gradients and extracting transport parameters. We developed an electrochemical cell composed of a narrow channel etched into a microscope coverslip with vertical electrodes running along its sides to drive a reaction in a ferrocyanide-based aqueous redox electrolyte. Applying a voltage while imaging the cell, we measure the evolution of concentration profiles through their changes to the local refractive index. Analysis of the evolving ion concentration gradients allows us to extract a diffusion coefficient consistent with that of aqueous ferrocyanide, demonstrating the ability to do label-free optical imaging of ion transport in an aqueous electrolyte. This work serves as a basis to proceed to study CO2 reduction for solar fuel generation. We anticipate imaging in situ mass transport to characterize the involved reactions and to compare local and global efficiency and durability across photovoltaic systems for improved device performance.

SESSION ES02.02: Operando X-ray Microscopy of Energy Storage Materials

Wednesday Afternoon, April 24, 2024
Room 424, Level 4, Summit

1:45 PM *ES02.02.01 Characterizing The Morphological and Crystallographic Behavior of Ni-Rich Li-Ion Cathodes Donal Finegan; National Renewable Energy Laboratory, United States

High Ni content cathodes display large volumetric changes and can incur crystallographic phase changes during formation and initial activation. The heterogeneous geometric and crystallographic evolution of the electrodes greatly influence their cycle-life performance. This work will focus on the application of advanced electron and X-ray microscopy techniques to characterize the evolution of heterogeneous particle morphology and crystallographic phases during formation, activation, and throughout the cycle-life of the cathodes. Focused-ion beam electron back scatter diffraction (FIB-EBSD) is applied to characterize the grain size distribution and orientations through the particle architectures. X-ray nano-computed tomography (nano-CT) is applied before and after formation and cycling to quantify morphological changes such as crack growth throughout the life of the cathode materials. Finally, synchrotron X-ray diffraction computed tomography (XRD-CT) captures the efficacy of high-voltage activation steps during formation to irreversible form a stable layered phase for high performance long-life cycling. The multi-modal approach provides a comprehensive description of the morphological and crystallographic phenomena that determine the performance of earth-abundant cathodes and sheds new light on performance limiting material properties.

2:15 PM ES02.02.02 Advanced Operando Analysis for Interface Observation using Synchrotron X-ray Computed Tomography for Lead-Acid Batteries Seongjun Kim1,2, Mark Wolfman1,2, Tiffany Kinniburgh1,2, Alan Kastengra1,2, Tim Fister1 and Paul Fenter1; 1Argonne National Laboratory, United States; 2Advanced Photon Source, United States

In the realm of battery technology, a field that has profoundly influenced various industries, including the automotive sector with the widespread adoption of lithium-ion batteries (LIBs), trust in these energy storage solutions remains challenged by issues related to safety, cost, and environmental impact. This has ignited an ongoing competition between traditional and emerging battery technologies.

Lead acid batteries (LABs), a technology dating back to 1859, have endured as preferred secondary power sources in many applications, primarily due to their economic advantages. Nevertheless, LABs face significant hurdles in order to compete effectively with other battery types. Deep discharges can lead to rapid sulfation, while the irreversible crystallization of lead sulfate (PbSO4) can compromise battery lifespan and performance. Therefore, understanding the structural transformations of two critical components, the positive active material (PAM) and negative active material (NAM), becomes imperative for enhancing battery capacity and cycle life. Variations in internal morphology can influence electrode porosity and surface area, both pivotal factors in determining battery performance. Traditional post-mortem analysis methods, such as scanning and transmission electron microscopy (SEM and TEM), fall short in capturing real-time changes during cycling.

Synchrotron X-ray computed tomography (XCT) emerges as a non-destructive methodology for characterizing material morphology and interfaces across a wide spectrum of scales, from sub-micron to centimeters. This technique facilitates both two-dimensional (2D) and three-dimensional (3D) visualization, proving invaluable for investigating interface transformations in solid-phase materials. In situ or operando measurements enable the identification of morphology changes due to phase transitions during cycling. XCT-generated images can be reconstructed into 3D slices and further assembled into 3D representations, aiding in the interpretation of porosity and particle evolution across different states of charge (SOC).

Additionally, complementary synchrotron X-ray techniques, such as diffraction (XRD) and transmission X-ray microscopy (TXM), contribute to unveiling the intrinsic chemo-mechanical dynamics within lead-acid batteries.

This presentation promises to shed light on LABs, offering insights into their mechanism through various synchrotron X-ray techniques. The application of in situ and operando X-ray measurements enhances our understanding of LABs, contributing to broader comprehension of this enduring energy storage technology.

2:30 PM BREAK
In this work we have demonstrated a state-of-the-art data workflow for processing CT datasets of electrode particle degradation. This method allows for large statistically relevant volumes to be analyzed during cell cycling whilst still tracking the changes in individual particles throughout time-lapse datasets. We believe that moving forward this workflow can be repackaged for a broad range of electrochemical materials that observe volume and density change during use.

4:30 PM ES02.07
Operando Detection of Cracking in High Ni Battery Cathode Materials by X-Ray CT
Huw Parks1,2 and Rhodri Jervis1,2; 1University College London, United Kingdom; 2Faraday Institution, United Kingdom

In a drive for ever-increasing energy density and reduction in use of cobalt in lithium ion battery cathodes, high-nickel content layered cathodes (Ni>80%) of the form Li(Ni0.8Mn0.1Co0.1)O2 (NMC811) have received significant recent attention. These materials undergo considerable anisotropic lattice changes during cycling (lithiation and delithiation) which have been attributed to the creation of microcracks in polycrystalline agglomerate cathode particles. This cracking behaviour has long been suspected to cause increased surface reactions leading to impedance rise, reduction of electronic conductive pathways and eventually complete particle detachment from the conductive matrix and pulverisation; however, the pre-existence of particle cracks and defects from manufacturing and calendaring of the electrodes can make it difficult to assess the contribution of the electrochemical history alone in causing cracks[1]. In a bid to reduce this, so-called single-crystal materials have been proposed to be more resistant to degradation[2] due to their resilience to cracking[3] and lower surface exposure to electrolyte, which can cause parasitic reactions and drive oxygen loss[4].

Assessing the origins of cracking and its evolution with battery ageing is complex due to the small and internal nature of the cracks, often requiring either destructive imaging techniques (such as FIB SEM or TEM on lamella) or small sample sizes in non-realistic environments to facilitate non-destructive imaging by methods such as X-ray computed tomography (CT). In previous work, we have developed methods for producing electrodes with optimised tab geometries for in situ and operando X-ray CT and related characterisation methods[5, 6], which we use here to allow for a pseudo-in situ nano-CT study of electrochemically induced cracking in NMC811 particles with minimal pre-existing damage[7]. This allows for direct observation of first-cycle cracking within the particles using lab-based CT on identical particles in the discharged and charged state, showing that even on the first cycle, significant intergranular cracks can develop in the polycrystalline materials. Additional ex situ studies on non-identical particles have revealed cracking in polycrystalline materials occurs at relatively low potentials, in the early stages of charging, and is at least partially recovered on discharge[8].

In this presentation we will extend this methodology to assess the progression of first cycle cracking throughout the charge and discharge range on thousands of identical particles from the same electrode within a realistic pouch cell environment. The use of the tab electrode geometry within a working pouch cell and larger field of view afforded by synchrotron micro-CT studies, combined with automated image processing and analysis, allows us to follow the behaviour of around 5,000 NMC particles through multiple states of charge, revealing the diversity of cracking behaviour within working, commercially relevant, Li ion battery electrodes. Advanced grey-scale analysis of the data reveals sub-resolution limit information about the damage to the particles throughout their states of (de)lithiation and provides a statistically relevant quantification of the extent of crack closure behaviour.

Heterogeneous Lithium Transport within Individual Single-Crystalline NCM Battery Particles

Bonho Koo1, Jinkyu Chung1, Danwon Lee1, Chihyun Nam1, Martin Z. Bazant2 and Jongwoo Lim1; 1Seoul National University, Korea (the Republic of); 2Massachusetts Institute of Technology, United States

Probing the lithiation kinetics in solid-state electrodes is foundational for advancing high-efficiency battery technologies. Typically, a consistent and monotonic lithium gradient is anticipated across solid-solution or single-crystalline battery constituents throughout the cycling process. Our exploration, centered on the heterogeneous lithium distribution within single-crystalline LiNi0.333Mn0.333Co0.333O2 nanostructures, utilized operando scanning transmission X-ray microscopy for precision. Contrary to the prevailing Pickian diffusion paradigm, our insights highlight the emergence of regions both rich and deficient in lithium, which exhibit dynamic behavior across battery cycles. This intricate interplay of intra-particle strain fields, capable of either concentrating or dispersing lithium, was authenticated using Bragg coherent X-ray diffraction methodologies. Significant, we elucidated that regions with sparse lithium proximal to the particle surface can modulate the overarching charge transfer resistance and offer avenues for in-situ optimization. This investigation provides a renewed perspective on the intricacies of nanoscale solid-state guest diffusion, heralding implications for battery rate performance and durability.

SESSION ES02.04: Operando Spectroscopy of Energy Storage Materials
Session Chairs: Raphaële Clement and Wenko Zhang
Wednesday Afternoon, April 25, 2024
Flex Hall C, Level 2, Summit

Improving The Sensitivity of Operando Nuclear Magnetic Resonance for Electrochemical Studies

Khashayar Bagheri1,2, Ludivine Afonso de Araujo1,2,3, Raphaël Praud1,2,3, Vincent Sarou-Kanian1,2, David Sicsic3, Michael Deschamps1,2 and Elodie Salager1,2; 1CNRS-CEMHTI, France; 2Réseau sur le Stockage Electrochimique de l’Energie (RS2E), France; 3Renault SAS, France

Nuclear Magnetic Resonance (NMR), as a bulk technique, is nicely suited for studying, operando, multi-component electrochemical cells. The NMR signal of atoms can be detected in many phases, independently of their degree of order: liquid, crystalline or amorphous. In addition NMR measurements deposit little power into the material, so that there is no risk of battery or material degradation during measurement. This comes however at the cost of a relatively low intrinsic sensitivity, which results in a limited temporal resolution.

In this talk we will present our latest developments to improve the sensitivity of operando NMR studies of batteries. Our approach is two-pronged: we work on reducing parasitic signals and on increasing intrinsic sensitivity, while controlling electrochemical behavior.

A first part will report on how we improved the operando setup and analysis for the early detection of the onset of metallic Li plating in NMC622/graphite cells at low temperature and fast charge [1]. Direct detection of metallic Li in the cell for various conditions of temperature and charging rate is precise to identify the exact conditions favoring metallic lithium plating and its evolution. A better grasp of this degrading phenomenon could lead to optimized charging protocols.

The second part explores how the sensitivity of the measurement itself can be increased. Most operando NMR measurements follow the signal of 7Li or 23Na atoms, as they are taking part in the redox reactions. The NMR signals from the paramagnetic solid electrodes however suffer from large broadenings, due to the interaction of the atomic spins with unpaired electrons. Here we approached the problem from another side and explored ways to exploit the NMR signal of the liquid electrolyte solvent inside the battery. Sensitivity is enhanced thanks to the narrower signal of liquid, and the intrinsic sensitivity of 1H higher than that of 7Li and 23Na. We demonstrate that the 1H NMR spectrum of the carbonates in the liquid electrolyte is mainly sensitive to the redox state of the positive electrode. This parameter is difficult to obtain without a three-electrode measurement, but is essential for understanding the mechanisms of capacity loss and developing adequate models for battery management systems.

Finally, proper electrochemical behavior may require pressure applied to the cell during cycling. This brings an additional challenge to NMR sensitivity, as the metallic parts applying pressure tend to disturb and shield the radio-frequency waves used for the measurement. We will present our progress on a design for operando NMR that is compatible with applying greater pressure on large pouch cells.

XES measures the chemical-energy dependent absorption coefficient of a material in the process of generating core electron holes. Chemical state sensitivity from the XAS near-edge structure (XANES) and local atomic structure sensitivity through extended x-ray absorption fine structure (EXAFS) allows us to keep track of changes in the constituent elements during cycling. XES, a complementary method is obtained by capturing characteristic photons resulting from quenching generated core holes. K-edge emission line (3p-to-1s transition) of XES obtain their chemical state sensitivity through interaction between the 3p and valence orbital (exchange interactions). Element-specific emissions of sufficient energy resolution are simple to process and inform us on the chemical state, spin state, and local structure of transition metal allowing us to study the redox processes in real-time (operando) during charge/discharge of batteries. The high flux requirement of such real-time (operando) experiments often limits these studies to synchrotron sources. Limited access to synchrotron radiation has hastened the development of lab-scale instruments that employ bremsstrahlung sources and monochromators with sufficient energy resolution. The lab-scale instrument used in this study can perform both XES and high energy-resolution XES experiments using a scanning setup which employs the Rowland circle geometry.

Here, we present the spectral changes of transition metal K1,3 and Kβ features of XES are utilized to track state of charge (SoC) and study redox processes during C/10 operando cycling for the following cathode materials: LiCoO2 (LCO), Li[Ni0.5Co0.5Mn1.5]O2 (NCM111), Li[Ni0.5Co0.5Mn1]O2 (NCM811), and LiFePO4 (LFP). The results obtained from operando Kβ XES are compared with K-edge XAS, which serves as a benchmark. Additionally, the sensitivity of XES towards the total spin of the transition metal valence is used to investigate the change in magnetic properties resulting from nucleation of a new phase in electrochemically delithiated LCO samples in the range of 2-10% lithium removal.

9:15 AM ES02.04.04 Investigation on Photo-corrosion of TiO2 during The Photoelectrochemical Process by In-Situ ICP-MS Characterization Vi Tran, Max Planck Institute for Iron Research, Germany

With the growing environmental deterioration and ever-increasing energy demand, exploring a renewable and clean energy for human development has been regarded as a promising research subject. Hydrogen is one of the most desirable energy carriers because of its abundance, high energy density and only byproduct of water. A breakthrough was made by Fujishima and Honda in 1972, who found that hydrogen could be generated from water splitting on a TiO2 photoelectrode under UV light. However, the energy conversion efficiency of TiO2 semiconductor for photolyss catalytic process is relatively low owing to their fast recombination of electron-hole pairs and its large bandgap (3-3.2 eV). Fortunately, various methods are designed to improve the performance of photo(electro)catalyst which is closely associated with its nanotechnology.

TiO2 is considered to be quite stable since its redox potential has been calculated to be more positive/negative relative to the water oxidation/reduction potential, which means that photocatalysts produced charge carriers, while driving the desired redox potential rather than oxidizing or reducing semiconductor photocathodes. Nevertheless, the real photocorrosion (decomposition or degradation) depends on specific kinetic parameters such as illumination intensity, electrolyte property, radiation adsorption, charge transport and mass transport. We use inductively coupled plasma mass spectrometry (ICP-MS) to reveal the dissolution products of TiO2 photoelectrode during PEC water splitting. It is unveiled that TiO2 photoanode experiences photocorrosion from its oxidation with photogenerated holes. We demonstrate how the atomic structure scale of TiO2 correlates with its PEC performance and photocorrosion process to enable a better understanding of the complex structure-activity-stability relationship in photoelectrocatalysis. ICP-MS analysis under solar water splitting conditions reveals the chemical instabilities that are not predicted from thermodynamic considerations of stable solid oxide phases represented by the Pourbaix diagram. Our investigation of photochemical corrosion pathway of TiO2 thin film proves the competition between water splitting and semiconductor oxidation experimentally.

9:30 AM ES02.04.05 Operando Raman Spectroscopy for Aqueous Organic Redox Flow Batteries Lara Lubian, Rubén Rubio-Presa, Virginia Ruiz, Álvaro Colina and Edgar Ventosa, University of Burgos, Spain

Generation of electricity from renewable sources is crucial for achieving the transition to a sustainable and decarbonization energy system. While solar and wind power are becoming increasingly popular, their intermittency requires the deployment of efficient and cost-effective energy storage systems (ESSs) to match energy production and demand. Among the various ESSs, redox flow batteries (RFBs) that are featured by their independent scalability of energy and power are promising ESSs candidates for stationary energy storage application. The all-vanadium redox flow battery (VRFB) is currently the state-of-art of RFB, but the large-scale implementation of VRFBs presents an intrinsic challenge; vanadium is considered a critical material. Aqueous organic redox flow batteries (AORFBs) gaining much interest as vanadium-based species are replaced by organic redox-active species. While many organic molecules have demonstrated suitable redox potentials, kinetics and solubilities, their cycle stability should be further improved for large-scale deployment. Therefore, advanced techniques are required to investigate the capacity fading mechanisms in operando conditions.

In this contribution, the implementation of Raman spectroscopy for AORFBs will be discussed. Raman spectroscopy is a very useful technique that provides chemical information on redox-active molecules. Surprisingly, this powerful analytical technique has not been exploited in RFBs despite its intrinsic advantages to investigate highly concentrated solutions of strongly colored active molecules. In this talk, we will present the experimental setup and discuss the results obtained during the characterization of AORFBs.

10:15 AM ES02.04.06 Hollow-Core Optical Fibre Sensors for Operando Raman Spectroscopy on Li-Ion Battery Liquid Electrolytes Ermanno Miele1,2, Wesley Dose3,2, Michael Froza4, Zach Ruff1,2, Michael Von De Volder1,2, Clare Greg3,2, Jeremy J. Baumberg1,2 and Timmen G. Euser4,5,6,7, Cavendish Laboratory, University of Cambridge, United Kingdom; 2The Faraday Institution, United Kingdom; 3University of Cambridge, United Kingdom; 4Max Planck Institute for the Science of Light, Germany

Liquid-filled hollow-core fibres (HCF) are excellent sample cells in which light propagates in well-defined modes at the centre of a microchannel. The internal sample volumes in HCF can be as small as a few nL per cm interaction length, while long optical paths enable sensitive absorption, fluorescence, and Raman spectroscopy [1,2]. This talk will introduce optical fibre hollow-core fibres and briefly review their applications as microreactors. It will then demonstrate a new operando Raman spectroscopy method that tracks the chemistry of liquid electrolytes during battery cycling. An optofluidic hollow-core fibre is integrated into a working Li-ion cell and used to analyse sub-microlitre electrolyte samples at different stages of the charge-discharge cycle by background-free Raman spectroscopy. The observed changes in electrolyte composition are related to the solid electrolyte interphase (SEI) formation [2]. In addition, Raman measurements over multiple cycles reveal early signs of battery electrolyte degradation and we demonstrate that lost capacity can be recovered by infiltration of fresh electrolyte into a degraded cell. The new methodology contributes to understanding better the limitations of Li-ion batteries and paves the way for studies of degradation mechanisms in different electrochemical energy storage systems.

Acknowledgments
This work has received funding from the European Union’s Horizon Europe research and innovation program – European Innovation Council (EIC) under the grant agreement No 101046742.

9:45 AM BREAK
reaction with Li⁺ during the charging and discharging process.

11:15 AM ES02.04.09
The Local Structure in Zn-Cl Electrolytes and The Potential for Operando Study of The Interfacial Electrolyte Structure in Zn Ion Batteries using Valence-To-Core X-Ray Emission Spectroscopy
Gerald Seidler 1, Diwah Dhakal 1, Darren Driscoll 2, Tim Fister 2, Nirajan Govind 3, Andrew Stack 4, Nikhil Rampal 4, Gregory Schenter 3, Christopher Mundy 2, John Fulton 2 and Mahaling Balasubramanian 1; 1University of Washington, United States; 2Argonne National Laboratory, United States; 3Pacific Northwest National Laboratory, United States; 4Oak Ridge National Laboratory, United States

The determination and modeling of the local structure around ions in electrolytes is a classic problem in physical chemistry that also has contemporary impact spanning electrical energy storage, geochemistry, and ionic liquids (broadly defined). This problem is greatly enriched by the occurrence of cation-anion correlations, such as in contact ion pairing, giving at its extreme the 'water in salt electrolyte' (WISE) regime that poses extreme theoretical challenges while also showing improved energy density in some batteries. Here, we report several studies of ion pairing in the aqueous Zn-Cl solutions as a function of concentration, anion activity, nanocoherence, and temperature. To this end, we demonstrate that laboratory-based valence-to-core x-ray emission spectroscopy (VTC-XES) gives an improved method to determine the local symmetry and average composition of the Zn(II) first shell coordination. Starting with bulk solutions at ambient conditions, analysis of VTC-XES gives a robust characterization of the first coordination shell without the analytical complications of extended x-ray absorption fine structure (EXAFS), for which the changing second-shell population at high concentrations generally requires independent theoretical modeling by advanced molecular dynamics simulation. Next, we find that nanocoherence by nanophosphorous ion electrode material increases the mean ion pairing and also, in agreement with prior WiSE results, increases the electrochemical window for Zn-ion batteries. Finally, we return to the bulk system to study the temperature dependence of ion pairing, giving new insight into the geochemical problem of Zn transport in brines while also clearly demonstrating the limitations of models based on extrapolation of solubility and thermodynamic information from the dilute regime. These results illustrate the power of VTC-XES to investigate electrolyte structure, even when measured in the laboratory rather than at synchrotron x-ray light sources. The future extension to non-aqueous electrolytes would have even more direct relevance for beyond-Li-ion batteries. In addition, the work here lays important groundwork for future operando studies of the near-electrode interfacial structure of Zn-ion and other metal-ion electrolytes via synchrotron-based measurements. Such studies would immediately interrogate the connection between electrolyte structure and the operating voltage window for Zn-ion and other metal-ion battery systems.

11:30 AM *ES02.04.10
Understanding Electrochemical Properties of LiNiO₂ as a Cathode for Lithium-Ion Batteries
Minhkvng Kim; Kwangwoon University, Korea (the Republic of)

Cathode materials have been developed toward having high energy density and low cost with decreasing cobalt and increasing nickel. However, as Ni content increases, structural and electrochemical stabilities become poor. Cathode materials exhibit a trade-off relation between capacity and stability. It is challenging to break the trade-off relationship because 'high capacity' generally accompanies high structural and volumetric change. However, both properties are important to utilize materials. Recently single crystal cathodes are paid attention to solve the issue. Here, we synthesized single crystal LiNiO₂ and investigated the electrochemical properties depending on surface planes, crystal sizes and anti-site defects. Its impact will be addressed in this presentation.

SESSION ES02.05: Operando Diffraction and Scattering of Energy Storage Materials
Session Chairs: Yujin Liu and Andrej Singer
Thursday Afternoon, April 25, 2024
Room 424, Level 4, Summit

1:30 PM *ES02.05.01
Characterization of Advanced Positive Electrode Materials for Li-Ion Batteries
Naoki Yabuuchi; Yokohama National University, Japan

The demand for electric vehicles equipped with Li-ion batteries is growing to develop low carbon society. Ni-enriched layered materials are used as electrode materials of Li-ion batteries for electric vehicle applications. However, available reversible capacity of Ni-enriched layered materials is approaching its theoretical limit. Therefore, innovation and development of new positive electrode materials is necessary. Recently, many cation-disordered rocksalt oxides have been proposed as a new series of electrode materials. Nevertheless, insufficient electrode kinetics for the cation-disordered rocksalt system limits its use for practical applications. One simple strategy is synthesizing nanosized materials to overcome a problem of electrode kinetics (for electrons, holes and ions), and electrode kinetics are significantly improved through nanosizing.4) Structural disordering also triggers unique electrode properties associated with different local environments for cations/anions.4-7 From these results, we discuss the advantage and uniqueness of nanostructured cation-disordered rocksalt materials for high-energy advanced Li-ion batteries.

References
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2:00 PM *ES02.05.02
Understanding The Dynamics of Electrodes (Crystalline and Amorphous) and Interphases in Lithium Batteries
Enyuan Hu, Muhammad Rahman, Sha Tan and Nan Wang; Brookhaven National Laboratory, United States

Lithium batteries are complicated systems of electrodes and electrolytes. The inherent thermodynamic instability between the electrode and the electrolyte frequently results in the formation of an interphase. Understanding the dynamics of the electrodes and this interphase during battery operation is pivotal to advancing battery technologies. However, several challenges render the characterization process particularly daunting: 1. the processes can be far from equilibrium, making them unpredictable through traditional methods like phase diagrams; 2. instead of a well-defined crystalline structure, the electrode may assume an amorphous form, complicating our understanding; 3. the interphase exists in extremely trace amount, making its observation and characterization process particularly daunting: 1. the processes can be far from equilibrium, making them unpredictable through traditional methods like phase diagrams; 2. instead of a well-defined crystalline structure, the electrode may assume an amorphous form, complicating our understanding; 3. the interphase exists in extremely trace amount, making its observation and characterization process particularly daunting.

2:30 PM ES02.05.03
Revealing the Sodium Storage in Hard Carbon Pores
Luis Kitsu Iglesias; Emma Antonio and Michael Toney; University of Colorado Boulder, United States

Sodium-ion batteries (NIBs) are an attractive candidate to support the increasing demand of energy, especially amid growing concerns about the sustainability of lithium resources for lithium-ion batteries. NIBs provide advantages due to the abundance of sodium, its low cost, and electrochemical performance. Hard carbon (HC) is the most promising anode for the commercialization of NIBs, however, due to its structural complexity, a general mechanism for sodium storage in HC remains unclear, obstructing the development of highly efficient anodes for NIBs. To elucidate the mechanism of sodium storage in HC pores, we combined operando synchrotron small-angle X-ray scattering, wide-angle X-ray scattering, X-ray absorption near edge structure, Raman spectroscopy, and galvanostatic measurements. Through this multidimensional investigation, we provide mechanistic insights into the sodium pore filling process across various HC microstructures including the pore sizes that are preferentially filled, the extent to which different pore sizes are filled, and how the defect concentration influences pore filling. We observe that sodium in the larger pores exhibits an increased pseudo-metallid sodium character, indicative of larger sodium clusters. Furthermore, we show that the hard carbons prepared at higher pyrolysis temperature have a larger capacity from sodium stored in the pores, and that sodium intercalation between graphene layers occurs simultaneously to the pore filling in the plateau region. Our results suggest that the engineering of defects in pore walls, together with increasing the pore size distribution and/or volume fraction of closed pores are key to designing superior HC anodes. Moreover, our study also gives a systematic approach to study other porous functional materials and to understand how ions store in the pores.

2:45 PM ES02.05.04
Comparing the Insertion Properties of Mg²⁺ into V₂O₅·H₂O in Organic and Aqueous Electrolytes
Daniela Söllinger and Simone Pokrant; University of Salzburg, Austria
Batteries are indispensable in our society due to their ability to store renewable energy efficiently and provide it on demand. [1] In this context, lithium-ion batteries offer one of the highest energy densities and are already used in numerous mobile applications. However, lithium reserves and their accessibility are limited, which motivates researchers to find alternatives with similar electrochemical properties, i.e. low redox potentials and high volumetric/gravimetric specific capacities as counter electrode in batteries compared to lithium.

In this context, magnesium is attractive because it is more abundant, has a low redox potential vs. SHE and a small ionic radius, comparable to lithium. [2] The double charge of magnesium results in advantages and disadvantages; on the one hand it offers the possibility to store a higher amount of charge, while on the other hand the stronger polarization of Mg$^{2+}$ compared to Li$^{+}$ leads to challenges concerning the intercalation process. Therefore, cathode materials, which allow the reversible intercalation of Mg$^{2+}$, offer high theoretical capacities and are stable in various chemical environments e.g. in organic and aqueous electrolytes, are of great interest in current magnesium-ion battery research. One promising cathode material, which can fulfill these requirements, is hydrated vanadium oxide V$_2$O$_5$·H$_2$O. [3]

In this context, we show via operando XRD how the structural evolution of V$_3$O$_7$·H$_2$O during ion insertion is affected by adding small quantities of water to the organic electrolyte. In addition, we study Mg$^{2+}$ insertion into V$_2$O$_5$·H$_2$O in a completely aqueous electrolyte for the first time. Then we compare the structural properties of hydrated vanadium oxide as cathode material with respect to Mg$^{2+}$ insertion in organic and aqueous electrolytes.

In the next step we investigate to which extent the chemical environment influences the electrochemical properties. Hereby, V$_2$O$_5$·H$_2$O shows promising initial specific capacities of ~300 mAh g$^{-1}$ in a pure aqueous electrolyte at practical current densities of 100 mA g$^{-1}$ which demonstrates the versatility of V$_2$O$_5$·H$_2$O as cathode material for Mg$^{2+}$ insertion.

References:
order polysulfide species ($\text{Li}_2\text{S}_8$ and $\text{Li}_2\text{S}_6$) on the cathode and quickly diffused to the entire separator. This polysulfide diffusion resulted in the majority capacity decay in Li-S batteries.

In summary, we highlight the crucial role of operando XAS and X-ray spectromicroscopy as a transformative tool to overcome the fundamental challenges in Li-S batteries. Our study offers the potential for high-energy-density and sustainable energy storage solutions.
Li$_3$PS$_4$ is an attractive solid-electrolyte material that possesses high RT ionic conductivity ($10^{-4}$ S.cm$^{-1}$) but the effects of specific synthesis parameters on the material's local structure and transport properties still demand clarifications. In particular, mechano-chemistry induces the formation of a variety of P$_x$S$_y^{4-}$ moieties that strongly influence the global transport properties of Li$_3$PS$_4$.

Na$_3$PS$_4$ is another very interesting material with complex crystal chemistry that we will present. The effects of mechanochemical synthesis that lead to increased ionic conductivity in an archetypical sodium ion conductor Na$_3$PS$_4$ were not fully understood and we undertook comprehensive analysis based on diffraction (Bragg and pair distribution function), spectroscopy (impedance, Raman, NMR and INS), and ab initio simulations.

**References**


SESSION ES03.02: General Session II

Session Chairs: Robert Sacci and Yan Yao

Tuesday Afternoon, April 23, 2024

Room 423, Level 4, Summit
4:30 PM *ES03.02.06
Constriction Susceptibility of Anode Materials in Solid State Batteries Xin Li; Harvard University, United States

This talk introduces a new concept of constriction susceptibility of anode materials found in all-solid-state batteries. X-ray diffraction, transmission electron microscopy, scanning electron microscopy, and elemental analysis techniques were used to characterize the structural and chemical details of the anode. Density functional theory simulation and high-throughput computation were used to analyze the constriction susceptibility of materials at anode, which helps categorize and design new anode materials. A proper utilization of the phenomenon can lead to fast plating and stripping of Li metal in the anode at high areal capacity in experiment. A pouch cell made by slurry-casting technique was used to demonstrate the stable and fast cycling capability of such anode design.

5:00 PM ES03.03.01
Formation of Intimate Interfacial Contact between The NCM and Li$_2$PS$_4$CI Solid Electrolyte for All-Solid-State Batteries Jaeik Kim, Seungwoo Lee, Hyunjejin Lee, Joonhyeok Park, Jiwoom Kim, Gunwoo Cha, Hongjun Park, Bobae Lee, Ungyu Paik and Taeseop Song; Hanyang University, Korea (the Republic of)

All-solid-state batteries (ASSBs) with sulfide-based solid electrolytes (SEs) have been considered the most promising next-generation energy storage system due to their high energy density. However, mechanical instability such as initial insufficient physical contact and physical contact loss during cycling at the cathode active materials/solid electrolyte interface impede the practical use of ASSBs. Here, we report high-performance ASSBs using a Ni-rich NCM as cathode active materials coated with argyrodite-type sulfide solid electrolyte through the mechanofusion method. The uniformly coated solid electrolyte layer guarantees solid physical contact between cathode active materials and solid electrolytes, enabling sufficient ion transport pathways. Furthermore, the firmly attached solid electrolyte does not detach from NCM when the cathode active material shrinks during de-lithiation. Making intimate initial physical contact and maintaining physical contact repress the interface resistance effectively. As a result, a full cell with argyrodite-coated NCM shows significantly enhanced electrochemical performances.

5:00 PM ES03.03.02
Multifunctional Covalent Organic Framework Solid Electrolyte Facilitating Fast Li-Ion Diffusion in Solid-State Batteries Jun-Hyeong Lee, Jaewoo Lee, Yoonhee So, Hong-Won Kim, Yujin Choi and Jong-Ho Kim; Hanyang University, Korea (the Republic of)

Ensuring the safety, high energy density, and long-term cycling performance of all-solid-state Li metal batteries (LMBs) requires the development of compatible organic solid electrolytes. However, it remains a challenge to develop an approach that enables organic solid electrolytes to easily dissociate strong Li-ion pairs and facilitate rapid Li-ion transport. In this study, a diethylene glycol-modified pyridinium covalent organic framework (DEG-PMCOF) with a well-defined periodic structure is prepared as a multifunctional solid electrolyte with a cationic moiety of high polarity, an additional flexible ion-transporter, and an ordered ionic channel for all-solid-state LMBs. The DEG-containing pyridinium groups within DEG-PMCOF lower the dissociation energy of Li salts as well as the energy barrier for Li-ion transport, resulting in an enhanced ion conductivity and a high Li-ion transfer number at room temperature in the solid electrolyte. Furthermore, the DEG-PMCOF solid electrolyte offers a wide electrochemical stability and effectively prevents the formation of Li dendrites and dead Li in all-solid-state LMBs. Molecular dynamics and density functional theory simulations provide insights into the mechanisms underlying the improved Li-ion transport in DEG-PMCOF, involving integrated diffusion processes such as hopping motion, vehicle motion, and free diffusion. The all-solid-state LMB constructed with a DEG-PMCOF solid electrolyte exhibits a high specific capacity, excellent retention, and outstanding Coulombic efficiency at various C-rates during long-term cycling. This DEG-PMCOF approach represents an effective strategy for designing a variety of solid-state Li batteries.

5:00 PM ES03.03.03
Enhancing Lithium Transport in Garnet-Type Solid Electrolyte for High-Performance All-Solid-State Batteries Young-Gyun Lee and Jay Whitacre; Carnegie Mellon University, United States

Garnet-type Li$_5$La$_2$Zr$_2$Ti$_3$O$_{12}$ (LLZTO) is a promising solid-state-electrolyte for all-solid-state batteries; it has a good chemical stability in contact with Li metal and high ionic conductivity. However, insufficient interfacial contact and associated voids caused by poor wetting between Li metal and LLZTO can lead to a huge interface resistance and thus poor electrochemical performance including a high overpotential and limited critical current density (CCD). In addition, Li dendrites can be formed and will propagate through the LLZTO microstructure within the pores and grain boundaries, which can cause cell short circuiting. In this work, LiAlO$_2$ (LAO) was used as a sintering additive to improve a LLZTO microstructure with a denser structure, lower porosity, and compacted grain boundary regions. LLZTO with LAO (LLZTO-LAO) showed a higher relative density (~95%) and reduced porosity (~4.2%) compared to pure LLZTO (88% of relative density and 9.5% porosity). To calculate the ionic conductivity and activation energy of the LLZTO, a blocking electrode sputterde by gold on both side LLZTO was fabricated. LLZTO-LAO displays an improved ionic conductivity (0.59 S cm$^{-1}$) and Li-ion activation energy (0.38 eV). In order to investigate interface resistances between LLZTO-LAO and Li metal, Li-Li symmetric electrochemical test cells were used. An enhanced interfacial resistance (72.5 Ω cm$^2$) was demonstrated for the LLZTO-LAO cell. Li plating/stripping tests with critical current density (CCD) and cycling performance of Li symmetric cells were investigated by galvanostatic cycling experiment. While LLZTO delivers a lower CCD of 0.1 mA cm$^{-2}$, a higher CCD of 0.3 mA cm$^{-2}$ is demonstrated within the symmetric cell with LLZTO-LAO. Furthermore, the firmly attached solid electrolyte does not detach from NCM when the cathode active material shrinks during de-lithiation. Making intimate initial physical contact and maintaining physical contact repress the interface resistance effectively. As a result, a full cell with argyrodite-coated NCM shows significantly enhanced electrochemical performances.

5:00 PM ES03.04
The Effect of Slurry pH Values on The Electrochemical Properties of Manganese-Based-Oxide Electrode for Solid-State Batteries Thu-Hao Kuo, I-Han Lee, Chia-Chien Ma and Tri-Rung Yew; National Tsing Hua University, Taiwan

With the rapid growth of electric vehicles, their conventional lithium-ion batteries (LIBs) are suffering from insufficient energy density and potential safety risks. High-capacity, earth-abundance, and low-flammability make manganese oxides a promising active material for anodes. Furthermore, the pH value of solid-state batteries (SSBs) influences lithiation and delithiation reactions, which in turn impacts the lithium wettability and interface resistance of SSBs. It is critical to study the effect of pH range so as to optimize the active materials and binders in manganese-based-oxide anodes.

In this work, the different pH values of electrode slurries will be investigated to improve the stability of binders and active materials. Furthermore, the pH value will be optimized to inhibit the unnecessary irreversible reactions during charge and discharge. It is expected that the optimized pH value of electrode slurries will enhance the retention, Coulombic efficiency, and rate-capability of the manganese-based-oxide anode in SSBs.

For the optimization of the pH value for manganese-based-oxide electrode slurries, water-based slurries will be produced by mixing manganese oxide powders, carbon black (super P), carboxymethyl cellulose (CMC), and styrene-butadiene rubber (SBR). The pH value of slurries will be adjusted with an oxalic acid. After that, the premixed slurries will be coated on copper foils by using a doctor blade, and then baked in a vacuum oven. After battery assembly, the electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge (GCD) analyses will be applied to analyze the Coulombic efficiency, cycling life, and impedance variation resulted from different pH values. The composition and structure of active materials will be characterized by field-emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). This work will shed a light on controlling the pH value of manganese-based-oxide electrode slurries, for the improvement of SSB retention.

5:00 PM ES03.05
Zwitterionic Covalent Organic Framework Solid Electrolyte with Ordered Ionic Channels for All-Solid-State Lithium-Metal Batteries Jaewoo Lee, Jun-Hyeong Lee, Jae-Hoon Shin, Yoonhee So, Yejoo Yu, Yujin Choi, Hong-Won Kim and Jong-Ho Kim; Hanyang University, Korea (the Republic of)

Organic solid electrolytes are considered a promising way to enhance the energy density of Li rechargeable batteries. However, practical applications of organic solid electrolytes have suffered from extremely low ionic conductivity at room-temperature due to strong ion pairs of Li salts and lack of ordered ionic channels for Li$^+$ diffusion. Covalent organic frameworks (COFs) with...
well-defined chemical and pore structures can be considered excellent candidates for solid electrolytes due to their uniform channels for the migration of ionic species. Herein, the zwitertonic covariant organic framework (Zwitt-COF) was developed as a solid electrolyte with not only the superior ability to dissociate strong Li-ion pairs but also well-organized ionic channels for fast Li\textsuperscript+ diffusion. Theoretical simulations revealed that zwitertion can effectively dissociate the strong Li-ion pairs, and the linear hexagonal ion channels can be reopened in the Zwitt-COF solid electrolyte by reconstructing AA stacking structures due to the dissociative adsorption of Li\textsuperscript+ on Zwitt-COF. The Zwitt-COF electrolyte exhibited high ionic conductivity at room-temperature and stable Li plating/stripping performance without formation of Li dendrite and dead Li. Furthermore, the Zwitt-COF electrolyte displayed a wide electrochemical stability window and outstanding thermal stability. All-solid-state Li metal full cells prepared with a Zwitt-COF electrolyte exhibited excellent cyclic performance for a long duration with high retention of discharge capacity. The strategy for incorporating zwitertin into a COF structure can provide an effective way to develop various all-solid-state batteries.

5:00 PM  ES03.03.06

Development of Solid Polymer Electrolyte with Excellent Electrochemical Properties Using High-Energy Electron Beam Irradiation  Wookil Chag and Taeshik Earmme; Hongik University, Korea (the Republic of)

Lithium-ion batteries (LIBs), an energy storage system used in various fields such as electronic devices, electric vehicles, and unmanned aerial vehicles, consist of a cathode, anode, separator, and electrolyte. Currently, commercialized LIBs employ a liquid electrolyte that utilizes carbonate-based organic solvents. When an exothermal reaction is triggered by overcharge or external shock, the thermally unstable organic solvent can generate flammable gases and lead to ignition, ultimately causing a thermal runaway in LIBs. Due to the safety concerns associated with organic solvent-based liquid electrolytes, research has been conducted on solid-state electrolytes (SSEs) as an alternative to liquid electrolytes (LEs). Among various SSEs, polymer electrolytes (PEs) have garnered attention for their advantageous interfacial properties, form factor, and processability. In this study, the fabrication method for PEs involves in-situ polymerization. PEs created through in-situ polymerization are prepared by injecting a liquid precursor comprising monomers, lithium salt, initiators, and other components into the cell. Typically, thermal initiation is employed as the primary method for PE fabrication. However, thermal initiation comes with drawbacks, including challenges in controlling precursor reactions and the requirement for extended heat treatments. To address these issues, solid polymer electrolytes (SPEs) are used for high-energy electron beam irradiation. SPEs are produced with just tens of seconds of electron beam exposure. Optimized SPEs exhibit an average ionic conductivity of 0.54 mS cm\textsuperscript{-1}, a lithium transfer number (t\textsubscript{Li}) of 0.69, a wide electrochemical stability window exceeding 5 V, and excellent properties in suppressing the growth of lithium dendrites. Furthermore, in the NCM811SPEsLi cell configuration, a discharge capacity of 183 mAh g\textsuperscript{-1} (0.1 C, 25 °C) was achieved, with 80% capacity retention after 200 charge/discharge cycles at 0.5 C and 25 °C.

5:00 PM  ES03.03.07

Rational Design of Electrolyte and Interface for High-Performance and Safer Solid-State Li Batteries  Dongjun Kim, Baozhi Yu and Ying Chen; Deakin University, Australia

Solid-state Li metal batteries (SSLMB) gained increasing attention from researchers. Free of flammable organic liquid electrolytes by replacing solid-state electrolytes (SSE) greatly enhances battery safety, and employing Li metal anode possesses ultrahigh specific capacity and lowest redox potential delivers higher energy density than current state-of-art Li\textsuperscript+ ion batteries. However, the safety crisis still exists, due to the extremely high reactivity of Li metal and the uneven plating-stripping behavior of Li anode. Unwanted side reactions pulverize SSE and electrode-electrolyte interface. Dendritic Li deposition accumulates dead Li, penetrates SSE, and eventually involves internal short-circuit. Moreover, incomplete solid-solid contact between SSE and electrode induces severe polarization during battery operation. The poor interfacial compatibility of SSE to Li metal, both (electro-)chemically and physically, hinders the practical application of SSLMB so far. Here, we suggest some effective approaches to resolve interface issues in the SSLMB. Firstly, we prepared an artificial solid electrolyte interphase (SEI) layer using poly(vinyl alcohol) and hydroxyl-functionalized boron nitride nanosheets. The artificial SEI alleviates the side reaction between Li metal and electrolyte, which mitigates electrolyte degradation. We found that this artificial SEI also assists uniform Li plating-stripping and suppresses dendritic Li deposition, by boosting Li\textsuperscript+ ion transport at the electrode-electrolyte interface. Secondly, we designed multi-layered SSE with inorganic-gel hybrid SSE and in-situ prepared SSE. The inorganic-gel hybrid layer supports excellent mechanical stability and fast Li\textsuperscript+ ion conduction with a high Li\textsuperscript+ ion transfer number. The in-situ prepared SSE greatly improves interfacial compatibility between SSE and Li metal anode. It provides intimate contact at the interface and prevents inorganic electrolyte decomposition in the hybrid. Moreover, by comparing different layered SSEs, we found that the bulk electrolyte layer assists cycling stability, while the interfacial layer dictates the practical current density of layered SSE. When this multi-layered SSE is applied in the Li-S full cell, the layered SSE only allows polysulfide dissolution in the in-situ SSE layer and halts its further diffusion into the bulk electrolyte.

5:00 PM  ES03.03.09

Development of an All-Solid State Li-Ion System  Damiel Mourraoub; CEA - LITEN - Grenoble Alpes, France

Li-ion batteries are considered as the most suitable electrochemical energy storage systems for a wide range of applications including automotive applications in order to contribute to the reduction of CO\textsubscript{2} emissions responsible for climate change. In recent years, the majority of the works on batteries has consisted in developing solid electrolytes with the goal to improve their safety and the possibility of using a negative electrode based on metallic lithium which will ultimately make it possible to achieve high energy densities. CEA-Liten and Saft have jointly developed a solid-state polymer electrolyte system. The polymer PTMC (Poly trimethylene carbonate) has been selected for its high transport number, over 0.7, and its stability with respect to lithium both at high potential and at low potential despite its modest conductivity. The Solid Polymer Electrolytes (SPE) realized is a crosslinked membrane based on PTMC, with good mechanical properties that allow an easy handling and integration into a complete system (Fig 1). The electrodes containing PTMC and NMC622, Graphite or SiOx as active material were manufactured with a surface capacities around 1mAh cm\textsuperscript{-2}. Their mechanical properties are similar to conventional Li-ion electrodes. Solid-state prototypes with a capacity around ten milliampere-hours have been assembled with these components. The performances of the all-solid prototypes containing PTMC are encouraging. Indeed, they operate correctly at a C/20 rate at 80°C but also at room temperature with the addition of plasticizers.

5:00 PM  ES03.03.11

Recent Advancements and Prospects Of Lithium-Ion Batteries: Smart Features, High Performance Anode, Cathode and Electrolyte Materials  Shaharia Ahmed, S M Anvett Ullah Shahge, Md Wankir Arabhan and Jasim Uddin; The University of Texas, United States

Nowadays, lithium-ion rechargeable batteries (LiBs) are the predominant source for energy storage and have promising prospects in the future. Monitoring the health status of the LiBs has become a pressing need to prolong the life and increase the security of Li-powered applications. This need has opened new possibilities for smart LiBs research, enhancing battery life and safety. Herein, the scheme of sensors for Li-ion smart batteries has been discussed, which use a straightforward beam structure towards the measurement of different parameters, for instance, force, temperature, and displacement. Besides, we have discussed the most recent high-performance anode, cathode, and electrolyte materials used for and the modification of the materials by using different techniques to make them suitable for high-energy density Li-ion batteries. Finally, it has been concluded with promising future outlooks of the LiBs research by using these high-performance materials.

5:00 PM  ES03.03.13

Investigation of Mechanical Characteristics of Cathodes in Composite Cathode of All Solid-State Batteries  Joseph M. Vazquez and Howard Qingsong Tu; Rochester Institute of Technology, United States

All-solid-state batteries (ASSBs), responsible for both ion transfer and resisting dendrite growth. A robust solid electrolyte that excels in these functions is essential for advancing ASSB technology. Existing solid electrolytes face challenges like poor interfacial contact, mechanical debonding, and mechanical failure. While the field predominantly focuses on ion transfer and micro-scale mechanical properties, there is a noticeable gap in understanding macro-scale mechanics. This study addresses this gap by examining prevalent solid electrolytes, including Li6PS5Cl, Li3YCl6, Li3YBr3Cl3, LPSCl, and Li1.4La1.4Zr1.4Ta0.6O12. Through traditional compression testing supported by video analysis, we reveal the correlations between pellet density and slenderness with elasticity, strength, and toughness across sulfide, halide, and oxide solid electrolyte materials. Our findings underscore the macro-scale mechanical advantages of LPSCl, exhibiting a relatively large elastic range (5–83 MPa), high compressive strength (~103 MPa), significant toughness (~16 MPa), and semi-ductile nature. The notable differences in elastic, non-linear, and failure mechanics among solid electrolytes emphasize the relevance of macro-scale mechanical properties in predicting cell failures such as capacity fading, dendrite growth, and contact loss.

5:00 PM  ES03.03.14

Long-Durable Three-Dimensional Garnet-Type Li6.4La1.4Zr1.4Ta0.6O12 Solid-State Li-Metal Batteries  Sung Ryoul Choi, Seojeong Yoo and Jun-Young Park; Sejong University, Korea
Lithium-metal (Li-metal) holds promise as an anode material for next-generation high-energy density lithium-ion batteries (LIBs) due to its exceptional theoretical capacity of up to 3860 mAh/g [1]. However, technical challenges are remain, notably concerning safety due to dendrite formation during charge-discharge cycles [2]. In conventional aqueous-LIBs, preventing the penetration of Li dendrites remains unresolved despite extensive efforts [3]. To address this challenge, solid-state electrolytes (SSEs) have emerged as promising alternatives due to their high ionic conductivity, stability against Li-metal, and wide electrochemical windows [4]. SSEs encompass various categories such as polymer electrolytes, inorganic sulfide electrolytes, and inorganic oxide electrolytes [5]. Among these, the garnet-type Li₆La₃Zr₂O₁₂ (LLZTO) stands out for its excellent ionic conductivity, ranging from 10⁻⁴ to 10⁻³ S cm⁻¹ and its thermodynamic stability against Li-metal [6, 7]. However, the formation of Li dendrites persists even at low current densities, primarily due to the inhomogeneity between Li-metal and the LLZTO electrolyte, particularly poor Li-metal wettability on the LLZTO electrolyte [8, 9]. Efforts to address the lithiophobic nature of LLZTO electrolytes have involved surface polishing, which enhances lithium wettability [10-12]. Another approach for improving Li-metal wettability is the introduction of nanometer-scale metal/metal oxide interlayers at the Li-metal–LLZTO interface [13, 14]. However, these strategies have not completely prevented dendrite formation, evident from low critical current density (CCD) results [15]. In our study, we present a three-dimensional (3D) tri-layer structure created via the tape-casting technique. This structure comprises porous-dense- porous regions. The porous layer plays a crucial role in enhancing the heterogeneity of the interface between the Li-metal anode and LLZTO electrolyte, facilitating Li-metal wetting and infiltration into the pores. Additionally, the dense morphology acts as a protective layer, impeding Li dendrite penetration, as dendrites tend to propagate along porous regions and grain boundaries of the LLZTO electrolyte. This architecture resulted in stable Li-metal cycling at high current density and improved critical current density performance.

**Keywords:** Lithium-ion batteries, Li₆La₃Zr₂O₁₂, solid-state electrolyte, dendrite.

**References**


**5:00 PM ES03.03.15**

Converting Primary Alkaline Batteries to Rechargeable Solid-State Batteries via Single-Anion Conducting Polymer Electrolytes Eric G. Ruzicka, Hunter O. Ford, Brian Chaloux, Jeffrey Long, Debra R. Rolison and Megan B. Sassin; Naval Research Laboratory, United States

**5:00 PM ES03.03.16**

Solid State Polymer Electrolyte for Lithium Ion Batteries Dianel Mouragzh, Lionel Picard and Thibaut Gutel; CEA - LITEN - UGA, France

Li-ion batteries are considered as the most suitable electrochemical energy storage systems for a wide range of applications including automotive applications in order to contribute to the reduction of CO2 emissions responsible for climate change.

In recent years, the majority of the works on batteries has consisted in developing solid electrolytes with the goal to improve their safety and the possibility of using a negative electrode based on metallic lithium which will ultimately make it possible to achieve high energy densities. Lithium-ion batteries currently dominate the rechargeable battery market, but their reliance on expensive and non-US sourced active materials and flammable electrolytes leave the door open for researchers to develop rechargeable batteries based on alternative chemistries.

Here, we report on the synthesis and characterization of a polymeric hydroxide-conducting solid-state electrolyte (SSE) and demonstrate that this SSE facilitates rechargeability in alkaline Ag-Zn cells that are conventionally used as primary batteries. Utilizing a library of inhouse-synthesized styrenic monomers to generate custom SSEs, we found that the architecture of the polymer not only influences the stability of the SSE, but also the capacity and cycle life. Infrared (IR) and x-ray photoelectron spectroscopies (XPS) were utilized in conjunction with scanning electron microscopy (SEM) to assess the SSE and electrode chemistry before and after electrochemical cycling to evaluate for stability and active material-crossover. Combining electrochemistry (impedance spectroscopy, cyclic voltammetry, and galvanostatic cycling) with these results, we determined that crosslinking, chemistry of the quaternizing agent, and the electrode quality/geometry influence Ag-Zn cell performance.

Demand for energy storage devices to supply society with its ever-increasing energy needs necessitates the development of portable power systems with enhanced energy efficiency, long cycle life, and improved safety. Lithium-ion batteries currently dominate the rechargeable battery market, but their reliance on expensive and non-US sourced active materials and flammable electrolytes leave the door open for researchers to develop rechargeable batteries based on alternative chemistries.

In this work, we present a pathway for the direct synthesis and processing of REAHs from concentrated aqueous solutions and we will discuss making thin membranes through dehydration and other casting methods.

The US Department of Energy's Energy Efficiency and Renewable Energy Vehicles Technologies Office provided funding for this work.
Unveiling The Mechanical and Electrochemical Evolution of Nano Silicon Composite Anodes in Sulfide based All-Solid-State Batteries

Hongli Zhu; Northeastern University, United States

The utilization of silicon (Si) anodes in all-solid-state lithium batteries (ASLBs) provides the potential for high energy density. However, the compatibility of sulfide solid-state electrolytes (SEs) with Si and carbon is often questioned due to potential decomposition. To investigate this, operando X-ray absorption near-edge structure (XANES) spectroscopy, ex-situ scanning electron microscopy (SEM) and ex-situ X-ray nano-tomography (XnT) were utilized to study the chemistry and structure evolution of nano Si composite anodes. Results from XANES demonstrated a partial decomposition of SEs during the first lithiation stage, which was further accelerated by the presence of carbon. But the performance of first three cycles in Si-SE-C was stable, which proved the generated media is ionically conductive. XnT and SEM results showed that the addition of SEs and carbon improved the structural stability of the anode with fewer pores and voids. A chemo-elasto-plastic model revealed that SEs and carbon buffered the volume expansion of Si, thus enhancing mechanical stability. The balance between the pros and cons of SEs and carbon in enhancing reaction kinetics and structural stability enabled the Si composite anode to demonstrate the highest Si utilization with higher specific capacities and better rate than pure Si and Si composite anodes with only SEs.

8:45 AM *ES03.04.03
On The Journey toward Competent All Solid State Electrolytes
Rana Mohaddes1,2; 1Toyota Research Institute of North America, United States; 2Tohoku University, Japan

Energy storage systems poised to offer improved performances beyond that afforded by Li-ion batteries are intensely being studied. Of these, all solid state batteries ASSBs promise to dramatically improve the energy storage densities and efficiencies by way of utilizing non-flammable solid state electrolytes SSEs that possess high compatibility with reactive anode and cathode materials, such as metallic anodes and high voltage cathodes. Unfortunately, all known families of SSEs fall short from fulfilling this demand and thus new SSE materials are required. We will herein discuss the status of these technologies and report critical SSEs advancements conducted in our group.

9:15 AM ES03.04.04
Fast Room-Temperature Mg-Ion Conduction in Clay-Like Solid Electrolytes
Xiaochen Yang1,2, Sunny Gupta1, Yu Chen2 and Gerbrand Ceder1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States; 3Rice University, United States

The discovery of mechanically soft solid-state materials with fast Mg-ion conduction is crucial for the development of solid-state magnesium batteries. Herein, we report a novel solid magnesium electrolyte that achieve high ionic conductivity of 0.47 mS/cm at room temperature. These Mg-ion conductors exhibit clay-like mechanical properties, enabling intimate contact at the electrode–electrolyte interface during battery cycling. With a combination of experimental and computational analysis, we identify that the soft-clay formation is induced by partial anion exchange. This partial anion exchange creates undercoordinated magnesium ions, yielding fast Mg-ion conduction. Our work demonstrates the potential of clay-like halide electrolytes for all-solid-state magnesium batteries, with possible further extension to other multivalent battery systems.

9:30 AM ES03.04.05
Scale-Up of Halide-Based All-Solid-State Batteries
Fengyu Shen1, Michael McGahan2, John D. Pietras3, Marka M. Dookf1, Vincent S. Battaglia1 and Mike Tucker1; 1Lawrence Berkeley National Laboratory, United States; 2SGR North America, United States

All-solid-state batteries (ASSBs) offer improved safety and potential higher energy density for energy storage. Among the components of ASSBs, the solid electrolyte plays an important role as it is the key component to prevent dendrite growth and forms interfaces with the cathode and anode. Halide solid electrolytes gain significant attention due to the high ionic conductivity, low processing temperature, good formability, oxygen resistivity and high-voltage stability. Our study demonstrated the feasibility of scaling up halide electrolyte and halide-containing cathode by tape casting, using toluene as a solvent and MSB1-13 as a binder. A low-voltage cathode (LiFePO4) was used and cell performance was tested in button cell with size of 0.5 cm² area. In this study, pouch cells are manufactured, involving 80% cathode active material (LiNi0.82Mn0.07Co0.11O2) loading and Li/In alloy anode. A pouch cell is cycled under a lower stack pressure and results of long-term cycling will be reported. The interfacial resistance of pouch cells is higher than that of button cells with the same composition as the stack pressure for button cells is much higher (100 MPa). Cells with Li metal anode are also explored with an anode interlayer, cycling in a voltage window of 3-4.3 V, and the cell performance will be compared with that of the cells with Li/In alloy anode.

Reference:

9:45 AM ES03.04.06
Robot-Assisted Sol-Gel Exploration of Cation-Disordered Rocksalt (DRX) Materials for Li-Ion Batteries
Tim Kodalle1, Yuxing Fei1,2, Nathan Szymanski1, Yan Zeng1, Gerbrand Ceder1,2 and Carolin M. Sutter-Fella1; 1Lawrence Berkeley National Laboratory, United States; 2University of California, Berkeley, United States

Rechargeable Li-ion batteries are omnipresent in our daily lives and demand is increasing. To satisfy the tremendous growth, there is a great interest in developing novel high-performance electrode materials at reduced cost, and nickel and/or cobalt free. [1] In this regard, Li-excess cation-disordered rocksalt (DRX) metal oxides have been identified as promising cathode materials with energy densities that can exceed traditional layered cathodes such as LiTMO2 with TM being a combination of transition metals.[1,2] Some drawbacks of these DRX materials include significant first-cycle capacity loss, limited cyclc life, and voltage fade.[1] Several factors have been identified to mitigate these drawbacks, including greater disorder of the TMs as well as controlled particle size and shape.[3] Each of these characteristics can be manipulated by modifying the choice of precursors and synthesis techniques.

Conventionally, solid-state synthesis is employed for the fabrication of electrophochemically active materials including Li-ion batteries.[4] The typical sequence of synthesis steps includes mixing, grinding, pelleting, and annealing. Such reactions are driven by solid-state diffusion, which is predominantly controlled by time and temperature.[4] In comparison, the sol-gel approach to synthesis consists of elements at the molecular level by dissolving precursors in a solvent (e.g. water) with the addition of chelating agents (e.g. citric acid) to form a viscous gel. This is followed by solvent evaporation, gel decompositon, and annealing to form powders or thin films.[4] In this study, we compare the nucleation and crystallization pathway of Li-Mn-Ti oxide (LMTO) deposited both by solid-state as well as sol-gel synthesis. Using automated, robot-assisted synthesis approaches, we systematically investigate the parameter space of both syntheses and the influence of precursors and precursor ratios on phase purity, final composition, oxidation states, reaction temperatures, and sample uniformity.

In the cathodes fabricated by solid-state synthesis, we find strong competition between two intermediate spinel-like phases, Li2MnO4 and Li2TiO3, depending on the oxidation state of the TMs as well as the Li-TM ratio in the selected precursors. While the intermediates forming in cathodes deposited via the sol-gel method appear to be less sensitive to these parameters, we find a strong dependency on the solvents and chelating agents used for fabrication. Additionally, we observe a strong interdependency between the choice of solvents and the ratio of Li:TM's influencing the reaction temperature of target phases and intermediates. Based on these findings, we will propose reaction pathways as well as a nucleation model for LMTOs prepared by sol-gel synthesis.

References:

10:00 AM BREAK

SESSION ES03.05: Conductivity and Transport I
Session Chairs: Pieremanuele Canepa and Richard Remsing
Wednesday Morning, April 24, 2024
Room 423, Level 4, Summit

10:30 AM *ES03.05.01
Chloride Solid Electrolytes: Structural Complexity, Ion Transport and Reactivity
Raphaëlle Clement; University of California, Santa Barbara, United States
Electronic Paddle-Wheels Facilitate Transport in Solid-State Ionic Conductors

Richard Remsing; Rutgers University, United States

Solid-state ionic conductors (SSICs) are promising alternatives to liquid electrolytes in energy storage technologies. The rational design of SSICs and ultimately their deployment in battery technologies requires a thorough understanding of their ion conduction mechanisms. In SSICs containing molecular ions, molecular rotations couple to translational diffusion to create a “paddle-wheel” effect that facilitates conduction. This paddle-wheel mechanism explains many important features of molecular SSICs. However, we lack a similarly detailed explanation for anharmonic lattice dynamics and ion conduction in SSICs composed of monatomic ions. I will discuss our recent theoretical work that provides such an explanation. We predict that ion conduction in many SSICs involves “electronic paddle-wheels,” in which localized lone pair electrons rotate, and these rotations couple to and facilitate ion diffusion. After discussing our evidence from simulation results, I will make analogies to molecular SSICs and argue that the electronic paddle-wheel mechanism creates a unifying principle for understanding ion conduction in both monatomic and molecular materials. We anticipate that a predictive understanding of electron paddle-wheels in ionic conduction can be leveraged to create design principles for engineering solid-state electrolytes from the electronic level on up.

How Correlated are Ion Hoppings in Inorganic Solid-State Electrolytes? Jisu Jung and Seungwoo Han; Seoul National University, Korea (the Republic of)

In this presentation, we present the use of Behler-Parrinello-type neural network potentials (NNPs) to overcome the aforementioned challenges and obtain Li-ion conductivities in argyrodite crystals and ab initio MD data at 600 and 1200 K. Several validations are conducted to ensure the quality of our NNP in terms of both structural and dynamic properties. To obtain the ionic conductivities, we select the SCAN functional, which reproduces the lattice parameter within 0.2% of the experimental value. To train the NNPs, we utilize the SIMPLE-NN package and employ strained bulk supercells containing 6500 atoms for up to 25 ns. In calculating the diffusivity, we neglect the initial 5 ns, where most of the Li-ions remain within the cage at room temperature, resulting in millions of atomic configurations. By doing this, we are able to (1) quantify correlations between many diffusing ions, (2) identify predominant collective migrating mechanisms and (3) determine how specific and novel migration descriptors such as the length and duration of individual ionic hops correlate with ionic diffusion coefficients, all under realistic finite-temperature conditions.

We show that the probability for N-ions to concertedly diffuse decreases exponentially with N, and that such many-ion correlations practically do not depend on temperature. Interestingly, it is found that despite N = 2 correlations are largest, higher order many ion (N > 2) coordination is more frequent in concerted diffusion. The explained unsupervised analysis approach has been implemented in the IonDiff software [3], a python code that is publicly available.

Path Integral Approaches to Ion Diffusion

Jarvist M. Frost and Lucius Liu; Imperial College London, United Kingdom

Classical ion diffusion theories rely on simplified hopping models lacking concerted motion. Molecular dynamics can capture correlations but requires extensive sampling. This fairly brute-force approach has become the normal way to calculate ion diffusion rates, recently accelerated with the use of machine learning force-fields trained against density functional theory calculations.

We revisit path integral techniques to bridge this gap. Integrating state-of-the-art graph neural network potentials [1], with the 1990s path-integral approach of Chakraborty et al. [2] offers an efficient route to model correlated transport, and understand the physical processes. Generally these more sophisticated mathematical models developed in the 70s to 90s, have mostly been neglected as attention has shifted to explicit simulation on fast computers.

We show how a semi-numerical path integral approach parameterised by lighter weight machine-learning force-field molecular dynamics, can describe and understand correlation effects in representative lithium, sodium, and halide ion conductors.


Enhancing Li-Ion Conductivity in Argyrodite Li$_6$PS$_5$Cl through Disorder Engineering Investigated by Machine Learning Potential

Jiho Lee; Suyeon Ju, Seungwoo Hwang, Jinmu You, Jisu Jung and Seungwu Han; Seoul National University, Korea (the Republic of)

Solid-state electrolytes (SSEs) have emerged as promising candidates for next-generation batteries, offering improved safety and higher energy density compared to conventional liquid electrolytes. Nevertheless, the practical utilization of SSEs has been hindered by the challenge of achieving high ionic conductivity at room temperature. Among SSEs, argyrodite systems have achieved a high conductivity of 10 mS/cm at room temperature through strategies involving disorder engineering and doping. To further optimize ionic conductivity and gain a comprehensive understanding of the underlying mechanisms, theoretical calculations based on density functional theory (DFT) have been applied. However, recent DFT studies have faced challenges in accurately quantifying transport properties in argyrodite systems compared to experiments, primarily due to computational limitations. For instance, small simulation cells introduce spurious correlations in Li-ion motions between periodic boundaries, while a scarcity of diffusion events makes direct simulation at room temperature difficult.

In this presentation, we present the use of Behler-Parrinello-type neural network potentials (NNPs) to overcome the aforementioned challenges and obtain Li-ion conductivities in argyrodite Li$_6$PS$_5$Cl with varying S/Cl disorders (0−100%). Utilizing cost-effective and accurate NNPs allows for direct simulations at room temperature, unraveling the effects of S/Cl disorders. We select the SCAN functional, which reproduces the lattice parameter within 0.2% of the experimental value. To train the NNPs, we utilize the SIMPLE-NN package and employ strained bulk crystals and ab initio MD data at 600 and 1200 K. Several validations are conducted to ensure the quality of our NNP in terms of both structural and dynamic properties. To obtain the ionic conductivity with a statistical convergence error range of 10%, we carry out systematic tests on the supercell and ensemble sizes. As a result, NNP MD simulations are performed using 5x5x5 supercells containing 6500 atoms for up to 25 ns. In calculating the diffusivity, we neglect the initial 5 ns, where most of the Li-ions remain within the cage at room temperature, resulting in non-linear mean squared displacements. Our predicted activation energies and ionic conductivities align well with experimental data. Interestingly, the conductivity peaks at 25% S/Cl disorder. By analyzing the diffusion mechanism, we find that the peak observed at 25% disorder arises from the synergistic effects of two contributing factors: the enhancement of rotational motion and the disorder effect which facilitates the Li diffusion between cages. Additionally, free energy analysis shows that these structures are thermodynamically accessible, suggesting the potential for optimizing Li-ion conductivity through disorder engineering in Li$_6$PS$_5$Cl. This work paves the way for estimating and studying the transport properties of SSEs using accurate and cost-effective NNPs.
Interfacial Engineering for Lithium Metal Batteries Employing Garnet-Type Electrolyte

Ju-Sik Kim¹, Sewon Kim¹, Gabin Yoom¹, Michael Badding², Zhen Song³ and Dongmin Im⁴;
¹Samsung Advanced Institute of Technology, Korea (the Republic of); ²Corning Incorporated, United States

Garnet-type solid electrolytes, represented by the composition Li₇La₂Zr₂O₁₂ and its derivatives, have recently garnered significant attention due to their good compatibility with lithium metal anode. However, several issues remain unsolved, hindering the commercialization of lithium metal batteries employing garnet-type electrolytes: (1) Carbonates and hydroxides easily form on the surface of garnet electrolytes, leading to high interfacial resistance when incorporated into batteries. (2) While the chemical stability of garnet-type electrolytes against lithium metal is reasonably good, it is frequently observed that lithium dendrites penetrate through the electrolyte layer, causing short circuits between the cathode and anode. (3) During cell discharge or lithium metal stripping, voids often form at the interface. This results in fluctuations in local current density, accelerates short-circuiting, and worsens cycling stability. In this presentation, we will demonstrate that surface treatment of garnet with acid and the introduction of a carbon or carbon-metal composite interlayer are highly effective in addressing these issues. Stable cell cycling performance is achieved even at room temperature, with an areal capacity comparable to that of commercial lithium-ion batteries. We will also discuss the working mechanisms of these methods.

2:00 PM *ES03.06.02

Sodium Solid-State Electrolyte and Electrode Interfaces

Jin An Sam Oh¹ and Y. Shirley Meng¹,²; ¹University of California, San Diego, United States; ²The University of Chicago, United States

An ideal solid-state electrolyte requires a high ionic conductivity, low electronic conductivity, and matched electrochemical window with the electrode. Often, it needs to possess mechanical properties with rigidity to acts as a separator while having the ability to form intimate interface with the electrode to realize the all-solid-state batteries. In this talk, I will share our recent efforts in material development and architecture design to enable all-solid-state sodium batteries as a complimentary and safe energy storage system.

2:30 PM BREAK

SESSION ES03.07: Electro-Chem-Mechanics

Session Chairs: David Stewart and Howard Qingsong Tu

Wednesday Afternoon, April 24, 2024

Room 423, Level 4, Summit

3:30 PM *ES03.07.01

High-Rate Cycling in 3D Dual-Doped NASICON Architectures toward Room-Temperature Sodium-Metal-Anode Solid-State Batteries

Prem Jaschin, Christopher Tang and Eric D. Wachsmann; University of Maryland, United States

Sodium metal-based solid-state batteries hold tremendous potential for next-generation batteries owing to low-cost earth-abundant sodium resources. However, fabricating thin free-standing solid electrolytes that could cycle sodium at high current densities has been a major challenge in developing room temperature solid-state sodium batteries. By developing high conducting Zn²⁺ and Mg²⁺ dual-doped NaₓZr₂SiPO₁₂ (NASICON) solid electrolytes and fabricating a 3D porous-dense-porous architecture (with an ultrathin, 25 µm, dense separator) coated with a nanoscale ZnO layer, an extremely low areal interfacial resistance of 3.5 Ω cm² was realized. This enabled a record high critical current density of 30 mA/cm² at room temperature with no stack pressure and a cumulative sodium cycling capacity of 10.8 Ah/cm² was achieved. Furthermore, pouch cells were assembled as a proof-of-concept with Na₃V₂(PO₄)₃ cathodes on dense-porous bilayer electrolytes with sodium metal anodes and cycled up to 2C rates at room temperature with no applied stack pressure.

4:00 PM ES03.07.02

Dynamic Coupling of Internal Strain-Stress Field and Lithium Pathway within Individual Cathode Particles governed by Solid Electrolyte in All-Solid-State Batteries

Jinkyu Chung, Junho Bae, Hanbi Choi and Jongwoo Lim; Seoul National University, Korea (the Republic of)

In all-solid-state batteries (ASSBs), (electro)chemo-mechanical aspects such as uneven interfaces, cathode-electrolyte interphase formation, delamination, fracture, defects, etc., are the major factors in capacity fade but remain largely unknown.

Nonhomogenous transfer of lithium ions can cause significant variations in strain and stress within battery electrodes, leading to degradation in battery performance. In all-solid-state batteries (ASSBs), the lithium pathway and the associated strain/stress field become more intricate due to the (electro)chemo-mechanical reaction at the electrode-electrolyte interfaces. The dynamic volume change in active particles are heavily influencing by strength of the solid electrolyte and interfacial conformality. This can continually alter the lithium pathway and the internal stress field, leading to recurrent redefinitions of (electro)chemo-mechanical environment.

Here, we have developed an operando coherent X-ray imaging platform and associated analysis methodologies. Named PICASSO (Primary particle In-situ X-ray imaging with Chemical-composition Analysis and Strain-Stress Observation), this technology can track the nanoscale transport of lithium and the strain evolution of individual electrode particles in ASSBs. With this platform, we gained a comprehensive electrochemical and mechanical understanding of the cycling properties of single electrode particles in ASSBs.

4:15 PM ES03.07.03

Competition Between Lithiation-Induced Stress and Concentration Gradients in 3D Geometries

David M. Stewart, Paul Albertus and Gary W. Rubloff; University of Maryland, United States

A comprehensive understanding of electro-chemo-mechanical (ECM) phenomena in solid-state batteries (SSBs) requires not only theoretical models, but validation of the models by direct measurement in well-defined geometries. We will highlight a few intriguing results using 3D models of SSBs and measurements on thin film electrodes, which motivate novel methods for measuring local stress and Li concentration in situ. These results emphasize that the inclusion of ECM effects is essential in understanding the fluxes in 3D geometries.

Using multi-physics modeling we have simulated the electrochemical behavior of a battery operating in the confined space of a nanopore. The 3D geometry produces large concentration gradients that affect the Li flux: rather than a conformal flux field, largely along the radial axis of the pore, the Li flows up and down the pore. However, the same geometry, when including electro-chemo-mechanical coupling, has entirely different behavior. Due to the stress gradients produced by the confined volume expansion of the cathode, the Li flux is further influenced, and achieves the fully conformal distribution that we expected from intuition.

Experimentally, we have measured ECM coupling in two model systems using Si electrodes, whose electrochemical and mechanical properties are well known. We employed micro-Raman mapping to measure the shift in the Si peak, and ultimately translated that to a strain/stretch profile in the electrode during lithiation. In single-crystal Si wafers we measured bi-axial stress maxima around 0.6 GPa, localized to the lithiation front, and post-mortem SEM shows lateral cracks that form at this same depth, causing delamination and breakdown the electrode. Furthermore, XPS depth profiles and EBSD cross sections show that the lithiation front is not sharp, as seen elsewhere in the literature. Due to ECM effects, the diffusion lengths in this experiment are 100x larger than predicted by concentration gradients alone.
In subsequent experiments, using a square Si island approximately 10 µm on a side, dynamic stress profiles are measured. The Raman stress measurement is fast enough to be done in operando, allowing us to see transient stress states for comparison with models. Existing literature treated the cracking and delamination of these islands entirely from a mechanical perspective. Our ECM models, parameterized to the experimental observations, reveal that the origin of the failure is not simply mechanical, but due to a competition between Li concentration gradients and stress gradients.

While the theory of ECM coupling is rather well studied, its application in 3D geometries is not well explored. At the same time, validation of the theory is nascent in electrochemical systems, where material properties change dynamically with state of charge. Together, our models and experiments are providing the fundamental understanding of SSB performance required for next generation designs.

4:30 PM ES03.07.04
Towards Improved All-Solid-State Batteries: A Multi-Scale Simulation of Cation Inter-Diffusion and Mechanical Failures at NASICON-Oxide/LiCoO2 Interfaces Ming-Yuan Hong and Hong-Kang Tian, National Cheng Kung University, Taiwan

All-solid-state batteries (ASSBs) hold great promise, yet their commercialization has faced challenges due to interfacial complications, which encompass issues such as solid electrolyte decomposition, mechanical degradation, and Li dendrite growth. Specifically, NASICON-type solid electrolytes, like Li1+4Al1−xTi2−x(PO4)3 (LATP) and Li1+4Al1−xGe2−x(PO4)3 (LAGP), have attracted attention because of their stability against LiCoO2 (LCO) and remarkable ionic conductivity (ranging from 10−4 to 10−3 S/cm). However, a decline in discharge/charge capacity due to mechanical breakdown at their interfaces has been a concern. Leveraging an integrated multi-scale simulation approach that combines Density Functional Theory (DFT) with Finite Element Analysis (FEA), we delve into the issues of cation inter-diffusion and the resulting mechanical challenges at LATP/LCO and LAGP/LCO interfaces. Our DFT studies pinpointed energetically favorable sites for Co to replace Ti atoms, mirroring atomic structures emerging from Co and Li inter-diffusion events. Evaluations of the elastic attributes of Co-LATP and Co-LAGP configurations showed a decline in modulus values (both Young’s and shear), signaling an interferential softening. However, the diffusion of Co and Li away from LATP transforms into Co2O4, characterized by a greater Young’s modulus compared to Co and LATP/LAGP. By channeling these insights into a 2D continuum model through FEA, we could visualize the Li-ion concentration gradient adjacent to the LATP particle and the subsequent stress distribution across various discharge phases. Our results identified peak first-principal stresses at the interfaces, reaching approximately 800 MPa for LATP/LCO and around 1000 MPa for LAGP/LCO. In comparison, non-interface scenarios registered values between 400-500 MPa. These findings accentuate the importance of inhibiting Co diffusion to safeguard ASSB integrity. Furthermore, simulations suggest that enhancing the interface contact area to 75% of optimal contact can effectively counteract peak stress induced by interfaces, underscoring the significance of this parameter in counteracting interface-induced mechanical degradation. In conclusion, this study offers a thorough exploration into the alterations in material properties and the potential mechanical decline triggered by cation inter-diffusion at these interfaces, urging its prevention in subsequent ASSB innovations. The analytical methods adopted here also present a valuable methodological framework for probing other ASSB material pairings, potentially guiding the prediction and alleviation of mechanical setbacks during the discharging phases.

4:45 PM ES03.07.05
Microstructure-Aware Mesoscale Modeling of Chemomechanical Stress Evolution during Cycling in Solid Electrolyte-Cathode Composite Bo Wang, Longsheng Feng, Kwangnam Kim, Liwen Wan, Tai Wook Heo and Brandon Wood, Lawrence Livermore National Laboratory, United States

The volume change of active material during charge-discharge cycling is responsible for the capacity fading of all-solid-state Li batteries due to mechanical degradation in the cathode such as delamination and crack formation. Many strategies to alleviate the chemomechanical stress build-up have been proposed in experiments but rationale of the stress release mechanisms at the mesoscale remain elusive. In this presentation, we present a microstructure-aware mesoscale model to quantitatively predict the stress distribution during cycling in a secondary particle agglomerate of the cathode active material embedded within a solid electrolyte matrix, taking the LiCoO2-Li1−xLa2ZrO12 (LCO-LLZO) as a model system. We find that the mechanical stress hotspots develop at different stages within the grain boundaries of the LCO agglomerate and the LCO-LLZO interfaces. We investigate the influences of microstructural morphology (columnar versus equiaxial), grain orientations (textured versus random), mechanical properties at the grain boundaries and heterogeneous interfaces, and anisotropy of chemical expansion on the stress hotspot evolution and provide optimal mitigation strategies. The theoretical results can help gain mechanistic understanding on cathode degradation and inform guidelines for experimental design of microstructurally optimized cathode materials for long-life solid-state batteries.

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

8:30 AM ES03.08.01
Phase Study of Lithium-Niobium-Tantalum Oxides as Cathode Coating Materials Hengning Chen1, Zeyu Deng1 and Pieremanea Canepa1,2; 1National University of Singapore, Singapore; 2University of Houston, United States

Although all-solid-state batteries (ASSBs) exhibit great potential for providing high energy density and enhanced battery safety, the stability of electrode–electrolyte interfaces is still a serious challenge. Niobate and tantalate materials have been widely applied as coating materials to mitigate the interfacial reactivities in ASSBs, especially amorphous LiMO3 (M=Nb or Ta) with high ionic conductivities and appreciable electronic resistance.1 Compared with pure LiMO3 (M=Nb or Ta), partially-crystallized Li-Nb-Ta oxides were found to show even higher ionic conductivity and higher permittivity, which can be more effective for fast charge-transfer reactions at the cathode/electrolyte interfaces in ASSBs.2 However, the mechanism behind Nb/Ta mixing and the improved properties needs to be further understood.

Leveraging a combination of density functional theory, cluster expansion formalism, grand canonical Monte Carlo (gMC) simulations, and machine-learned molecular dynamics, we reveal the phase transition nature of Li2Ta2−xNb2xO8 and the improved Li-ion conduction properties brought by Nb/Ta mixing. As studied in our previous work, the crystalline Li-M-O coating contains mixtures of Li2O3 and Li3MO4, and we extend the mixing study into Li3MO4 as well.3 Our investigation of the phase behavior and the structure-property relationships in the Li-Nb-Ta oxides helps to develop more suitable synthesis protocols to maximize the functional properties of these coating materials.

References:

8:45 AM ES03.08.02
Interplay of Interfacial Adhesion and Mechanical Degradation in Anode-Free Solid-State Batteries Imtiaz Ahmed Shozib and Howard Qingsong Tu; Rochester Institute of Technology, United States

Degradaions at the interface between the solid electrolyte (SE) and the anode have been identified as one of the primary reasons for solid-state battery (SSB) failure. Interfacial adhesions and mechanical conditions are important factors need to be investigated for SSB. This article investigates the impact of assembling pressure on the performance of an anode-free solid-state battery (ASSB) with an AgC | Li1+4Al1−xTi2−x(PO4)3 | LPSO | NCM811 full cell configuration. Results demonstrate that an optimal assembling pressure of 530 MPa significantly improves specific capacity. Notably, an increase in capacity is observed when the assembling pressure is increased from 350 MPa to 530 MPa, while pressures beyond this threshold lead to a significant decrease in capacity due to soft short effect. The highest discharge capacity was achieved at an optimal assembling pressure of 530 MPa, corresponding to a high gravimetric energy density of 409.62 Wh/kg. This notable enhancement over alternative assembling pressures is likely a result of the intricate interplay between interfacial adhesion and mechanical stability. This assembling pressure incrementally improves the interfacial adhesion between the SE and the AgC interlayer. At 450 and 530 MPa, where interfacial adhesion is moderately higher, lithium deposition...
Because of the ongoing demand on energy consumption, high energy density batteries are needed. Solid-state batteries can lead to higher energy densities compared to commonly used liquid lithium batteries and avoid the flammable organic solvents. The class of halide electrolyte (Li$_x$MX$_y$, $M = $ metal, $X = $ Cl, Br, I) provide promising characteristics in solid-state batteries due to their reasonable conductivity values and larger electrochemical stability window compared to sulfides. Due to the good conductivity value of 1 mS/cm$^{-1}$, the broad theoretical electrochemical stability window and the water-based synthesis possibility the electrolyte Li$_3$InCl$_6$ is a good candidate for the use with high potential cathode materials like LiNi$_{0.8}$Mn$_{0.1}$Co$_{0.1}$O$_2$. It was shown that the Li$_3$InCl$_6$ is not stable at the lithium metal anode, therefore a bilayer setup with a sulfide and a halide layer is commonly used to study halides at the cathode side. Omitting the halide layer and only using a sulfide layer, like Li$_3$PS$_4$,Cl lead to a capacity loss over the cycling and decomposition products.

Based on this literature we studied three different cell setups with the halide electrolyte Li$_3$InCl$_6$ and sulfide electrolyte Li$_3$PS$_4$,Cl in combination with the cathode material LiNi$_{0.8}$Mn$_{0.1}$Co$_{0.1}$O$_2$. Cycling of the cells over 100 cycles revealed the fast capacity fading of the cell setup with the LiNi$_{0.8}$Mn$_{0.1}$Co$_{0.1}$O$_2$:Li$_3$InCl$_6$ cathode composite in direct contact to the Li$_3$PS$_4$.Cl whereas the cells with avoiding this triple phase boundary cycle more stable. Within the cycling process, electrochemical impedance spectroscopy performed and showed a significant increase of the interfacial resistance in the fast capacity fading cell, which was not the case for the pure sulfide and the bilayer cell setup. For further analysis of the fast capacity fade, time-of-flight secondary ion mass spectrometry and focused ion beam scanning electron microscopy analysis were performed to understand the interfacial resistance increase. At the buried interface of the cathode composite to the sulfide separator an indium-sulfide species could be detected, which were also slightly less present at the separator-separator interface of the halide and sulfide electrolyte.

This indicates the incompatibility of the Li$_3$InCl$_6$ and Li$_3$PS$_4$,Cl electrolytes, which is more pronounced in the presence of LiNi$_{0.8}$Mn$_{0.1}$Co$_{0.1}$O$_2$.

This work highlights that in the search for new battery components the chemical stability of the materials to each other should not be overseen. Adding more components in a battery cell, like bilayers, increases the number of interfaces and possible degradation areas. Therefore, studies of solid-state batteries should also consider more properties besides electrochemical stability windows of single components.
Herein, we employ first-principles calculations and experiments to investigate the conduction mechanism, propose, and validate our design strategies for enhancing ionic conductivity, using Li$_x$YCl$_6$ (LYC) as a model system. Consistent with previous reports, we find that the lithium diffusion occurs three-dimensionally in LYC, which exhibits anisotropic behavior with faster ionic conduction along the c-axis channel than in the ab-plane. However, it is revealed that the lithium diffusion in the ab-plane leverages the superionic conduction in LYC, and, more importantly, it is primarily determined by the partial occupancies of the yttrium (Y) ion in the structure. Our theoretical calculations demonstrate that the presence of Y in the ab-plane interrupts the lithium diffusion with the electrostatic repulsion associated with the tetrahedral site hopping mechanism of lithium ions, resembling that of conventional layered lithium transition-metal oxides. Furthermore, the partial occupancy of Y over a certain ratio entirely disconnects the percolation diffusion pathways of lithium ions in the ab-plane. On the other hand, it is conversely observed that the lack of Y in the ab-plane leads to the collapse of the interlayer space, indicating that Y cations serve as a pillar of the layered lithium diffusion framework. This contradicting effect of Y in the structure signifies the importance of the composition/ordering of M cations in the trigonal Li$_x$MCl$_6$. Accordingly, we propose a target region for M partial occupancy that can lead to cation arrangements with percolating and non-collapsed lithium diffusion pathways. Our design rules for the target cation arrangement are experimentally confirmed by a M-deficient Li$_{1-x}$M$_{0.5}$Y$_{0.5}$Cl$_6$ (i.e., Li$_{1-y}$Y$_{0.5-y}$Zn$_{y}$Cl$_6$) new halide superionic conductor that exhibits the highest reported room-temperature ionic conductivity (1.19 $\times$ 10$^{-3}$ S cm$^{-1}$) among trigonal halide superionic conductors. This study illuminates the detailed superionic conduction mechanism in halides for the first time and suggests that searching for a new compositional space that balances the lithium percolation and stacking slab distance is an unexplored and efficient strategy for the design of superionic halide SEs.

Reference

10:45 AM ES03.09.02
Free-Standing Sulfide Electrolyte Thin Film for Solid-State Lithium Battery Applications
Seokyoung Yoon1,2, Dong Ok Shin1,2, Seok Hun Kang1, Jaecheol Choi1, Ju Young Kim1, Young-Gi Lee1 and Young-Sam Park1,2, 1Electronics and Telecommunications Research Institute, Korea (the Republic of), 2University of Science and Technology (UST), Korea (the Republic of)

The great attention to low carbon economy through the electric vehicles grows the market of lithium ion battery (LIB) rapidly because of its high power and energy density. However, a liquid carbonate electrolyte employed in the LIB is flammable, thus being able to cause severe safety issues. To reduce the safety issues, a solid electrolyte (SE) instead of the currently commercialized liquid electrolyte has been introduced to fabricate solid-state lithium batteries [1,2]. Even though the prevailing SEs (that is, sulfide, polymer, garnet and sodium superionic conductor) do not simultaneously satisfy all the stability requirements such as mechanical, chemical, electrochemical and thermal stabilities, sulfides have the highest ionic conductivities and the favorable mechanical properties among them, thereby being considered to work reasonably well in the conventional sandwich battery structure [2]. To prepare the sulfide SE, a slurry coating technology has been generally used. However, the traditional wet method charges additional cost coming from using an environmentally harmful organic liquid solvent and the resulting production of a solvent recovery system. In addition, strong reactivity between a polar liquid solvent and the sulfide leads to the decrease in the ionic conductivity of the sulfide SE [2]. Thus, the introduction of a liquid-free dry process is necessary to obtain the sulfide electrolyte. Furthermore, thin and free-standing SEs are preferred for high efficiency batteries with a high degree of freedom of electrode material selection.

In this work, separate sulfide electrolyte films with a thickness of several dozens of micrometers are demonstrated by a dry procedure which is composed of the following three steps [3]: first, an agyrodite-type sulfide and a binder powders are mixed. Next, the two nonsticky powders are ground homogeneously to fabricate a sticky sulfide-binder dough. Then, the dough is fed into rollers to obtain the independent SE layer with a thickness of below one hundred micrometers. Microstructural and elemental analyses are carried out utilizing a field emission scanning electron microscope and energy dispersive X-ray microanalysis, respectively. Alternating voltages are applied by a frequency response analyzer (10$^{-1}$-10$^{-6}$ Hz, Solartron HF 1225, AMETEK Scientific Instruments) to get Nyquist plots and calculate ion conductivities of dry- and wet-processed sulfide SE samples. Charging-discharging cycling experiments are performed under galvanostatic cycling condition from 3.0 to 4.3 V (Toscat-3000, Toyo System). The test results are presented and discussed in the talk.


Acknowledgement
This work was supported by internal fund/grant of Electronics and Telecommunications Research Institute (ETRI). [23YB2600, Development of Fundamental Technology for Non-Lithium Resources Based Next Generation Aqueous-Type Multivalence-Metal-Ion Battery.]

11:00 AM ES03.09.04
Fabrication of Y-Doped and Ce-Doped NaSICON through Integrated Mechanical and Thermal Activation Method
Madeline Barickman, Abigail Barickman and Shan-Ju Chiang; North Central College, United States

NaSICON (Na Super Ionic CONductor) materials have emerged as promising candidates for a wide range of applications such as all-solid-state Na-ion batteries, sodium-air batteries, electrochemical sensors, and electrolytes for thermoelectric generators, and membranes due to their high availability, profound ionic conductivity, high thermal and chemical stability, and good electrochemical compatibility. To be used in energy storage devices, the high ionic conductivity with relatively low interfacial resistance has to be possessed. However, the Na-ion conductance at room temperature remains several orders of magnitude lower than organic electrolytes even NaSICONs have relatively high ionic conductivity at elevated temperature. Therefore, there is still a need in developing a consistent manufacturing process to further increase the ionic conductivity of NaSICON and reducing the production cost for synthesizing NaSICON membranes. This study aims to improve the density and ionic conductivity of yttrium and cerium-doped NASICON materials through mechanical activation and one-step sintering process while suppressing the manufacturing cost of NaSICONs. Here, we report the feasibility of integrated mechanical and thermal activation method in doping the zirconium site in NaSICON. Fully densified Y-doped NaSICON has 100% higher total conductivity at the room temperature then the same material prepared from general solid-state sintering method, while Ce-doped NaSICON demonstrates the good bulk conductivity of 4.7 $\times$ 10$^{-5}$ S/cm. This study will provide an alternate solution for synthesizing high ionic conductivity NaSICON at low cost for many energy storage systems.

11:15 AM ES03.09.05
Assessing Correlations between Phonon Features and Migration Barriers in Multivalent Solid Electrolytes
Samuel M. Greene and Donald Siegel; The University of Texas at Austin, United States

Solid ionic conductors with high ionic conductivity can enable the development of solid-state batteries with improved safety and performance. Most materials exhibit insufficient conductivity for commercial applications, particularly for multivalent ions. High-throughput computational approaches, which involve screening large databases of compounds, can accelerate the discovery of new materials with sufficient conductivity. Directly calculating ionic conductivity from first principles is expensive and difficult to automate, which renders such calculations incompatible with screening approaches. Previously, others have proposed the phonon band center (mean phonon frequency) as a metric that is easier to calculate and measure, and they have demonstrated that it is correlated with the energetic barrier for ion migration in lithium and sodium conductors. I will discuss our efforts to extend this approach to investigate magnesium, calcium, and zinc conductors using first-principles calculations of phonon features. In addition to frequencies, we consider the directions of phonon modes as predictors for migration barriers. We compare our results with previous trends for monovalent conductors.

SESSION ES03.10: Fabrication and Scale Up II
Session Chairs: Deok-Hwang Kwon and David Mutlin
Thursday Afternoon, April 25, 2024
Room 423, Level 4, Summit
Stable anode-free all-solid-state battery (FA-ASSB) with sulfide-based solid-electrolyte (SE) (argyrodite Li6PS5Cl, LPSCl) is achieved by tuning wetting of lithium metal on “empty” copper current-collector. Lithiophilic 1 μm Li2Te is synthesized by exposing the collector to tellurium vapor, followed by in-situ Li activation during the first charge. The Li2Te significantly reduces the electrodeposition/electrodissolution overpotentials and improves Coulombic efficiency (CE). During continuous plating experiments using half-cells (1 mA cm-2), the accumulated thickness of electrodeposited Li on Li2Te-Cu is more than 70 μm, which is the thickness of Li foil counter-electrode. Full FA-ASSB with NMC811 cathode delivers an initial CE of 83% at 0.1 C, with a cycling CE of 99.5%. Cryo-FIB sectioning demonstrates uniform electrodepositied metal microstructure, with no signs of voids or dendrites at the collector-SE interface.

Electrodissolution is uniform and complete, with Li2Te remaining structurally stable and adherent. By contrast, unmodified Cu current-collector promotes inhomogeneous Li electrodeposition/electrodissolution, electrochemically inactive “dead metal”, dendrites that extend into SE, and thick non-uniform solid electrolyte interphase (SEI) interspersed with pores.

Density functional theory and mesoscale calculations provide complementary insight regarding nucleation-growth behavior. Unlike for conventional liquid-electrolyte metal batteries, the role of current collector/support lithiophility has not been explored for emerging FA-ASSBs.

As a synthesis-oriented material scientist within the optoelectronics field, I hope that this contribution will promote discussion and potential future collaboration with battery experts.

Due to its pseudocapacitive, one-dimensional, rapid ion channels, TiO2(B) holds promise as a Li-ion rechargeable battery anode electrode. Despite its potential for high capacity and superior rate capability, realizing its theoretical capacity and full rate capability remained challenging. Partly owing to its metastability, instead of pure or single crystalline TiO2(B) materials, multiphase or polycrystalline samples are synthesized. In this study, assisted by an isostuctural VO2(B) template layer, we successfully synthesized single-phase TiO2(B) films epitaxially, with well-aligned ion diffusion channels. Using a liquid electrolyte, TiO2(B) epitaxial electrode demonstrates a capacity close to the theoretical value of 335 mA h g–1 and exceptional charge–discharge cyclability for ≥200 cycles, surpassing the performance of other TiO2(B) or alternative phase nanostructures. Moreover, by applying LiPON as a solid electrolyte, we demonstrated the feasibility of an all-solid-state configuration, showing excellent stability. These findings suggest significant potential for downsizing all-solid-state nanobatteries for application in self-powered integrated circuits.

Stable lithium lanthanum zirconium oxide (LLZO) and other solid-state electrolyte (SSE) materials are widely heralded for their high lithium ionic conductivity, low electrical conductivity, and stability against lithium metal. However, the difficulty in manufacturing solid electrolytes, especially in the thin film geometry, has hindered widespread deployment. Multiple critical challenges need to be solved to produce low-cost SSEs for solid-state batteries at-scale: reproducibility of the thin-film deposition to achieve dense mixed-metal oxides, the intrinsic reactivity of lithiated metal oxides to environmental species like water and carbon dioxide that result in the formation of secondary surface phases like Li2CO3, and the necessity of low-throughput and energy-intensive curing steps.

Here, we present a rapid spray plasma process to manufacture large-area thin-film LLZO SSEs for solid state batteries. The LLZO is first generated via blade coating to form an oxide network. The oxide is then cured and densified in one step at 3.6 cm/min linear processing speed by a nitrogen plasma discharged into a low-humidity, ambient pressure environment. Plasma allows for a reduction in processing time by orders of magnitude compared with many traditional vacuum-based thin film routes owing to the combination of radical ions, ultrafast photons, and heat present in the curing process along with the lack of processing. The resulting amorphous phase LLZO thin films have low carbonate contamination, high ionic conductivity of 1x10-5 S/cm at room temperature, low surface and through-plane defect density, and surface roughness of <40 nm. This work is a step toward the high-throughput manufacturing of LLZO for solid state batteries.

Three-dimensional printed additive manufacturing of battery components presents a promising solution: compared to conventional micromachining, this approach enables rapid prototyping with complex architectures.

Stable solid-state batteries (SSBs) using lithium metal anodes are the best candidates for high energy density battery applications. The energy density can be further increased by eliminating the lithium metal excess in an “anode-free” cell format. However, low Columbic efficiency from heterogeneous lithium metal plating and stripping along with charge loss due to solid electrolyte interphase (SEI) formation severely limit the cycle life of anode-free SSBs. Here, we explore the use of ultra-thin (5-20 nm) Al2O3 and ZnO coatings deposited by atomic layer deposition (ALD) on copper electrodes for anode-free cells with a solid polymer electrolyte. Voltammetry shows that lithium inventory loss due to SEI formation is reduced by over 50% with Al2O3@Cu electrodes, but these electrodes experience order of magnitude higher interface resistances than bare Cu and ZnO@Cu electrodes due to their inherently low ionic and electronic conductivities. The electrochemical differences between Al2O3 and ZnO coatings are examined in X-ray photoelectron spectroscopy (XPS) experiments that show Al2O3 undergoing a self-limiting lithiation reaction with Li metal, while ZnO reacts completely with Li to form a Li2O alloy and Li2O. These chemical differences at the interface result in higher and lower lithium plating nucleation overpotentials for Al2O3 (up to 220 mV) and ZnO (down to 15 mV) coatings, respectively, relative to uncoated Cu electrodes (35 mV). Time-of-flight secondary ion mass spectrometry (ToF-SIMS) reveals lithium plating underneath a reacted Li4AlOx coating and through emergent defects and pinholes with Al2O3@Cu electrodes, while it plates exclusively on top of the electronically conductive converted ZnO@Cu electrodes. Scanning electron microscopy (SEM) corroborates these mechanisms by showing sparse coverage of isolated Li clusters plated with
Al2O3/Cu electrodes, while Cu and ZnO@Cu grow more dense and interconnected lithium deposits. Despite both coatings improving different aspects of anode-free battery design, unmodified Cu electrodes show higher Coulombic efficiencies (~77%) than Al2O3/Cu (up to 70%) and ZnO@Cu (up to 75%) electrodes. Increasing Al2O3 coating thickness decreases the practical current density compared to unmodified Cu (30 μA/cm²) but increasing ZnO coating thicknesses can double or triple this value. These (electro)chemical and morphological observations lead to the proposal of two mechanisms, where less-reactive metal oxides develop lithium-ion conductivity through the metal oxide structure to plate lithium underneath the coating, while more-reactive metal oxides undergo full reduction and conversion reactions that allow lithium to plate above the coating. The fundamental research here open paths for future work to leverage these mechanisms and explore other materials for high-efficiency anode-free SSBs.

3:45 PM ES03.11.02
Electrothermal Transport and Reaction in Polymer and Hybrid Electrolytes for Lithium Metal Batteries Daniel Hallinan, Longsheng Feng, Anna Mills, and Jie-Tsong Kiang; Florida A&M-University Florida State College of Engineering, United States; Oak Ridge National Laboratory, United States; SLAC National Accelerator Laboratory, United States

Increasing the energy density of lithium-ion batteries requires, among other advances, electrolytes that are compatible with lithium metal and next-generation cathodes. Polymer electrolytes play an important role in this regard, but overcoming slow ion transport is a major challenge. Recent advancements in time-resolved infrared spectroscopy to characterize salt diffusion in polymer electrolytes will be reported as well as efforts to electrochemically measure transference number and electrochemical reaction kinetics in these electrolytes. In addition to our efforts in developing characterization techniques, we will report recent progress in solid electrolyte development. Hybrid electrolytes that combine fast ion transport of ceramic electrolytes and processability of polymer electrolytes are promising. This requires either 1) low binder contents that maximize ceramic transport pathways or 2) unity polymer transference number that takes advantage of transport in both phases. Our progress in both of these directions will be discussed, focusing on 1) free-standing solid electrolytes with small amounts of inert binder and 2) polymer blend electrolytes. Both exhibit single-ion conduction, which yields numerous transport and efficiency advantages. The effect of processing solvent on binder-containing sulfide electrolyte properties will be covered. State of the art in the polymer blend electrolytes will also be reviewed including recent advancements from our team using precision polyanions with polyether solvating polymer. This presentation will cover miscibility, conductivity, and transference numbers as a function of composition and temperature. Distinct differences between blends containing different anionic forms will be explained in the context of ion correlation. Important future directions for polymer blend and hybrid electrolytes will also be discussed.

4:00 PM ES03.11.03
Enhancing Li Ion Conduction in Argyrodite Solid Electrolytes through Anion Site-Exchange Jie-Sen Yang and Ping-Chun Tsai; National Taiwan University of Science and Technology, Taiwan

The superionic solid electrolyte Li₆PS₅Cl (LPSC), featuring ionic conductivity on par with those of liquids, has gained intense interest in the development of all-solid-state batteries. However, the mechanisms behind such extraordinarily high ionic conductivity remain unclear. In previous works, a phenomenon involving positional exchange between S and Cl anions was observed, which we referred to as “S/Cl site-exchange.” We disclosed the correlation between Li ion conduction and the S/Cl site-exchange by integrating DFT, AIMD and NEM simulations, along with 7Li PFG NMR diffusivity measurements for the first time. A remarkable increase of ~10² times in Li ionic conductivity and a substantial reduction of ~160 meV in energy barriers are observed when the S/Cl site-exchange is introduced. We found out that transportation bottlenecks of Li ions are overcome through beneficial neighboring Li configuration induced by the S/Cl anion exchange. The comprehensive understanding of ion transport mechanisms in LPSC would help the design of solid-state fast ion conductors.

4:15 PM ES03.11.04
Partial Transport Optimization and Mechanical Characterization of The Cathode Active Material LiFeS₂ in all Solid-State Batteries Tim Bernese; Inorganic and Analytical Chemistry, University Muenster, Germany

Solid-state batteries spark tremendous interest given their potential to overcome the limitations of energy density that are present in conventional Li ion batteries. At the same time, with current state-of-the-art cathode active materials (CAM) employing critical elements such as Nickel and Cobalt, concerns regarding their scarcity and cost are raised even before the wide-spread implementation of the technology. To overcome these concerns, in this work, we evaluated the cation- and anion-redox (cathode) active material Li₂FeS₂ as an alternative candidate for solid-state batteries with a promising theoretical specific capacity of 400 mAh/g. By combining electrochemical characterization with studies of the partial conductivities, cathode composites are optimized in regard to their CAM and solid electrolyte composition, leading to an optimum between high initial capacities and capacity retentions. Half cells employing 50 to 60 wt.% CAM are shown as most promising candidates, without the necessity of carbon additives due to the intrinsically high electronic conductivity of Li₂FeS₂ >30 mS/cm. The kinetic limitations of the cales are further elaborated by current density dependent cycling (rate testing), showing that higher electronic conductivities, i.e., higher intermediate CAM loadings, benefit faster charging rates in comparison. This is a promising result given that higher loadings are thought after to reduce the amount of electrochemically inactive materials in solid-state batteries. The study of kinetic limitations is complemented by mechanochemical characterization of the cathode. Tracing the pressure changes during cycling, both with lithium-indium and LTO as reference electrodes, is used to gather insights into the origin of capacity fading. While usage of lithium-indium allows to capture the mechanochemical response of the system including effects of lithium intercalation and deintercalation in the reference anode, the use of LTO, i.e., a zero-strain material during cycling, allows characterizing the response of the cathode specifically. Thereby, the latter approach could be utilized to characterize not only the general mechanochemical response of LiFeS₂ cathodes, but also to capture how these change as a function of cathode composition, ultimately providing insights into the failure mechanism of LiFeS₂ containing cathodes.

In conclusion, this work represents an initial introduction of LiFeS₂ as a cathode active material candidate for all-solid-state batteries. Furthermore, partial transport and mechanochemical characterization are utilized to optimize the cathode composition to achieve both, high average specific capacities, i.e., active material utilization, and high capacity retention. With that, this work is a foundation for further optimization of cells employing LiFeS₂ as CAM, and allows a general comparison to established solid state battery CAM, e.g., Li(Ni,Mn,Co)O₂ (NMC).

4:30 PM ES03.11.05
Investigation of Microstructural Impacts on Ionic Transport in Li₄La₃Zr₂O₁₂-LiCoO₂ Composite Structures Longcheng Feng, Bo Wang, Kwangnam Kim, Liwen Wan, Brandon Wood and Tae Wook Heo; Lawrence Livermore National Lab, United States

The ionic transport property of a solid composite cathode is sensitive to its microstructure, which has a critical impact on variability of the overall solid-state battery performance. In this presentation, we will discuss our recent microstructure-aware modeling effort on unraveling the relationship between microstructural features and effective ionic transport properties. Specifically, using Li₄La₃Zr₂O₁₂-LiCoO₂ composite as a model system, we combine atomistically informed mesoscale modeling approach and machine learning (ML) analysis to examine how the local transport properties of individual microstructural constituents and their topological features affect the effective diffusivity of Li in the two-phase composite. In addition, our ML analysis identifies key microstructural descriptors for the effective transport property. Our framework can be extended for elucidating the intricate microstructure-transport property relationship in generic multiphase materials, which offers insights highlighting the importance of microstructure engineering in tuning the properties of composite materials in diverse energy applications. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

SESSION ES03.12: Inorganic Electrolyte II
Session Chairs: Stefan Adams and Xi Chen
Friday Morning, April 26, 2024
Room 423, Level 4, Summit

8:15 AM ES03.12.01
Mechanical Milling – Induced Microstructure Changes in Argyrodite Li₄PS₅Cl Solid-State Electrolyte and Influence on Electrochemical Performance Yixian Wang and David Mitlin; The University of Texas at Austin, United States

In the early stages of sulfide solid-state electrolyte (SSE) research, sulfides like Li₄PS₅Cl (LPSC) were primarily synthesized in laboratories using fine precursors such as Li₂S, LiCl, and P₄S₈, employing meticulous synthetic procedures involving milling and sintering. This approach resulted in grains of as-synthesized SSE materials with a uniform particle size distribution and well-controlled morphology. Consequently, large-scale synthesis methods for LPSC SSE have been developed, leading to the availability of commercial LPSC SSE. Nonetheless, compared to lab-scale, commercial production of LPSC SSE often yields a wide range of particle sizes and particle distributions. In-depth understanding is needed regarding how microstructural features such as the average particle size and distribution, and pore size and distribution, affect the compressed SSE’s electrochemical performance.
In this presentation, we investigate mechanical milling – induced microstructure changes of LPSCI SSE and their influence on electrochemical performance. Planetary mechanical milling in wet media (m-xylene) is employed to alter commercial LPSCI powder. Quantitative stereology demonstrates how extended milling progressively refines grain and pore size/distribution, increases particle compactness, and geometrically smoothens the SSE-Li interface. Mechanical indentation demonstrates that these changes lead to reduced site-to-site variation in the compact's hardness. Microstructure, in turn, profoundly influences electrochemical behavior. For example, symmetric cells with 8 and 24-hour milled electrolytes remain stable after 190 cycles at 1 mA cm⁻²/2 mAh cm⁻², while the unmilled baseline cells short-circuit during initial activation. The Li/Ni asymmetric half-cells with milled electrolytes allow for stable electrodeposition of approximately 20 mAh cm⁻² (100 µm Li thickness), while the baseline shorts at 1.2 mAh cm⁻². Combined cryogenic focused ion beam (cryo-FIB) and X-ray photoelectron spectroscopy (XPS) demonstrate that milled microstructures promote uniform early-stage electrodeposition on foil collectors and stabilize solid electrolyte interphase (SEI) reactivity. Mesoscale modeling reveals the relationship between Li-SSE interface morphology and the onset of electrochemical instability, based on underlying reaction current distribution.

8:30 AM ES03.12.02
Formation of Lithium Lanthanum Zirconium Oxide Nanofibers: Insight from In-Situ Synchrotron X-Ray Scattering Study Jumukk Lee¹, Michael J. Counihan¹, Woosoo Go², Pallab Barai¹, Sanja Tepavcević¹, Mike Tucker², Marco M. Doeff³, Venkat Srinivasan⁴ and Yuepeng Zhang¹; ¹Argonne National Laboratory, United States, ²Lawrence Berkeley National Laboratory, United States

Lanthanum lanthanum zirconium oxide (Li₃La₂Zr₂O₇) with a cubic crystal structure is a promising candidate for a solid-state electrolyte due to its good ionic conductivity, thermal stability, and relatively large electrochemical window against Li metal anodes. The formation of the cubic phase usually requires elevated temperatures and a relatively long annealing time. However, we have observed cubic phase LLZO at significantly lower temperatures in nanofibers than their bulk counterparts. To understand the phase transformation and stability of the LLZO nanofibers, we performed in-situ simultaneous Small-Angle and Wide-Angle X-ray Scattering (SAXS/WAXS) for the LLZO precursor nanofibers during their annealing between RT and 800 °C. In this study, we investigate the structure evolution and microstructural changes of the nanofibers as a function of the temperature. The electrochemical properties of the LLZO nanofibers were also evaluated.

8:45 AM ES03.12.03
The Effect of Particle Size and Spatial Distribution on the Ion Transport Barrier in Polymer-Ceramic Composite Electrolytes Xi C. Chen¹, Ji-young Ock¹, Abigali Lee², Amit Bhattacharya², Tao Wang¹, Catalin Gainaru¹, Md Anisur Rahman¹, Sheng Dai¹, Raphaële Clement³ and Alexei Sokolov¹; ¹Oak Ridge National Laboratory, United States; ²The University of Tennessee, Knoxville, United States; ³University of California, Santa Barbara, United States

Significant efforts have been made to develop composite electrolytes combining polymer matrix with Li-ion conducting inorganic solids for feasible construction of solid-state batteries. Two main mechanisms have been proposed to enhance the ionic conductivity of the polymer matrix: 1) through a fast ion-transport interface layer along the ceramic particle-polymer interface, and 2) through percolated ceramic particles. However, without proper selection of ceramic and polymer chemistries and control of interfacial interactions, the resulting composite often even exhibits decreased conductivity. Furthermore, even with favorable interfacial interactions, the size and spatial arrangement of the ceramic particles may significantly impact the electrochemical performance of the composite electrolyte. In this work, we investigate the effect of particle size and spatial distribution in polymer-ceramic composite electrolytes. Two sizes of ceramic particles, Li₃La₂Zr₂O₇ (LLTO) nanorods with average diameter of approximately 20 nm, and commercial LLTO particles with average diameter of 1 µm are dispersed in two polymer matrices, a single-ion-conducting polymer electrolyte and a dual-ion-conducting polymer electrolyte. The total ionic conductivity in composites made with the single-ion-conducting polymer electrolyte shows a two-fold increase with the addition of LLTO nanorods, compared with neat polymer electrolyte. In addition, Li ion diffusion is also getting faster in this composite. In comparison, composites made from commercial LLDO does not show improvement in conductivity. We explain these results by increased Li ion mobility in the polymer interfacial layer surrounding nanoparticles. The ion transport energy barrier in the composites is analyzed and quantified as a function of temperature through broadband dielectric spectroscopy (BDS) analysis.

The spatial distribution of LLTO particles within the polymer matrix also plays a role in ion transport of the composite. Two morphologies of composites are created for this comparison, a relatively uniform morphology where particles dispersed throughout the matrix, versus a layered morphology where the majority of the particles reside on one side of the matrix. Constriction factor significantly decreases the total ionic conductivity in the layered morphology. Through these investigations, we shed light on how to design composite electrolytes to maximize favorable ion transport paths and minimize barriers.

Acknowledgements: This work was supported as part of the Fast and Cooperative Ion Transport in Polymer-Based Materials (FaCT), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Basic Energy Sciences at Oak Ridge National Laboratory.


9:00 AM ES03.12.04
Preparation of Structured Garnet LLZO Composite Solid Electrolyte Using Graphene Oxide as a Template Daniel Chang, Wan-Yun Lee and Che-Ning Yeh; National Tsing Hua University, Taiwan

All-solid-state lithium-ion batteries are viewed as a promising candidate for next-generation batteries due to their safety and high energy density. Despite the enhanced safety of these batteries owing to the use of solid-state electrolytes (SSEs), there is still ample room for improvement in terms of their ionic conductivity. Among various types of SSEs, composite solid electrolytes (CSEs) stand out as they combine the benefits of polymer matrix and ceramic fillers. The ionic conductivity and transport behavior of CSEs is strongly influenced by the tortuosity and continuity of the ceramic fillers. Thus, achieving low tortuosity structures with straight, interconnected ion pathways in CSEs is highly desirable but challenging. In this work, we choose the garnet-type Li₃La₂Zr₂O₇ (LLZO) as the ceramic filler, because of its high ionic conductivity (10⁻⁴–10⁻⁵ S/cm) at room temperature and its great chemical stability against lithium metal anodes. Additionally, we use poly(ethylene oxide) (PEO) as the polymer matrix to form the CSE. While most aligned ceramic scaffold are made by templating fixed structures, such as wood, cotton, or cellulose, we harness graphene oxide (GO) as a template to fabricate oriented LLZO structures. This method allows us to establish versatile processing techniques for designing distinct ceramic structures with interconnected pathways, utilizing honescomb and layered structure. Utilizing a uni-directional freeze-drying process, we successfully create interconnected ceramic structures with low tortuosity. Consequently, the corresponding CSE exhibits significantly improved ionic conductivity compared to CSEs with randomly mixed ceramic fillers. Our work provides a promising approach to the realization of CSEs with superior ionic conductivity and further advancing the prospects of safer, more efficient, and higher energy density batteries.

9:15 AM ES03.12.05
Understanding The Reactivity between Li₁ₓAlₓTi₂₋ₓ(PO₄)₃ and Sintering Aids to Minimize Densification Temperatures in All-Solid-State Batteries Morgan Guilleux¹, Christel Gervais², Arnaud Perere² and Christel Libearty Robert¹,²; ¹LCMCP, Sorbonne Université, France; ²Réseau sur le Stockage Electrochimique de l’Energie (RSE), France

NaSICON-type materials like Li₁₋ₓAlₓTi₂₋ₓ(PO₄)₃ (LATP) are considered promising solid electrolytes for all-solid-state batteries due to their good total ionic conductivity of 10⁻⁴ S cm⁻¹ at room temperature. However, a critical issue concerns the processability of the solid electrolyte in the composite positive electrode. Indeed, LATP must be densified by heat treatment (~900°C) to approach its maximum ionic conductivity and form an intimate contact with the active material. Nevertheless, chemical reactivity in the composite cathode has been observed as low as 700°C for some systems.

To prevent this reactivity, one strategy is to lower the densification temperature of this solid electrolyte. Multiple reports in the literature propose to use lithium salts as a sintering aid to achieve this goal. For example, LiBF₄ and LiF have been shown to densify the solid electrolyte LATP to relative densities above 90% of the theoretical density at temperatures ranging from 800°C to 900°C, respectively. However, these sintering temperatures remain too high and close observation of powder X-ray diffraction data reported in the literature, confirmed by our own experimental results, shows that resistive impurity phases such as LiTiPO₄ and Li₃PO₄ already form.

In this work, we investigated the chemical reactivity mechanism during the densification and sintering processes. We first studied the reactivity of several lithium salts with LATP (x = 0.3), using in situ and ex situ X-ray diffraction, Raman spectroscopy and ex situ solid-state NMR spectroscopy. We identified new intermediate phases for the first time, bringing a new light on the reactivity and sintering mechanisms. We show that lithium salts react with LATP at low temperature, long before they melt. This result interrogates the liquid phase sintering mechanism proposed in the literature and explain that the sintering temperature is not correlated to the melting point of the salt.

Decreasing the sintering temperature of LATP is a key challenge to achieve a viable composite positive electrode for all-solid-state batteries. Our work shows that the chemical reactivity...
between lithium salts and LATP is a limiting factor in decreasing the sintering temperature of the material below 700°C. This new knowledge enables us to reexamine sintering of oxide ceramics and explore new paradigms to address this challenge.

(5) Kwatel, K.; et al. Structural and Electrical Properties of Ceramic Li-Ion Conductors Based on Li1.3Al0.4Ti1.6PO4-LiF. Journal of the European Ceramic Society 2020, 40 (1), 85–93.
Three-dimensional (3D) electrodes and architectures are becoming more prevalent in next generation batteries leading to enhanced performance. For instance, in the case of Zn-based batteries, Klug, Youngchan Kim, Xiao Liu, Battogtokh Jugdersuren, Jeffrey W. Long, Debra R. Rolison, Rachel Carter and Megan B. Sassin; U.S. Naval Research Laboratory, United States.

11:00 AM DISCUSSION TIME

In this study, we introduce a novel method for synthesizing argyrodite materials, employing Li1Na as the primary starting material instead of Li2S. Li6PS5Cl can be efficiently prepared through a one-step ball milling process. The resulting material (Li6PS5Cl) demonstrated an ionic conductivity of 1.1 mS cm–1, comparable to the room temperature conductivity of established Li6PS5Cl.

11:30 AM ES03.15.05

Submicron-Thick Single-Column Conducting Polymers via Initiated Chemical Vapor Deposition Hunter Ford, Ramsay B. Nuwayhid, Brian Chaloux, Michael Swift, Christopher Klug, Youngchen Kim, Xiao Liu, Battogtokh Jugdersuren, Jeffrey W. Long, Debra R. Rolison, Rachel Carter and Megan B. Sassin; U.S. Naval Research Laboratory, United States

Three-dimensional (3D) electrodes and architectures are becoming more prevalent in next generation batteries leading to enhanced performance. For instance, in the case of Zn-based batteries, a 3D Zn electrode alleviates close hotspots mitigating shape change, while in the case of Li-S batteries a 3D porous carbon nanofibers help to prevent dissolution and diffusion of active material.\(^1\) Additional functionality and flexibility can be unlocked via modification of the extensive surface area of the 3D components, such as incorporating coatings to enhance electrolyte wettability, serve as an artificial solid-electrolyte interface, or as a solid-state electrolyte. Conformally and homogeneously coating the interior and exterior surfaces of a complex, macroscopically thick 3D structure necessitates the use of non-line-of-sight deposition techniques.

Initiated chemical vapor deposition (iCVD) is a non-line-of-sight method that has demonstrated utility to generate conformal polymer coatings with tunable thickness on both 2D and 3D substrates. Recently, we have reported on the post-deposition modification of iCVD-derived polymer films to produce a submicron-thick anion-conducting polymer electrolyte.\(^2\) To build off of these results, we move to generate crosslinked co-polymer systems via iCVD, based off of divinylbenzene and 4-dimethylaminomethylstyrene (DVB-DMAAM), and use post-processing protocols to impart specific performance functionalities. The co-polymer can be rendered as a single-anion conducting solid-state electrolyte (SSE) and we show that the ionic conductivity of the SSE depends upon the DVB/DMAAM ratio, the mobile ion identity, and network plasticization, with anion conductivity nearing 1 \(10^{-3}\) S cm\(^{-1}\) under optimal conditions. Molecular dynamic (MD) simulations are further used to probe ion transport, which coupled with mechanical property analysis enables structure-chemistry-property relationships to be determined. The iCVD generated SSEs facilitate anionic redox chemistry (Zn/ZnO, Ag/ZnO) without the use of an additional separator or free salt, a major advancement for improving specific cell capacity. Coupling iCVD with mass-scalable post-processing protocols to impart specific performance functionality of submicron-thick SSEs opens the door to advanced 3D electrodes and components to enable next-generation energy storage systems with high performance metrics.


11:45 AM ES03.16.03

Facile Synthesis of Li Argyrodite Materials as a Solid Electrolyte JaeSeong Yoo and Jae-Hun Kim; Kookmin University, Korea (the Republic of)

Recently, research on next-generation secondary batteries has been actively pursued to develop high-energy-density and safe battery technologies. Currently, liquid electrolytes are utilized in Li-ion batteries (LIBs), which are flammable and volatile. Replacing the liquid electrolyte with solid materials could facilitate a high-capacity Li metal anode and enhance the safety of LIBs. Solid electrolyte materials in all-solid-state batteries (ASSBs) are categorized into oxides, sulfides, and polymers. Among these, sulfide-based materials offer several advantages, including high ionic conductivity and excellent processability.

The Li-argyrodite materials (Li\(_2\)PS\(_4\)X, X = Cl, Br, and I) are exemplary sulfide-based materials renowned for their high ionic conductivity and electrochemical stability. However, a challenge exists in the current synthesis of argyrodite due to the elevated cost of lithium sulfide (Li\(_2\)S), an essential precursor for producing argyrodite-type materials. The high expense associated with Li\(_2\)S amplifies the production costs of solid electrolytes, presenting a significant barrier that impedes the widespread commercialization of ASSBs. Consequently, there is a growing demand for an economical method to synthesize Li\(_2\)S at a lower cost. Another approach involves synthesizing sulfide-based materials without the reliance on Li\(_2\)S.

In this study, we introduce a novel method for synthesizing argyrodite materials, employing Li\(_1\)Na as the primary starting material instead of Li\(_2\)S. Li\(_2\)PS\(_4\)Cl can be efficiently prepared through a one-step ball milling process. The resulting material (Li\(_2\)PS\(_4\)Cl) demonstrated an ionic conductivity of 1.1 mS cm\(^{-1}\), comparable to the room temperature conductivity of established Li\(_2\)PS\(_4\)Cl solid electrolytes. This approach has the potential to lower the cost of solid electrolyte synthesis and enhance time efficiency.
8:00 AM ES03.14.01
Sequencing Polymers for Room-Temperature Solid-State Batteries Xinrong Lin1, Shantaoo Han2 and Mao Chen2; 1 Duke Kunshan University, China; 2 Fudan University, China

For decades, liquid electrolytes have been adopted in lithium-ion batteries to bridge the interspace between electrodes and transport ions. In an era aspiring deep electrification and decarbonization in transportation and power sectors, polymers are expected to double energy density at the system level when combined with lithium anode, and enable all-solid-state battery (ASSB) that offers enhanced safety, processability and flexibility. Unfortunately, the long-standing crux to designing high-performance polymer electrolytes is their poor ion conductivity, which is limited by chain mobility and number of dissociated ions in polymer matrix. Previously, researchers have almost always focused on increasing segmental chain motion to improve ion transport, such as adding plasticizing additives or changing molecular compositions, which could lead to compromised mechanical integrity and polarization-related transport loss. In the meantime, though the importance of dissociated ions is empirically considered, the sequence strategy to modulate polymer transport and achieve delicate control of ion dissociation is almost universally overlooked.

Inspired by natural macromolecules that can achieve complex regulation by delicately controlling sequential arrangement of the backbone, we envision that manipulating polymer sequence could facilitate ion dissociation and strengthen control of transport in polymers. Herein, with a combination of experimental and computational methods, we prove the fundamental significance of polymer sequencing in ion transport and create homogeneous Li⁺ distributions, non-aggregated Li⁺ solvation structures and enhanced Li⁺-anion dissociation in a designed solid-state fluorinated single-ion polymer electrolyte with alternating sequence (alter-SIPE). Perhaps most remarkably, in dry polymers, the alternately sequenced polymer leads to a concerted PEO-Li⁺-anion migration pathway, allowing conductivity tuned up by 1-3 orders of magnitude at 30 degC, which is comparable to that of liquid-state polyethylene oxide (PEO). In addition, we demonstrate that the exceptional ionic conduction capacity of our alter-SIPE could enable dendrite-free operation and reversible cycling in Li|LiFePO4 (LFP) ASSBs with a high coulombic efficiency.

8:15 AM ES03.14.02
A Metal-Free Quasi-Solid-State Battery for Better Safety and Sustainability Ying Wang; Louisiana State University, United States

Solid-state rechargeable batteries promise high energy, low cost, and improved safety/stability. Hence, they are considered as the new-generation battery technology for electric vehicles and grid-scale electricity storage, and expected to meet other critical needs for more compact and higher-capacity energy storage devices. On another note, current commercial batteries are mainly metal based, with metal elements in charge carriers and/or electrode materials, which poses potential economic and environmental concerns due to the heavy use of nonrenewable metals. Thus, metal-free batteries provide a more sustainable and environmentally-friendly alternative to these batteries, though the relevant research is still in its infancy. Recently, rechargeable batteries based on aqueous electrolytes have shown high potential attributed to their low cost and intrinsic safety. An appealing choice is an aqueous battery using non-metal ions as charge carriers, such as ammonium ion with a lighter molecular weight (18 g/mol) and a small hydrated ionic size of 3.31 Å, leading to faster ion diffusion in the electrolyte. Furthermore, by combining with organic solvents, the electrolyte will function as a solid electrolyte (SCE) consists of a liquid immobilized in a solid skeleton, for example the ionogel which confines an ionic liquid within an inorganic or hybrid solid matrix.

In order to increase the energy density as well as the safety of alkali ion batteries, efforts over the past years have focused on solid electrolytes, mainly for Li⁺ conduction. Among these, the solid composite electrolyte (SCE) consists of a liquid immobilized in a solid skeleton, for example the ionogel which confines an ionic liquid within an inorganic or hybrid solid matrix. Since deep eutectic solvents have advantages over ionic liquids, such as ease of preparation, cost etc. we proposed a eutectogel (ETG) for lithium ion batteries composed of a DES (LiTFSI/NMA) in a solid silica matrix with a high ionic conductivity of 1.46 mS/cm, high thermal (130°C) and electrochemical stability (up to 4.8V)[1]. However, these materials also are brittle, which in the final cell will influence the interfacial resistance as the contact with the electrode may be limited, besides cracking, limiting the cell performance. Therefore, two strategies were followed for improvement.

First, the silica matrix was replaced by a polymer matrix, called the P-ETG, achieving 0.78 mS/cm, stability up to 4.5 V and improved fire safety in comparison to the conventional liquid electrolyte (1M LiPF6 in EC/DEC)[2]. Depending on the polymer that is used to build the matrix, the stability could be further improved (1.5-5.0V), which allows stable cycling with high energy density NMC622 cathodes[3]. Furthermore, insights into the DES-polymer interaction allow to optimize the conductivity from 0.4 mS/cm to 1 mS/cm at 25°C[4]. Second, turning to sodium ion batteries, the silica matrix was organically modified with phenyl groups in ionogels, which reduces the Young’s modulus from 29 to 6 MPa. This improves the charge transfer resistance in Na/Na2Ti3O7 half cells, but also decreases the ionic conductivity somewhat to 3 mS/cm; the anodic stability was 3.9V vs. Na+/Na [5]. The reason that the latter material was an ionogel, was that to the best of our knowledge, at the time there wasn’t any suitable sodium ion conducting DES available in literature. Therefore, its development became the subject of our research as well. A first DES consists of NaTFSI and NMA, demonstrating that high concentrations of salt are needed to improve the electrochemical (up to 4.65 V) and fire hazard stability, while compromising the conductivity, which for the most stable electrolyte is 0.3 mS/cm at 20°C[6]. A remaining issue for this DES is that even the highest concentrated one is not stable in contact with Na metal. This is tackled by a novel composition, with optimized sodium metal compatibility and anodic stability up to 4.0 V vs. Na+/Na, and half cells with cycle life and coulombic efficiency on par with cells built with conventional carbonate-based electrolytes[7]. The development of these novel Na⁺ conducting DES, paves the way to their incorporation into a solid matrix towards the formation of Na⁺ conducting eutectogels[8].

In this presentation, an overview of the group’s work of the past 5 years will be given, to show that quite a distance has been travelled on the road from ionic liquids to deep eutectic solvents as liquid electrolytes for sodium ion batteries, and from ionogels to eutectogels in both lithium ion batteries and sodium ion batteries. This has allowed to achieve improvements in cell performance regarding energy density, stability, safety and compatibility with metal anodes.


8:30 AM ES03.14.03
Electrolytes for Lithium and Sodium Ion Batteries: The Road from Ionic Liquids to Deep Eutectic Solvents and from Solid Ionogels to Eutectogels An Hardy1,2,3, Jonas Mercken1,2,3, An-Sofie Kelchtermans1,2,3, Bjorn Joos1,2,3, Dries De Sloovere1,2,3 and Marlies K. Van Baels1,2,3; 1 Hasselt University, Belgium; 2 IMEC, Belgium; 3 Energyville, Belgium

In order to increase the energy density as well as the safety of alkali ion batteries, efforts over the past years have focused on solid electrolytes, mainly for Li⁺ conduction. Among these, the solid composite electrolyte (SCE) consists of a liquid immobilized in a solid skeleton, for example the ionogel which confines an ionic liquid within an inorganic or hybrid solid matrix. Since deep eutectic solvents have advantages over ionic liquids, such as ease of preparation, cost etc. we proposed a eutectogel (ETG) for lithium ion batteries composed of a DES (LiTFSI/NMA) in a solid silica matrix with a high ionic conductivity of 1.46 mS/cm, high thermal (130°C) and electrochemical stability (up to 4.8V)[1]. However, these materials also are brittle, which in the final cell will influence the interfacial resistance as the contact with the electrode may be limited, besides cracking, limiting the cell performance. Therefore, two strategies were followed for improvement.

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Hydroborate solid electrolytes offer high ionic conductivity and are stable in contact with alkali metal anodes, but are challenging to integrate into batteries with high-voltage cathodes [1-3]. Here, we demonstrate stable dis-/charge cycling of solid-state lithium-ion batteries combining a Li3(CB11H12)2(CB9H10) hydroborate electrolyte with a 4 V-class LiNi0.8Mn0.1Co0.1O2 (NMC811) cathode, exploiting the enhanced kinetic stability of the LiCB11H12-rich and LiCB9H10-poor electrolyte composition [4]. Cells with lithium metal and indium/lithium anodes achieve a discharge capacity at C/10 of ~145 mAh g–1 at room temperature and ~175 mAh g–1 at 60 °C. Indium/lithium cells retain 98% of their initial discharge capacity after 100 cycles at C/5 and 70% after 1000 cycles at C/2. Capacity retention of 97% after 100 cycles at C/5 and 75% after 350 cycles at C/2 is also achieved with a graphite anode without any excess lithium. The energy density per cathode composite weight of 460 Wh kg–1 is on par with the best solid-state batteries reported to date.


**Synergistic In-Silico Design and Electrochemical Characterization of Solid-State Electrolytes with Fully Earth Abundant Chemical Compositions for Na/K-Metal Batteries**

**Ivano Eligio Castelli, Chiara Spezzati, Benjamin Sjolin and Mohamad Khoshkalam; Technical University of Denmark, Denmark**

The concept of corner-sharing frameworks is fundamental to the design of oxide solid-state electrolytes with superionic conductivity for alkali-metal ions such as Li⁺ and Na⁺. These structures are composed of a highly covalent skeleton of corner-sharing polyhedra, allowing alkali-metal ions to diffuse through interconnected and highly metastable interstitial positions within the framework. In this study, our focus is on a class of earth-abundant rock silicates as solid-state electrolytes (SSE) for Na/K-metal batteries. Through a synergistic approach involving in-silico design and electrochemical characterization, we investigated the relationship between structural features—such as migration energy barriers for Na⁺ and K⁺, bottleneck pathways in the skeleton structure, polyhedron packing ratio, and continuous symmetry measure—with SSE performance indicators such as ionic conductivity and phase stability under ambient conditions. Our preliminary investigations indicate that a high Continuous Symmetry Measure value in Na/K-polyhedra, along with a low packing ratio of the skeleton structure, are key features in achieving fast kinetic transport for Na⁺ and K⁺. Experimental results demonstrate that by applying this hypothesis, it is possible to achieve Na⁺/K⁺ ionic conductivity levels in the range of 10–0.1 mS/cm at 50 °C, using a fully earth-abundant chemical composition without relying on rare-earth or multi-valent transition metal ions. An SSE based on the Na-Mg-Al-Ca-Si-O oxide system was fabricated into thin, self-standing tape-cast layers under ambient conditions. These thin, self-standing layers, in a symmetrical cell configuration of Na/SSE/Na, cycled for more than 50 cycles up to 1 mA/cm² at 50 °C. The utilization of earth-abundant rock silicates as SSE, demonstrated through synergistic in-silico design and experimental characterization, offers a promising avenue for the development of high-performance and sustainable solid-state batteries, showcasing significant potential in achieving enhanced ionic conductivity and phase stability without relying on rare-earth or multi-valent transition metal ions.

**SYMPOSIUM ES04**

**Metal Anodes in Rechargeable Batteries—Electrolyte, Interface and Mechanism**

April 23 - April 26, 2024

**Symposium Organizers**
Betar Gallant, Massachusetts Institute of Technology
Tao Gao, University of Utah
Yuzhang Li, University of California, Los Angeles
Wu Xu, Pacific Northwest National Laboratory

* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

**SESSION ES04.01: Li Metal—Solid State**
Session Chairs: Tao Gao and Yuzhang Li
Tuesday Morning, April 23, 2024
Room 422, Level 4, Summit

**10:30 AM ES04.01.05**

**Polymerized Acrylonitrile Artificial SEI for Long-Life Li-Metal Battery and Enhanced Stability for Li/Li10GeP2S12 Interface**

Binh K. Hoang¹, Roya Damircheli¹, Madison Brausch¹, Victoria Castagna Ferrari², NHI Nguyen¹ and Chuang-Fu Lin¹; ¹The Catholic University of America, United States; ²University of Maryland, United States

Lithium metal anode batteries have attracted significant attention as a promising energy storage technology, offering a high theoretical specific capacity and low electrochemical potential. Utilizing lithium metal as the anode material can substantially increase energy density compared to conventional lithium-ion batteries. However, the practical application of lithium metal anodes has encountered notable challenges, primarily due to the formation of dendritic structures during cycling. These dendrites pose safety risks and degrade battery performance. Addressing these challenges necessitates the development of a reliable and effective protection layer for lithium metal. This study presents a cost-effective and convenient method to produce lithium metal protective layers by creating ex-situ polymer layers using acrylonitrile (AN). This method extends the lifetime of lithium metal anodes by a remarkable factor of six under high current (1
m(Acm²) cycling conditions. While the cycle life of bare lithium metal is approximately 150 hours under high current conditions, AN-treated lithium metal anodes exhibit an impressive longevity of over 900 hours. Furthermore, with the increasing attentions on solid-state electrolytes – which address the safety concerns and energy density limitations associated with conventional liquid electrolytes in lithium-ion batteries, the interface between Li metal and solid-state electrolytes has been the major challenges. For example, Li₁₀GeP₂S₁₂ (LGPS) stands out among these solid electrolyte materials, boasting high ionic conductivity (1 × 10⁻² S cm⁻¹). Nonetheless, the severe instability of the interface between lithium metal anodes and solid electrolytes, including dendrite formation and electrolyte degradation, hindering their practical implementation. This work also goes deeply to explore the stability and performance of Li | LGPS systems by utilizing a polymerized acrylonitrile interfacial. By elucidating the mechanisms governing the interfacial layers, this low-cost fabrication of AN-treated lithium metal holds significant potential for advancing the commercialization of future lithium-metal batteries, surpassing the capabilities of traditional lithium-ion batteries.

Solid state electroplating offer the potential to drastically increase the overall stability of rechargeable lithium batteries as well as provide the means to realise the usage of Li-metal anodes maximising the charge capacity of a device. At present, batteries use liquid electrolytes such as [LiPF₆] which although they possess high ionic conductivities of 1x10⁻² S cm⁻¹ limit the safe temperature ranges a battery can be operated at as well as forbidding the use of Li-metal anodes due to dendrite formation leading to short circuiting and “thermal runaway”. Solid electrolytes such as the Li-rich garnet materials, LLZO, or anti-perovskites, Li₃OCl, have demonstrated low migration barriers (<0.3 eV), however issues arise regarding stability or a competing lower conductivity phase. In this work, we have identified a promising Earth-abundant, non-toxic, stable Li-solid electrolyte. Using a combination of density functional theory and experiment, we show that this material possesses thermodynamic, dynamic and electrochemical stability, ideal defect chemistry and low migration barriers leading to undoped conductivities of ~10⁻² S cm⁻¹ which are expected to rise to at least 10⁻¹ S cm⁻¹ with minimal doping.

11:00 AM *ES04.01.07 Lithium Metal Solid-State Batteries: Anode-Free vs. Lithium Excess Matthew McDowell; Georgia Institute of Technology, United States

Solid-state batteries offer the promise of improved energy density and safety compared to lithium-ion batteries. The electro-chemo-mechanical evolution of materials at solid-solid electrochemical interfaces is different than at solid/liquid interfaces, and contact evolution in particular plays a critical role in determining the behavior of solid-state batteries. Lithium metal anodes in solid-state batteries are intrinsically limited by void formation during stripping and dendrite growth during plating. Anode-free solid-state batteries, in which there is no initial lithium metal at the anode interface, offers extremely high energy density, but there is a lack of understanding of how their behavior differs from excess-lithium electrodes. Using X-ray tomography, cryo-FIB, and fine-element modeling, we show that anode-free solid-state batteries are intrinsically limited by current concentrations at the end of stripping due to localized lithium depletion. This causes accelerated short circuiting compared to lithium-excess cells. Based on these results, the beneficial influence of metal alloy interfacial layers on controlling lithium evolution and mitigating contact loss from localised lithium depletion, including at low stack pressures, will be discussed. X-ray tomography is further shown to be particularly useful in observing the dynamic evolution of lithium metal, including void formation and filament growth. Finally, lithium metal composites offer a “middle ground” between lithium-excess and anode-free electrodes, and we show that composite electrode structure can act to enhance the effective transport of Li to the interface and therefore enable improved lithium operation at practical stack pressures < 2MPa.

11:30 AM *ES04.01.08 Critical Current Densities for Short-Circuiting of Solid-State Electrolytes Ryo Kurose¹, Yasutoshi Iriyama¹ and Munekazu Motoyama²; ¹Nagoya University, Japan; ²Kyushu University, Japan

The cubic phase Li₃La₂Zr₂O₁₂ (LLZ) exhibits Li⁺ conductivity on the order of 1×10⁻⁴ S cm⁻¹ at room temperature and has sufficient stability even in contact with molten Li¹. Additionally, its shear modulus is several times greater than those of sulfide solid electrolyte materials², and it is thus expected to act as a promising solid-state electrolyte for preventing dendrite growth of Li metal. However, it has been reported that repeated charging/discharging of Li metal anodes causes short circuits, even with LLZ. Similar results were reported by subsequent researchers, and it was gradually realized that the short-circuit problem was more difficult to solve than originally thought. Various models of the short-circuit mechanism of LLZ have been discussed³⁴, but there is no experimental confirmation of what determines the critical current density (CCD) that induces shorts. This is partly because Li voids are easily formed at the Li/LLZ interface, making it difficult to compare the CCD values under fair conditions. In the present study, the CCD was measured by keeping the Li/LLZ interface constant. The temperature dependence of the CCD was also clarified, and the short-circuit mechanism was discussed based on the activation energy values of the CCD.

Acknowledgments
This work was supported by JSPS KAKENHI Grant Number JP22H04611 (Grant-in-Aid for Scientific Research on Innovative Areas “Interface IONICS”), JP 22H02178, and JST GriteX Grant Number JPMJMX23SS.

References

SESSION ES04.02: Li Metal—Electrolyte and Interface
Session Chairs: Tao Gao and Yuzhang Li
Tuesday Afternoon, April 23, 2024
Room 422, Level 4, Summit

2:00 PM ES04.02.01 Indigo as Single Additive in Liquid Electrolyte for Lithium Metal Batteries Charlotte Mallet, Emmanuelle Giratte and Rochon Sylviane; Center of Excellence in Transportation Electrification and Energy Storage, Canada

Rechargeable lithium ion batteries (LIBs) have been successfully developed and widely used to power today’s portable electronic devices. The long term success in electric vehicles and energy storage system relies on rising the energy density, low temperature efficiency, safety and increased cycle life. In parallel, lithium metal batteries (LMBs), described as a system with Li⁰ as anode and metal oxide as cathode (NMC, LFP, LMO) are arising as aim of research for a plethora of groups. Lithium metal anode is considered as ideal anode due to high theoretical capacity (3860 mAhg⁻¹), lower negative electrochemical potential and lower density (0.534 g.cm⁻³).¹ Researchers used complex liquid electrolyte (ionic liquid, etc.) systems in order to avoid lithium dendrite and degradation, conventional liquid electrolyte ([LiPF₆], carbonate solvents) degraded faster than expected, and consequently, generated cells fading. Therefore conventional liquid electrolyte in such cell was not used. Use of organic additives in electrolyte and/or electrodes is considered as one of the most economical and effective approaches for solving many problems as cited previously. The additive can interact with electrolyte or anode to prevent degradation or enhanced cell performances. This presentation will outline commercial organic compounds: Indigo and its derivatives use as single additive in NMC/Li batteries with conventional liquid electrolyte, which considerably increased the cycle life of Li metal batteries. Dyes such Indigold contain electron density donor (-NR-) and acceptor (-C=O) groups linked by conjugated bonds, which participate to their versatile electrochemical properties.

When used as additive in cathode materials or electrolyte, indigo modified the electrode structure and changed the composition of the Li-ions battery electrolyte and solid electrolyte interface (SEI) on lithium metal.
Li-ion and Li-metal batteries performance limitations are associated with physico-chemical processes at electrode/electrolyte interfaces, which lead to high impedance, electrochemical instability, and inhomogeneous Li plating and stripping. In fact, battery performance is largely determined by thermodynamic, kinetic, and mechanical properties of such electrochemical interfaces and interphases. These electrochemical systems tend to operate far away from equilibrium. A thin passive film, the so-called solid electrolyte interphase (SEI) layer, that forms at the electrode/electrolyte interface during battery assembly/formation, which gradually reforms during its operation is critical for its basic function and lifetime. However, our overall understanding of heterogeneous ionic interfaces and interphases is still very limited due to two main reasons. First, characterizing such interfaces and interphases in their native environment is extremely challenging, as they are buried between two dissimilar materials. Second, the interfaces and interphases have complex structure and chemistry, and can even evolve by chemical inter-diffusion, lattice strain, defects, and space charge effects which lead to a variety of chemical reactions across multiple spatial and temporal scales. Interface evolution is further propelled by the large amount of charge and mass transfer between electrodes in a battery over its lifetime (generally leading to degradation, performance loss, and eventual battery failure). In this work, we overview and exploit the nanoscale spatial resolution, chemical selectivity, and surface sensitivity of near-field infrared nanospectroscopy to characterize electrode/liquid and solid electrolyte interfaces. Near-field infrared measurements in combination with standard surface characterization tools reveal that intrinsic molecular, structural, and chemical heterogeneities at the interface. This work provides a unique insight into the mechanisms of early-stage interphase formation at electrochemically active buried interfaces, and an experimental diagnostic means to aid in the development of methods to control local nanoscale variations in electrolyte chemistry, structure, and ionic conductivity at the surface of the electrode.

Stable and Ion-Conductive Polymeric Lithicone for Lithium Metal Anode Protection


2.5 PM + ES04.02.03

SINS of The SEI Layer: On The Origins of Electrode Passivity of Li-Metal Anode Robert Kostecki, Jonathan M. Larson, Andrew Dopilka and Asiya Sarycheva; Lawrence Berkeley National Laboratory, United States

Li-metal batteries are becoming increasingly appealing for electric mobility and other high-tech applications as they offer high energy density advantage coming from the utilization of Li metal anode with an ultrahigh theoretical specific capacity and an extremely low reduction potential. However, the practical application of Li metal anode is hampered by a variety of issues. These include dendrite formation which poses a risk for fire, formation of unstable solid electrolyte interphase (SEI) and “dead” Li resulting in a fast capacity fading, which are aggravated at high current densities. In this work, we report Li metal protection by a lithium-glycerol lithicone (LGL) layer formed by utilizing tert-butoxide and glycerol precursors in a molecular layer deposition process. The as-formed protection layer shows a good stability and a high ionic conductivity. The performance of the LGL-protected Li metal anode (LGL@Li) is demonstrated in both symmetric and full cell configurations at high current densities. The LGL@Li/LGL@Li cells demonstrate improved cycling stability compared with Li/Li cells during Li metal stripping/plating process at ~2.3 mAcmm⁻² (2C) and areal capacity of 1.1 mAhcm⁻². Furthermore, LGL@Li/NMC622 cells show a capacity retention of ~87% compared with ~35% for Li[NMC622 cells after 200 cycles at a high current density of 2.1 mAcmm⁻² (C/2). Our results show that LGL protection strategy is promising for practical Li metal batteries.

3:00 PM BREAK

3:30 PM + ES04.02.05

Lithium Metal Batteries with Improved Thermal Stabilities Xia Cao, Wu Xu and Ji-Guang Zhang; Pacific Northwest National Laboratory, United States

Lithium Metal Batteries with Improved Thermal Stabilities

Xia Cao, Wu Xu, Ji-Guang Zhang

Energy and Environment Directorate, Pacific Northwest National Laboratory

Richland, Washington 99354, United States

Development of lithium (Li) metal batteries (LMBs) has attracted worldwide attention in recent years due to their much higher theoretical energy densities than those of conventional Li ion batteries. 1,2 Other metal batteries (MBs), such as Na metal batteries (NMBs) and potassium metal batteries (PMBs) also attracted more and more attention due to their abundance in earth crust and low cost. 3,4 Although long cycle life of metal batteries have been demonstrated,5,6 their large-scale applications are still hindered by several barriers. One of the main barriers is the thermal stability of the electrolytes, especially when they are in contact with high voltage cathode. Therefore, development of electrolyte with improved thermal stability is critical for large scale application of metal batteries

In this work, factors affecting thermal stability of electrolytes for Li metal batteries will be discussed. First, electrolyte components should be selected to enable preferential decomposition of its salt rather than solvent so an inorganic rich interphase layer can be formed on electrodes, especially on metal anode to block its continuous reaction with electrolyte. These inorganic rich SEI layers can also enable the formation of large size of metal particles instead of nano powders, therefore minimize the surface area of anode. Formation of a stable SEI layer can not only minimize the formation of powder metal particles, but also prevent exposure of large amount of pure metal powder to ambient air in case of mechanical damage of batteries. Second, electrolyte solvents with high boiling point, low vapor pressure, and low reactivity with oxygen species are desired. These features will largely slow down the formation of flammable vapor when the cell is exposed to ambient air. Third, electrolyte should be stable at elevated temperature even at fully charged (high voltage) conditions. In any case, selection of solvent properties should not compromise electrochemical property es of the electrolytes. At last, examples of novel electrolytes based on these design principles will be reported in this work.


4:00 PM + ES04.02.06

Prediction of Electrode-Electrolyte Degradation through Data-Driven Massive Reaction Networks Kristin A. Persson1,2; 1UC Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

Despite decades of work, there is still considerable uncertainty regarding the major components of the solid-electrolyte interface (SEI) and its dynamic formation mechanism as a function of electrolyte and anode composition. Here we present a new data-driven first-principles framework using a combination of high-throughput calculations, reaction networks, machine learning, and microkinetic modeling. Our automated methodology is based on a systematic generation of relevant species using a general fragmentation/recombination procedure which provides the basis for a vast thermodynamic reaction landscape, calculated with density functional theory. We explore this landscape using stochastic methods and shortest pathfinding algorithms, which yield the most likely reaction pathways which are then refined with transition state calculations and kinetic information. The results of the framework show promise in being able to automatically recover previous insights on single reaction pathways, as well as successfully predicting the early dynamics and competitive nature of the SEI formation. As examples, we present i) formation mechanisms of LEMC as compared to LEDC, ii) decomposition mechanisms of the lithium hexafluorophosphate salt and iii) recover the Peled-like separation of the SEI into inorganic and organic domains resulting from rich reactive competition. By conducting accelerated simulations at elevated temperature, we track SEI evolution, confirming the postulated reduction of lithium ethylene monocarbonate to dilithium ethylene monocarbonate and hydrogen gas. These findings furnish fundamental insights into the dynamics of SEI formation and demonstrate a path forward toward a predictive understanding of electrochemical passivation.

SESSION ES04.03: Li Metal—Characterization and Mechanism

Session Chairs: Tao Gao and Yuzhang Li

Wednesday Morning, April 24, 2024

Room 422, Level 4, Summit

Electrodeposition of lithium (Li) metal is critical for high-energy batteries. However, the simultaneous formation of a surface corrosion film termed the solid electrolyte interphase (SEI) complicates the deposition process, which underpins our poor understanding of Li metal electrodeposition. Here we decouple these two intertwined processes by outpacing SEI formation at ultrafast deposition current densities while also avoiding mass transport limitations. By using cryogenic electron microscopy, we discover the intrinsic deposition morphology of metallic Li to be that of a rhombic dodecahedron, which is surprisingly independent of electrolyte chemistry or current collector substrate. In a coin cell architecture, these rhombic dodecahedra exhibit near point-contact connectivity with the current collector, which can accelerate inactive Li formation. We propose a pulse-current protocol that overcomes this failure mode by leveraging Li rhombic dodecahedra as nucleation seeds, enabling the subsequent growth of dense Li that improves battery performance compared with a baseline. While Li deposition and SEI formation have always been tightly linked in past studies, our experimental approach enables new opportunities to fundamentally understand these processes decoupled from each other and bring about new insights to engineer better batteries.

**8:30 AM** Integrating Multi-Functionality that enables In-Situ TEM probing of Solid Electrolyte Interphase Characteristics

Chongmin N. Wang; Pacific Northwest National Laboratory, United States

For better battery performances, solid electrolyte interphase (SEI) layer is expected to possess three ideal characteristics: electrically insulative, ionically conductive, and constant thickness. These three characteristics are interactively correlated, typically, the thickness of SEI layer is controlled by the electrical properties of SEI layer. However, SEI layers do not seem to behave the ideal characteristics, rather the thickness of the material continuously increases during charge-discharge cycling and shelf storage, indicating that the SEI does not behave as an electrical insulator. We use in-situ bias transmission electron microscopy to directly measure the electrical properties of SEI. We discover that the current-voltage characteristics of SEIs resemble certain electrical conductance, rather than electrical insulation as conventionally assumed. We further demonstrate by tailoring the solvation sheath of the electrolyte, the electrical properties of the SEIs can be readily tuned, which inherently correlate to electrochemical properties. The work highlights the significance of electrical properties of the SEI layer and their tuning towards the enhanced performance of an electrochemical cell.

**9:00 AM** Real- and Reciprocal Space Characterization of Advanced Solid State Batteries

Kelsey B. Hatzell; Princeton University, United States

New and re-imagined energy materials play a critical role in decarbonizing a range of industries related to transportation, chemical fuels, separations, power production and beyond. Transportation accounts for approximately 23% of energy related carbon dioxide emissions and electrification approaches are widespread for personal vehicles. Batteries currently play an outstanding role in a range of applications involving electric vehicles and portable electronic applications and there is a growing interests in expanding the frontier for batteries. Applications such as electric aviation, batteries in space applications, and undersea propulsion is a solid rather than a liquid. I will also discuss the materials and chemo-mechanical principles which impact ion transport and electronic transfer reactions in this class of material systems. Understanding how to engineer materials for coordinated and/or concerted transport is critical achieving reversible operation of these materials and devices. Using real- and reciprocal- space techniques I will show how we can measure and visualize material utilization and reaction heterogeneity in solid state batteries in space and time. The work will conclude by exploring emerging applications for energy and climate materials through highlighting some of our team’s emerging directions that focus on batteries for space applications and novel moisture-swing direct air capture processes.

**9:30 AM BREAK**

**10:00 AM** Mechanical Properties and Deformation Behavior of Lithium Metal

Lara C. Pereira dos Santos1,2 and Robert Spatschek1,3; Forschungszentrum Jülich, Germany; 2RWTH Aachen University, Germany; 3JARA-Energy, Germany

Lithium metal is the ideal candidate as anode material for reaching high energy densities. However, comprehensive and reliable research on its complex mechanical deformation remains scarce, hindering an in-depth understanding of Li-based solid-state batteries. Lithium mechanical properties vary widely depending on length scale, orientation, strain rate and temperature. Besides, lithium is extremely reactive, creeps at room temperature and has a strong anisotropy, making experimental characterization a considerable challenge. This work aims to study the mechanical properties and deformation of lithium as a combination of experimental and modeling tools. On the theoretical side, techniques such as first-principles, molecular dynamics and effective medium theory are applied. Information not only from the elastic parameters, but also from the plastic regime is obtained. Simulations are carried out for different temperatures, specimen sizes and crystal orientations. On the experimental side, micro-indentation is performed and the hardness of lithium foils is evaluated. With this study, we expect to support investigations regarding the size and orientation dependency of Li mechanical properties. Additionally, we aim to contribute to bridging the gap between theory and experiments, as well as understanding plasticity on small scales, high strain rates and high homologous temperatures.

**10:15 AM** Liquid Madelung Potential as The "Beyond Debye-Hückel" Concept Validated for Several Metal Electrodes

Atsuo Yamada, Norio Takenaka, Atsushi Kitada, Seongjae Ko and Hinata Koyama; The University of Tokyo, Japan

Achievement of carbon neutralities requires the development of electrochemical technologies suitable for practical energy storage and conversion. In any electrochemical system, electrode potential E is the central variable that regulates the driving force of redox reactions. However, quantitative understanding of the electrolyte dependence of E has been limited to the classic Debye-Hückel theory that approximates the Coulombic interactions in the electrolyte under the dilute limit conditions. Therefore, accurate expression of E for practical electrochemical systems has been a holy grail of electrochemistry research for over a century. Here we show that the "liquid Madelung potential" (E_M) based on the conventional explicit treatment of solid-state Coulombic interactions enables quantitatively accurate expression of the electrode potential, with the E_M shift obtained from molecular dynamics reproducing a lithtero-unexposed huge experimental shift for the several metal electrode. Thus, a long-awaited method for description of the electrode potential in any electrochemical system is now available. Examples of battery system optimization based on this new concept will be demonstrated.

**10:45 AM** First-Principles Modeling of Deposition Processes at Metal Anodes

Axel Groß1,2; 1University of Ulm, Germany; 2Helmholtz Institute Ulm (HIU), Germany

Metal anodes in batteries of the rocking chair type promise to lead to high energy densities as they yield the lowest possible binding energy for the metal atoms and require no host material. On the other, they are often rather reactive causing the decomposition of commonly used electrolyte components. This may lead to the formation of a passivation layer known as the solid electrolyte interphase (SEI). A better understanding of these reaction mechanisms can lead to an improved electrolyte and substrate design to achieve highly reversible metal anodes in this contribution, recent purely computational [1] and joint theoretical-experimental [2,3] studies addressing the most likely decomposition products of electrolyte components at a number of alkaline metal anodes are presented. It will be demonstrated how the analysis of the first-principles electronic structure calculations based on density functional theory (DFT) allows to identify the crucial steps in the decomposition reactions.

In addition, metal anodes also play a crucial role in batteries using anionic charge carriers such as chloride. Based on periodic DFT calculations, the initial steps in the conversion of a Mg anode to a magnesium chloride salt will be analyzed [4] which represents the driving force in the operation of such Cl-ion batteries.

[1] D. Stottmeister and A. Groß, Batterie Supercaps 2023, 6, e202300156.
Unveiling Lithium Metal Anode Behavior through The Advancements and Applications of Titration Gas Chromatography
Y. Shirley Meng
and Wurigumula Bao
The University of Chicago, United States;
Argonne National Laboratory, United States

Lithium metal anodes have long been the ideal anode for a variety of cell chemistries owing to their high gravimetric capacity. Dendrite growth, during cycling, however, restricts their practical deployment. Here, a new class of nanomaterials TiB2 derived 1-dimensional lepidocrocite quasi two-dimensional nanoflakes (1DL) are used as basic for creating a Li scaffold, that can be used as an anode-free setup. The 2D nanoflakes comprised of 1DL nanofilaments are synthesized with a bottom-up reaction, directly from commercial 3D-bulk solids at near ambient temperatures and pressures1,2. The morphology of the 1DL is highly tunable based on processing parameters and can be intercalated with a variety of cations3,4. Here 1DLs are oriented vertically to guide Li-metal deposition and serve as a Li metal scaffold. This is achieved with a control freezing of an aqueous blade casting slurry. Freeze-drying results in an organized vertically oriented structure. These vertical-1DLs enable easier Li nucleation, with lower overpotentials compared with bare Cu or a normal cast slurry of 1DLs. The vertical-1DL shows a superpotential of ~0.06 mV vs -0.08 mA for Cu, a 25% reduction. Leading to a more spatially uniform deposition of Li. Further, 1DL flakes can be intercalated with lithiophilic cations to further improve Li metal deposition and nucleation. Lastly, the OH rich surface groups on the 1DL NFs surfaces help improve the formation of a uniform solid-electrolyte interphase. These properties enable 1DL nanoflakes that are oriented vertically to serve as a Li scaffold in an anode-free setup.

1:45 PM *ES04.04.02 Vertically Orientated TiO2 1D Lepidocrocite Nanoflakes as Scaffold for Enhanced Li-Metal Anodes
Neel A. Cardoza, Mary Qin Hassig, Tabor Yim, Michel Barsoum and Vibha Kalra;
Drexel University, United States

This presentation covers the recent advances in my lab on enabling Li metal anodes. Topics include: 1) A breakthrough tool of cryogenic electron microscopy, leading to atomic scale resolution, 2) ~0.08 mA for Cu, a 25% reduction. Leading to a more spatially uniform deposition of Li. Further, 1DL flakes can be intercalated with lithiophilic cations to further improve Li metal deposition and nucleation. Lastly, the OH rich surface groups on the 1DL NFs surfaces help improve the formation of a uniform solid-electrolyte interphase. These properties enable 1DL nanoflakes that are oriented vertically to serve as a Li scaffold in an anode-free setup.

2:00 PM *ES04.04.03 Materials, Electrolytes and Tools for Lithium Metal Anodes
Yi Cui; Stanford University, United States

This presentation covers the recent advances in my lab on enabling Li metal anodes. Topics include: 1) A breakthrough tool of cryogenic electron microscopy, leading to atomic scale resolution of fragile battery materials and interfaces. 2) Electrochemical measurement techniques for deep understanding of solvation entropy and free energy, charge transfer and electrodeposition kinetics. 3) Materials design to enable Li metal anodes. 4) New electrolyte design for stabling cycling of Li metal anodes.

2:30 PM BREAK

3:30 PM *ES04.04.04 Microstructural Design Principles for Achieving Stable Metal Anode Interphases with Liquid and Solid-State Electrolytes
David Mitlin; The University of Texas at Austin, United States

Lithium metal battery systems (LMBs) are being sought as an ultimate replacement to LIBs, potentially increasing the cell energy over by fifty percent due to the high capacity and low voltage of the metal anode. Analogous improvement in energy is possible with sodium metal batteries (NMBs) and with potassium metal batteries (KMBs), where existing solid ion insertion anodes can be replaced by plating/stripping metal. However, in all three cases safety and performance are compromised by an unstable solid electrolyte interphase (SEI) that consumes metal ions and electrolyte, and ultimately leads to dendrites. This presentation provides a series of case studies derived from the group's LMB, NMB and KMB liquid and solid-state research on the microstructural design principles that provide for long-term cycling and fast-charge stability of metal anodes. The approaches may be categorized as the following: a) design of plating/stripping supports and templates with tuned geometry and functionality; b) design of secondary interlayers placed between the metal anode and the separator; and c) design of multifunctional hybrid separators to replace the conventional polymer separators employed with LIBs. It is demonstrated that despite appearing distinct, the efficacy of each in enabling electrochemical stability originates from three fundamental features that are directly interrelated. The wetting behavior of the electrolyte on the anode must be optimized, the wetting/stripping behavior of the anode on the current collector must be controlled, and a geometrically and chemically modified SEI must be established. Simultaneously achieving all three leads to stable plating/stripping, while missing even one leads to rapid dendrite growth. Cryogenic FIB cross sections and cryo-TEM are combined to yield new insight regarding film wetting behavior and early dendrite formation in optimized versus baseline specimens, analyzing growth in several representative electrolytes.

4:00 PM *ES04.04.05 Interfacial Pressure Improves Calendar Aging of Lithium Metal Anodes
Katharine Harrison1, Kimberly Bassett2, Kathryn Small2, Daniel Long3, Laura C. Merrill2 and Benjamin Warren2;
1National Renewable Energy Laboratory, United States; 2Sandia National Laboratories, United States; 3Air Force Research Laboratory, United States

Lithium metal is a very attractive anode material because its theoretical specific capacity is approximately 10 times higher than conventional graphite anodes. Despite great promise, Li anodes suffer from capacity fade due to instabilities with the electrolyte as well as stranding of active Li. We have previously shown that applied interfacial pressure improves Li anode cycling because the pressure reduces the propensity for Li isolation and enables easier reconnection. Many researchers have also shown that calendar aging can lead to Li capacity loss and this has been attributed to either electrolyte decomposition with concurrent Li corrossion or to the formation of stranded Li. Our prior research focused on calendar aging during cycling suggests the mechanism for calendar aging is largely related to stranding of Li during rest and reconnection of the stranded Li upon further cycling, evidenced by similar average Coulombic efficiencies and Li loss in cells with and without rest. Because our calendar aging studies suggest Li stranding as a major cause of Coulombic efficiency losses and our Li cycling studies suggest this can be mitigated partially through applied interfacial pressure, we hypothesized that applied pressure would improve calendar aging by reducing stranded Li and enabling reconnection.

We systematically varied applied pressure (0-1000 kPa) on Li metal anodes during cycling tests with and without intermittent calendar aging periods. Though the Coulombic efficiency decreases during aging periods, the lost capacity is recovered during subsequent cycles, as shown through average Coulombic efficiency and cumulative Li capacity loss analysis. We find that application of pressure partially mitigates calendar aging, in accordance with our hypothesis that calendar aging is caused by Li standing and can be mitigated to some degree with interfacial pressure. This is further supported by our results showing that calendar aging can lead to Li capacity loss and this has been attributed to either electrolyte decomposition with concurrent Li corrossion or to the formation of stranded Li. Our prior research focused on calendar aging during cycling suggests the mechanism for calendar aging is largely related to stranding of Li during rest and reconnection of the stranded Li upon further cycling, evidenced by similar average Coulombic efficiencies and Li loss in cells with and without rest. Because our calendar aging studies suggest Li stranding as a major cause of Coulombic efficiency losses and our Li cycling studies suggest this can be mitigated partially through applied interfacial pressure, we hypothesized that applied pressure would improve calendar aging by reducing stranded Li and enabling reconnection.

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The authors were supported by a Laboratory Directed Research and Development (LDRD) program. This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC (NTESS), a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration (DOE/NNSA) under contract DE-NA0003525. This written work is authored by an employee of NTESS. The employee, not NTESS, owns the right, title and interest in and to the written work and is responsible for its contents. This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the

Final_Abstract_Book_PF_Sessions_mrsspring2024-20-Jun-2024-14-29-03 (1).html [6/20/2024 2:34:09 PM]
Stress-Driven Diffusion of Lithium into Copper Current Collectors during Plating and Stripping

Kurt Hebert; Iowa State University, United States

Stresses in lithium metal anodes determine their stability during inevitable volume changes experienced upon cycling. Lithium deformation during cycling in liquid cells can initiate surface morphological instabilities which lead to capacity loss, e.g. whiskers and moss (1-3). Evidence suggests that whiskers grow by solid-state diffusion to the whisker base (3), and that whiskers relieve compressive stress in the metal generated by electrodeposition (4,5). While quantitative characterization of these processes is challenging, diffusion accompanying morphology instability can be detected when the whisker or moss is not too high (6,7). Lv et al. reported operating neutron depth profiling (NDP) measurement measurements of Li diffusion into Cu during plating–stripping cycles in pouch cells (7).

A model is presented for lithium diffusion in copper current collectors during cycling in a liquid cell. Diffusion is driven by gradients of elastic stress in the current collector, induced by the combination of mist-indent strain due to displacement Li atoms and bending of the copper film due to the Li concentration gradient (8). The Li diffusion flux at the copper surface (inward and outward during plating and stripping respectively) is assumed to be a constant fraction of the plating or stripping rate, consistent with the NDP measurements. We show that the model quantitatively accounts for all aspects of the measured concentration distributions. In particular, the model captures the unique “wave-like” concentration profiles revealed by NDP, in which the maximum lithium concentration is always at the copper surface, even when lithium diffuses out of the metal during stripping.

The constant flux boundary condition is justified by a model for surface morphology evolution, in which the lithium surface is covered by spheroidal protrusions that grow and contract, respectively, during plating and stripping (3,9). We show that plating on the spheroids through an intact solid-electrolyte interphase (SEI) layer generates inward stress-driven diffusion and outward creep within the protrusion. At the base of the spheroid, the diffusion flux continues into the substrate. This flux represents a small fraction of the plating rate, and thus accounts for the diffusion inferred from analysis of NDP measurements. Therefore, surface morphology evolution appears to be driven by stresses due to plating/stripping through an intact SEI layer.

REFERENCES

4:45 PM ES04.04.07
The Influence of Copper Current Collector Crystal Orientation on Long and Short Term Lithium Metal Plating

Josefine McBrayer, Alexander Heusser, Cooper Bryant and Noah Schorr; Sandia National Laboratories, United States

Lithium metal is a practical anode of choice for beyond lithium ion battery technologies due to its high capacity and low potential. However, recharging (plating) lithium metal has proven difficult because of the formation of lithium dendrites and an unstable solid electrolyte interface (SEI). Both are root causes of poor performance and safety issues as internal short circuits, fire, and thermal runaway. To mitigate these undesirable qualities of lithium anodes for secondary battery applications, more uniform lithium plating is necessary. Here we investigate the performance and lithium morphology on single crystal (111, 100, and 110) and polycrystalline copper current collectors to control Li plating, especially in early cycles. The 111 orientation was determined by cryo scanning electron microscopy (with focused ion beam cross sections) and energy-dispersive X-ray spectroscopy to lead to a more compact lithium morphology and uniform SEI. Plating/stripping experiments supported that this improved morphology also manifested in a greater coulombic efficiency in early cycles in lithium-copper cells.

Low-Cost Carbonaceous Metal-Free Wetting Layer as Sodiophilic Treatment for Solid and Molten Na Batteries

Mark Wellers, Hyungkyu Han, Eugene Polikarpov, Kee Sung Han, Keyyoung Jung, David Reed, Vincent Sprekle, Vaiyihalingam Shuttthanandar, Yiin Wang and Guosheng Li; Pacific Northwest National Laboratory, United States; Research Institute of Industrial Science and Technology (RIST), Korea (the republic of)

Sodium-metal batteries are a promising alternative to Li-metal batteries due to the natural abundance of Na, especially for grid scale energy storage where the cost premium of Li puts strain on the economic feasibility of scalable renewables-plus-storage. Low temperature Na-metal batteries, like their Li-based counterparts, suffer from Na-dendrite formation and dangerous cell failure upon extended cycling or plating at high current densities. Also like their Li-metal counterparts, Na-metal solid-state batteries (SSB) are unable to prevent dendrite intrusion without careful engineering of the Na-metal/solid-electrolyte interface. An alternative approach is to use elevated temperature batteries with a molten anode, which can enable categorically higher current densities with no dendrite issues. Where classically molten Na-batteries such as high temperature Na-S or 'ZEBRA' batteries operate well above 200 °C, it is desirable to reduce operating temperatures to unlock lower cost materials of construction and increase energy efficiency by reducing thermal losses. Unfortunately, it is well known that molten Na has poor wettability in contact with common solid electrolytes like sodium beta-alumina solid-electrolytes (Na-S-Al2O3, "BASE") or NaSICON (Na-Superionic Conductor) ceramic electrolytes.

Various wetting agents and interface modification strategies have been employed to improve wettability of molten Na and reduce interface resistance in Na-SSBs. Some rely on sputter deposition of a suitable metal such as Sn or deposition of metal precursors from solution followed by a heat treatment to form pure metals such as Pb, Sn, or Bi. Some strategies utilizing exotic phases of carbon such as graphene or carbon nanotubes have also been employed. Still others rely on high temperature annealing to drive off surface contaminants under vacuum or inert atmosphere. All of these strategies lack one or more crucial components such as low-cost, non-toxicity, simplicity, or scalability. This has motivated the development of a ‘metal-free wetting layer’ (MFWL) based purely on low-cost carbon resources which can be applied via scalable processes such as spin coating, spray-coating, or even drop-casting from solution. Our MFWL shows excellent uniformity when applied to a suitable solid-electrolyte such as BASE or NaSICON, and facilitates excellent wetting of molten Na as low as the melting point of Na. The meso/microstructure of MFWLs and mechanism of Na-wettability will be discussed in detail. Symmetric Na-Na cell data confirm that cells with low specific resistance and excellent cycling stability can be achieved when the NaF solution (T ~ 100 °C), forming extremely intimate contact between Na and the underlying solid-electrolyte. Further, the utility of this MFWL can be extended to solid-state symmetric Na-Na cells, showing that even without applied pressure, initial experiments with BASE electrolytes treated with MFWL demonstrate a critical current density of ~ 0.5 mA cm-2 at 30 °C. This simple, inexpensive, and scalable interfacial modification strategy shows great promise for enabling pure Na-anoxides across solid-state and elevated temperature batteries.

Cryogenic Focused Ion Beam Milling of Intact Na Metal Battery Stacks Reveals Separator Infiltration and Delamination Failure Mechanism

Kevin Matthews and Jamie Warner; The University of Texas at Austin, United States

Metal anodes are the next frontier of high-energy-density rechargeable batteries. Sodium (Na) metal batteries are particularly promising due to the widespread abundance and low cost of Na precursors. The structure, composition, and function of the solid-electrolyte-interphase (SEI) as well as the metal growth mechanisms must be understood to improve and commercialize Na metal batteries. We developed a cryogenic workflow utilizing a cryo-freeze sample transfer system to prepare intact electrode:separator:electrode stacks, allowing us to probe the intrinsic structure and composition of undisturbed battery interfaces. By milling with a gallium ion beam at cryogenic temperatures, we produced clean milled surfaces of the electrodes and separator with minimal beam-induced artifacts allowing for high resolution imaging, spectroscopic mapping, and 3D reconstructions generated from serial milling and imaging. Using these techniques,
we studied how the Na electrode, SEI, and separator evolve during cycling in both symmetric and asymmetric cells with a tri-layer porous polymer separator and either a carbonate- or ether-based electrolyte. Though often discarded before characterization, we find that the separator is a crucial piece of the puzzle when investigating battery performance and failure. We found overwhelmingly that cells begin with a conformal interface between the Na metal and the electrolyte-filled polymer separator instead of being separated by a layer of electrolyte. After extended cycling, Na infiltrates the separator pores, growing towards the opposing electrode. At the interfaces between the tri-layers, the Na can grow laterally, delaminating the separator layers. High resolution imaging and electron dispersing X-ray spectroscopy (EDS) mapping capture the Na metal in-between and within the polymer layers. 3D reconstructions of the electrodeposited Na and SEI suggest that the robustness of the SEI and the heterogeneity of its distribution (or lack thereof) relate to the ability of the Na to grow into the porous network of the separator. We combine these results to suggest a new failure model that relies on short-circuiting via the formation of a conductive pathway of Na templated by the porosity of the separator, rather than a penetration of the separator by discrete dendrites.

9:30 AM ES04.05.05
Weakly-Coordinating Cyclic Ether-Based Electrolytes Improve Potassium Metal Battery Cycling Stability and Capacity Retention
Austin Choi1, Zheng Li1,2,1 and Vilas Pol1,2
Purdue University, United States; 1University of Maryland, United States

As the scientific community holistically seeks alternative energy sources to traditional fuels such as coal and natural gas, attention has turned towards renewable energy generation such as wind and solar. In tandem, methods of storing energy are also being developed as a way to mitigate the intermittent nature of such methods of energy generation. Among these, electrochemical energy storage solutions are of particular promise given their flexibility and performance, allowing them to suit the needs of an increasingly growing number of industries such as chemical production and automotive manufacturing that are trending towards electrification. Lithium-ion batteries (LIBs) especially have become a mainstay in this space owing to their portability, high energy densities, and cycle lifetimes, and are the principle driving force for the growth of the global battery market to beyond US $100 billion today.

The “holy grail” anode material for LIBs is lithium metal itself, offering an excellent theoretical capacity of 3860 mAh g⁻¹, yet the scarcity and uneven distribution of lithium in the Earth’s crust precludes its more widespread utilization. Hence, “Beyond Li-ion” batteries featuring more readily available charge carriers are also being thoroughly investigated to address this concern. Potassium-ion batteries (KIBs) in particular are suitable alternatives as potassium is available globally and at roughly 1000 times the abundance of lithium. Similar to Li metal, K metal is seen as a promising anode material for KIBs, but its proliferation is hindered by the propensity for dendritic growth, difficulty in maintaining a robust solid electrolyte interphase (SEI), and loss of material in the form of “dead potassium.” Further, the larger ionic radius of potassium ions as compared to lithium ions further strains the SEI and corresponding cathode electrolyte interphase (CEI) during repeated cycling. Strategies to mitigate these effects are thus of paramount importance in successful realization of K metal anodes for KIBs.

As the SEI is deemed primarily by decomposition of the electrolyte-electrolyte-based methodologies are the most direct avenue for improving SEI stability and performance. Specifically, the formation of a mechanochemical role for the SEI and CEI is key in protecting the electrolyte from further degradation through polymerization and deintercalation of the cathode. Specifically, components such as KF that are produced via the decomposition of the fluorine-containing salt are instrumental in the composition of an SEI/CEI that are resistant to intense stresses. Thus, electrolyte solvents that enable preferential salt decomposition rather than organic solvent decomposition are preferred. Such behavior is governed by the solvation structure around the dissolved cations in the electrolyte, where maintaining the presence of salt anions in the solvation shell is critical for development of an inorganic SEI/CEI and is influenced by a variety of factors including the solvent dielectric constant and steric effects.

As compared to conventional carbonate-based electrolytes, ether-based electrolytes have been shown to promote such behavior to an increased degree in LIBs, but this effect remains comparatively unexplored in KIBs, especially paired with the K metal anode. This work demonstrates the efficacy of two cyclic ethers in enabling increased cycling stability and Coulombic efficiency against a K metal anode with regards to plating/stripping performance when compared against a typical carbonate-based electrolyte system. Further, these benefits extend to KIBs with a conventional Prussian blue cathode and K metal anode. These performance enhancements are correlated with the corresponding solvation structures, establishing a framework by which electrolyte solvents can be assessed with metal anodes and presents opportunities for further electrolyte design in other metal anode systems.

9:45 AM ES04.05.06
Probing The Redox -Mediation of Transition Metal Phthalocyanine in Metal-Air Battery
Subhankar Mandal and Aninda J. Bhattacharyya; Indian Institute of Science, India

Metal air batteries have garnered significant attention as a potential alternative to Li-ion batteries due to their high theoretical potential. In lithium-air batteries, during the oxygen reduction reaction (ORR), O₂ is reduced to solid insulating LiO₂, Li₂O₂ and in the reverse charge process, which is the oxygen evolution reaction (OER), discharge products convert back to O₂ and Li⁺. However, the practical implementation of O₂ battery has been hindered by several challenges, primarily due to the sluggish kinetics of ORR and OER. In recent times, a liquid-based redox mediator (@ electrocatalyst) has been demonstrated as an effective approach to increase battery efficiency and modify the reaction pathways to alleviate side reactions. In this presentation, we have systematically explored the solution-based redox mediation of first-row transition metal phthalocyanines for lithium-oxygen batteries. Our findings, based on experiment and theory, convincingly demonstrate that d⁶ (Mn), d⁷ (Co), and d⁸ (Ni) configurations function better compared to d⁶ (Fe) and d⁸ (Cu) in redox mediation of the discharge and charge step. The d⁸ configuration (Zn) and non-d analogs (Mg) do not show any redox mediation because of the inability to binding to O₂. During the discharge process, the LiO₂ coordinate with metal phthalocyanines and leads to a solution phase reaction pathway and reverse process controlled by the RM, thus confirming a bifunctional redox mediator. Apart from the reaction pathways predicted based on thermodynamic considerations, density functional theory calculations also reveal interesting effects of electrochemical perturbation on the redox mechanism mechanisms and the role of the transition-metal centre. In addition, to account for the interaction between RM mediator and the discharge products (KO₂ LiO₂, Li₂O₂ and parasitic products (LiCO₃ and LiOH), further spectroscopic and theoretically investigations were conducted. Our finding reveals that discharge/parasitic product coordinated to metal centre with the unfilled d orbital and oriented in between to M-N bond.in the case of filled d system, the discharge/parasitic products along the M-N bond and interacting with the imidazole moiety of the phthalocyanine ring leads to the poisoning the catalytic activity in battery performance.

10:00 AM BREAK

10:30 AM *ES04.05.09
First Principles Investigation into The Dynamics at Ca Anodes and Electrolyte Interfaces
Hashan C. Peiris and Manuel Smeu; Binghamton University, The State University of New York, United States

Motivated by recent experimental progress, we have utilized an approach combining density functional theory (DFT) and ab initio molecular dynamics (AIMD) to gain atomistic perspectives into the dynamic processes governing anode-electrolyte interactions. First principles based molecular dynamics allow one to capture the bond-breaking/forming processes, and interfacial interactions between the anode and the electrolyte, while preserving theoretical accuracy independent of empirical parameterizations. The DFT approach allows one to study the charge transfer during reactions energetic, capture transition states, and evaluate the potential energy landscapes in detail.

The transition to sustainable energy systems is predominantly influenced by the effectiveness of energy storage technologies. While Li-ion batteries have been the industry standard, there is a growing interest in multivalent ion battery systems. These alternatives offer advantages such as higher storage capacities, abundant material resources, and reduced geopolitical risks. Specifically, Ca-ion batteries garner attention as a promising option for high-energy density, low-cost batteries. Still at a nascent stage of development, understanding the interactions between the electrolyte and the Ca anode at the interface is crucial for optimizing the performance of these emerging battery technologies.

To gain insights into the initial formation of the solid-electrolyte interphase (SEI) at the interface, we first looked into the decomposition of pure ethylene carbonate (EC) and an EC/Ca(CO₃)₂ electrolyte on a Ca metal surface. We found that CaCO₃, CaO, and Ca(OH)₂ are the most common byproducts of the initial interfacial reactions. A fast two-electron reduction reaction producing CO₃²⁻ and CH₄ is found to be thermodynamically and kinetically favorable, while a reaction producing CH₂O⁻₂ and CO takes precedence when multiple EC molecules are considered. Investigating the EC-based electrolyte decomposition at Li, Ca, and Al anode interfaces, we found that pure EC only decomposes to CO and CH₃CO₂⁻ species on each surface. However, upon the introduction of a salt molecule into the electrolyte, a second EC decomposition route resulting in the formation of CO₃²⁻ and CH₃ begins to occur. Li and Ca surfaces are more active in EC breakdown than Al due to the rate of charge transfer being much faster due to lower electronegativity and ionization energies.

However, we looked at the use of preformed solid electrolyte interphase (SEI) using Al₂O₃ to retard the interfacial reactions with the electrolyte (EC) in Ca anodes. The amorphous oxide layer was found to be thermodynamically stable while allowing for the diffusion of Ca through the layer. The oxide coating remained insulating up to the equilibrium stoichiometry. More significantly, the calcinated oxide layer slowed or prevented the decomposition of solvent molecules.
Lastly, we examined the ether and ester electrolyte stability on Ca anodes with different solvent and salt combinations. Tetrahydrofuran (THF) was observed to be the most stable relative to EC, even in a highly reductive environment. We attribute this to the charge distribution in THF on its backbone while the EC concentrates charge on its ester oxygens and carbonyl carbon, resulting in decomposition. We find Ca(H$_2$)$_4$ and THF to be the most stable solution in our investigation, corroborating experimental evidence of its suitability as a CIB electrolyte.

More recently, inspired by the recent advances in machine learning-assisted techniques for computational materials research, we have been actively investigating the interactions of Ca metal anodes with S-based cathodes. We report on our current progress in modeling the Ca anode interactions with polysulfides.

SESSION ES04.06: Li-ion and Li metal
Session Chairs: Tao Gao and Yiru Zhang
Thursday Afternoon, April 25, 2024
Room 422, Level 4, Summit

1:30 PM ES04.06.01
Investigating Large Deformation and Amorphous Intermediates in Sb Electrodes
Ananya Ronika Balakrishna and Tao Zhang; University of California, Santa Barbara, United States

The key objective is to provide insight into how amorphous intermediates that form in high-capacity anodes during electrochemical cycling accommodate large volume changes and prevent microcracking in Antimony (Sb) electrodes. The electrochemical cycling of alloy anodes introduces an abrupt crystalline to amorphous structural transformation (in Na-based electrodes). This transformation, in turn, is accompanied by anisotropic volume expansion (>100%), abrupt changes to elastic stiffness, and an alteration to the Na-diffusion kinetics and alloying-reaction pathways. We hypothesize that these sudden changes to intrinsic material properties alter local stress distributions and phase transformation pathways in high-capacity anodes, which contributes to their characteristic mechanical response. We are developing a theoretical framework to understand the energy dissipation and deformation mechanism in large-volume change electrodes and to use these mechanistic insights to guide materials design.

1:45 PM *ES04.06.02
Quantifying Li Plating on Graphite during Fast Charging of Li-Ion Batteries
Bryan D. McCloskey; University of California-Berkeley, United States

Li-ion battery fast charge is limited due to challenges posed by plating lithium on the graphite anode, whereby the large overvoltage necessary to drive high Li$^+$ insertion rates results in favorable thermodynamic conditions for Li metal deposition on the graphite surface. Li plating is difficult to detect, particularly in small quantities, and results in safety risks and capacity fade due to lithium metal’s high reactivity with conventional electrolytes. Here, we present our efforts to develop both chemical and electrochemical methods to precisely quantify Li plating and detect the state-of-charge (SOC) onset of lithium plating on graphite electrodes during constant current fast charging. We will discuss titration mass spectrometry (TiMS), a highly sensitive (~20 nmol resolution, or 0.5 mAh of plated Li) chemical analysis where gases evolved from harvested graphite electrodes immersed in acid are used to quantify various solid electrolyte interface species, including electrically isolated (inactive) Li metal. TiMS is then used to determine the precise onset of Li plating and to distinguish between the various capacity fade mechanisms that arise during fast charge. We will then discuss the use of simple electrochemical cycling techniques to quantify irreversible Li plating in Li|Graphite half-cells as a function of energy density (electrode thickness), charge rate, temperature, and SOC. Similar methods are developed to quantify in-situ Li plating for commercially relevant Graphite|LiNi$_{0.5}$Mn$_{0.3}$Co$_{0.2}$O$_{2}$ (NMC) cells. In combination, all of these techniques provide a highly accurate measure of the onset of Li plating and quantitative insight into capacity losses during fast charging.

2:15 PM ES04.06.03
Reaction and Ionic Migration at The Electrode-Electrolyte Interface in Solid State Batteries from Machine Learning Molecular Dynamics
Jingxuan Ding, Albert Musaelian, Yu Xie, Menghang (David) Wang, Laura Zichi, Anders Johansson, Simon L. Batzner and Boris Kozinsky; Harvard University, United States

Atomistic-level understanding of the chemical reactions forming the solid-electrolyte interphase (SEI) in solid-state lithium batteries has remained challenging, primarily due to the limited resolution in experimental techniques and the insufficient accuracy in large-scale simulations. In this work, we combine on-the-fly active learning based on Gaussian Process regression (FLARE) with local equivariant neural network interatomic potentials (Allegro) to construct a machine-learning force field (MLFF) to perform large-scale long-time explicit reactive simulation of a complete symmetric battery cell with ab initio accuracy. The MLFF is validated with experimental values of mechanical properties of bulk lithium and diffusion coefficient of solid electrolyte. For the symmetric battery, we observe prominent fast reactions at the interface and characterize the dominant reaction products along with their evolution time scales, using unsupervised learning techniques based on atomic geometry descriptors. Our simulation reveals the kinetics and the passivation involved in the chemical reaction responsible for the SEI formation. The methods in this study are promising for acceleration analysis of atomistic mechanisms in complicated heterogeneous systems and provide design insights for the development of solid-state batteries.

2:30 PM ES04.06.04
Understanding Lithium Plating from Solid and Liquid Electrolytes Using Dynamic Impedance Spectroscopy
Robert L. Sace1, Zhiao Yu2, Ritu Sahore3, Andrew S. Westover4 and Zhenan Bao2; 1Oak Ridge National Lab, United States; 2Stanford University, United States

A potential strategy for increasing energy density of lithium batteries is to implement the so-called anode-free design. Here, the lithium metal anode is solely sourced from the cathode, traveling through the electrolyte. However, such Li batteries suffer from short cycle life due to lithium loss from passivation layer formation (solid-electrolyte interface), which require multiple cycles to stabilize. Anode-free batteries are required to have high Li metal coulombic efficiencies over the whole cycling life, particularly during the initial activation cycles. A holistic approach to electrolyte design, mechanism understanding, and battery engineering is needed to fulfill these requirements.

We used dynamic electrochemical impedance spectroscopy (deIES) to probe the formation and evolution of the SEI during Li plating and stripping on copper current collectors. deIES superimposes a multisinus waveform atop the applied charge and discharge current. We applied a sliding window fast Fourier transform protocol that converts the complex ratio of the measured potential and current signals into complex impedance. We will discuss two Li plating systems, Lipo (an amorphous ceramic) and a liquid electrolyte with stabilizing additives. We observed drastic changes in the cells’ impedance during plating and stripping. We will show how the passivation layer's impedance continues to evolve during Li cycling and accounts for a significant amount of the overall cell resistance. This knowledge enables us to predict the relative length of cycle life without long term continual measurements.


2:45 PM BREAK

3:15 PM ES04.06.05
Designing Stable Li Metal as Anode Electrode in Lithium Metal Batteries
Junjie Niu; University of Wisconsin–Milwaukee, United States

Rapid increasing demand on electrical vehicles and portable electronic devices place expectation of battery with energy density at 400-500 Wh/kg or higher. Developing stable Li metal anode for both liquid and solid-state electrolyte-based battery systems is critical to achieve this goal. Metallic lithium has the highest theoretical specific capacity of 3860 mAh/g and lowest electrochemical potentials of -3.04V versus the standard hydrogen electrode. However, the uncontrollable solid electrolyte interface (SEI) and growth of mossy/dendritic Li induced safety concerns as well as low columbic efficiency. Several strategies on stabilizing the Li metal-electrolyte interface have been reported such as adding electrolyte additives, constructing Li host for uniform Li deposition and regulating Li ion flux, and developing artificial SEI for Li metal-electrolyte interface stabilization.

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Li-O₂ batteries. The charging overpotential of Li-O₂ batteries is high, which provokes parasitic reactions and worsens the cycling stability of the batteries. Redox mediators (RMs) are widely used to decrease the charging overpotential by altering the electrochemical processes in Li-O₂ batteries. However, unwanted side reactions between RMs and Li metal anode may severely damage both the anode and the RMs; therefore, it is necessary to suppress the shuttle effect of RMs to extend the lifespan of Li-O₂ batteries. To improve the interfacial stability of the Li anode, 4A zeolite, a molecular sieve with a narrow aperture size of ~0.4 nm, was used to restrain the diffusion of RMs in this work. A polymer membrane containing 4A zeolite was synthesized to evaluate the performance of the molecular sieve. With the membrane, the Li-O₂ batteries with 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as the RM showed greatly improved performance. The charging overpotentials were kept at low levels and the cycle life of the batteries was extended eight times. The results from Raman spectroscopy indicated that the small pores of 4A zeolite physically blocked the movement of TEMPO, thus stabilizing the interface between the Li anode and the electrolyte. Furthermore, lithiated 4A zeolite was directly coated on the surface of the Li anode to study its effectiveness in suppressing the shuttle effect of RMs. The protective layer composed of lithiated 4A zeolite not only suppressed the shuttle effect of TEMPO, but also reduced the formation of Li dendrites. As a consequence, the cycle life of Li-O₂ batteries was prolonged more than ten times and the full-discharge capacity of the batteries at room temperature was greatly enhanced. In summary, with the assistance of 4A zeolite-type molecular sieves, it is promising to fabricate interface-stable, high-energy-density, and long-cycle-life Li metal batteries.

Stabilizing Anode/Electrolyte Interface in Li-O₂ Batteries by Molecular Sieves


**References:**


**3:30 PM ES04.06.06**

Proximity Matters: Interfacial Solvation Dictates Solid Electrolyte Interphase Composition

*Solomon Ovaykoh* , Yi Cui and Stacey F. Bent; 1Stanford University, United States; 2University of California, Berkeley, United States

The composition of the solid electrolyte interphase (SEI) plays a crucial role in controlling lithium-electrolyte reactions, yet the underlying cause of SEI composition differences between electrolytes remains unclear. Many studies have correlated SEI composition with the bulk solvation of Li ions in electrolytes, but this correlation does not fully capture the interfacial phenomenon of SEI formation. In our work, we present a direct mechanistic relationship between SEI composition and Li-ion solvation by forming SEIs using polar substrates that modify interfacial solvation structures. We avoid the deposition of Li metal by forming the SEI above the Li+/Li redox potential. Using theory and spectroscopy, we demonstrate that an increase in the probability density of anions near a polar substrate enhances anion incorporation within the SEI, establishing a direct correlation between interfacial solvation and SEI composition. We demonstrate the generalizability of this SEI-solvation correlation using three distinct classes of electrolytes. Finally, we employ this concept to generate stable, anion-rich SEIs, leading to high-performance lithium metal batteries. In summary, our work clarifies the mechanistic relationship between electrolyte solvation and SEI composition, resulting in a discovery that can be applied to the design of improved lithium metal batteries.

Stabilizing Anode/Electrolyte Interface in Li-O₂ Batteries by Molecular Sieves

Haining Wu, Xibin Wu, Shundong Guan and Liangliang Li; Tsinghua University, China

Lithium-oxygen (Li-O₂) batteries with an ultra-high theoretical specific energy (3500 Wh kg⁻¹) has recently attracted enormous attention. Due to the difficulty in decomposing discharge product Li₂O₂, the charging overpotential of Li-O₂ batteries is high, which provokes parasitic reactions and worsens the cycling stability of the batteries. Redox mediators (RMs) are widely used to decrease the charging overpotential by altering the electrochemical processes in Li-O₂ batteries. However, unwanted side reactions between RMs and Li metal anode may severely damage both the anode and the RMs; therefore, it is necessary to suppress the shuttle effect of RMs to extend the lifespan of Li-O₂ batteries. To improve the interfacial stability of the Li anode, 4A zeolite, a molecular sieve with a narrow aperture size of ~0.4 nm, was used to restrain the diffusion of RMs in this work. A polymer membrane containing 4A zeolite was synthesized to evaluate the performance of the molecular sieve. With the membrane, the Li-O₂ batteries with 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as the RM showed greatly improved performance. The charging overpotentials were kept at low levels and the cycle life of the batteries was extended eight times. The results from Raman spectroscopy indicated that the small pores of 4A zeolite physically blocked the movement of TEMPO, thus stabilizing the interface between the Li anode and the electrolyte. Furthermore, lithiated 4A zeolite was directly coated on the surface of the Li anode to study its effectiveness in suppressing the shuttle effect of RMs. The protective layer composed of lithiated 4A zeolite not only suppressed the shuttle effect of TEMPO, but also reduced the formation of Li dendrites. As a consequence, the cycle life of Li-O₂ batteries was prolonged more than ten times and the full-discharge capacity of the batteries at room temperature was greatly enhanced. In summary, with the assistance of 4A zeolite-type molecular sieves, it is promising to fabricate interface-stable, high-energy-density, and long-cycle-life Li-O₂ batteries.

**4:00 PM ES04.06.07**

Spatially Resolved *Operando* Synchrotron Studies of Li Metal Anode Strippping and Plating - Heterogeneity and Correlations with Cathode Performance

Peter Khalifah and Stacey F. Bent; 1Stanford University, United States; 2Stony Brook University, United States; 2Brookhaven National Laboratory, United States

Operando high energy lateral mapping (HELM) synchrotron diffraction studies have been used to carry out spatially resolved studies of the stripping and plating of Li metal anodes during battery cycling. Although it is very helpful to directly quantify the signal from Li metal layers that are only a few microns thick, this can be accomplished when the data collection is carried out in a carefully designed experiment at a modern synchrotron source and the subsequent Rietveld refinements are performed with suitably constrained structural models. In this manner, we have been able to interrogate the heterogeneity that develops during the cycling of "anode-free" pouch cell batteries with different metals used as the current collector. Furthermore, our data has enabled us to identify correlations between the heterogeneity in the anode and the cathode as well as to better understand the effect of this heterogeneity on the local current densities at different regions of the anode. Our synchrotron measurements probe local variations in electrochemical performance that cannot be resolved through traditional electrochemical testing, thereby providing novel insights into processes contributing to the loss of capacity and the reduction in the lifetime of pouch cell batteries.

**4:30 PM ES04.06.09**

Materials Processing to Create Fibrous Structures and its Application to Battery Manufacturing

Jae Chul Kim; Stevens Institute of Technology, United States

We have developed electrospinning-based manufacturing processes for battery systems that involve metallic lithium. With manufacturing feasibility, electrospinning is a widely used to create nano- and micro-porous layers of functional fibers. The electrospinning-produced layers can afford a wide variety of functionalities applicable to biomedical templates, separation membranes, and energy storage by tailoring fiber compositions. However, its manufacturing capability is limited at producing randomly-oriented fibrous structures. Topology and tortuosity of the electrospun fibers are poorly controlled, making it difficult to systematically investigate structure-property relationships for any given applications, especially electrochemical systems.

In this presentation, we will demonstrate how to design and fabricate high-performance lithium-ion battery systems with controllable and well-defined fiber architectures. Our work will also provide a fundamental understanding of the processing parameters and their effect on the electrochemical performance of lithium-ion batteries.

**SESSION ES04.07: Poster Session II**

**Session Chairs:** Tao Guo and Wu Xu

Thursday Afternoon, April 25, 2024

Flex Hall C, Level 2, Summit
N, S-Doped Graphene Quantum Dots for Affordable and High-Performance Aqueous Zinc-Ion Batteries

Keywords: energy storage, solvation structure, aqueous Zn ion batteries, DOD

The exorbitant costs linked to cutting-edge energy storage technologies, exemplified by lithium-ion batteries, present formidable obstacles to the widespread adoption and maintenance of new analyses. As a result, there is an urgent call to expedite the development of the next generation of energy storage technology—one marked by both low cost and high performance. Aqueous zinc-ion batteries (AZIBs) have emerged as promising candidates, offering an enticing blend of affordability and superior performance, positioning them as pivotal contenders for next-generation energy storage solutions. Nevertheless, the practical application of AZIBs faces significant challenges due to spontaneous surface corrosion and uncontrolled dendrite growth.

In pursuing a pragmatic solution while upholding cost efficiency, we propose a design strategy that involves N, S-doped graphene quantum dots (GQDs) derived from lemons and kitchen soda as a stable lithium metal host via carbide-mediated catalytic hydrogenolysis. Unlike conventional carbon hydrogenolysis, this approach aims to regulate interlayer, also achieves an improved cycling performance in the argyrodite Li6PS5Cl based high energy density all-solid-state battery full-cell configuration.

Facile Solvothermal Synthesis of Binder Free 1T-VS2/MXene Hybrid Electrode Materials for Li-Ion Batteries

Keywords: energy storage, nanomaterials, GQDs, aqueous Zn ion batteries

The findings suggest that TPP could serve as an effective additive in LiBs, particularly in complex, interconnected hybrid energy systems, offering a safer and more reliable energy storage solution. This research bridges knowledge gaps about TPP's role in LiBs and paves the way for designing safer batteries in the context of evolving energy storage demands.

References
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The development of high-capacity batteries has become crucial to meet the growing demands for modern electric applications like electric vehicles, smartphones, and various smart wearable devices. However, their widespread adoption of Li-ion batteries is hindered due to the limited capacity, low energy density, poor cycling stability, and high cost of traditional electrode materials. To resolve these challenges continuous efforts to design and development of novel electrode materials are required. Due to their unique properties, transition metal chalcogenides (TMCs) and MXene hybrid composite materials have emerged as promising electrode materials for high-capacity Li-ion batteries. In this study, we explore the facile solvothermal synthesis of binder-free 1T- VS₂/MXene hybrid electrode materials for high-capacity Li-ion battery applications. The facile solvothermal synthesis offers several advantages, including simplicity, binder-free, cost-effectiveness, and scalability. It involves the simultaneous growth of 1T-VS₂ and MXene nanosheets within a single reaction vessel, resulting in a homogeneous growth of 1T-VS₂ on the MXene sheets. This method eliminates the need for separate synthesis and post-deposition steps, restructuring the fabrication process and improving the efficiency of electrode materials. The 1T-VS₂ decorated MXene serves various roles in the hybrid composite, firstly they act as conductive pathways, facilitating electron transport and reducing internal resistances. This results in enhanced charge/discharge rates and improved power density of the electrode material. Additionally, MXene provides mechanical stability to the fragile VS₂ nanoparticles, preventing agglomeration and ensuring long-term stability. The electrochemical properties of the binder-free 1T-VS₂/MXene hybrid electrode materials were systematically investigated using several techniques such as voltammetry, galvanostatic charge-discharge, C-rate, stability, and electrochemical impedance spectroscopy. The results demonstrated significant improvements in electrochemical performance compared to pure VS₂ electrodes. The hybrid composite electrodes revealed high capacity, improved rate performance, and excellent cycling stability. The binder-free 1T-VS₂/MXene electrode materials' enhanced electrochemical performance can justify the VS₂ and MXene synergistic effects. The MXene provides high conductivity, efficient ion diffusion, and structural stability, while the VS₂ nanoparticles offer large redox sites and high energy density. The amalgamation of these properties results from a well-balanced electrode material with improved Li-ion battery performance.

Keywords: 1T-VS₂/MXene hybrids, facile solvothermal, high-capacity, Li-ion battery

Acknowledgments: This work was supported by the National Research Foundation of Korea (NRF) grants (No. 2021M3H4A3A02099204, and 2022M3C1A3081178 (Ministry of Science and ICT) and No. 2022R1H1A2073224 (Ministry of Education)) funded by the Korean Government.

5:00 PM ES04.07.12 Enhancing Zn-Ion Battery Performance with Thioacetamide Electrolyte Additive Minji Yeon1, Yujin Kim1, Jihoon Kim1, Sukena Yoon1 and Kuk Young Cho2, *1Kongju National University, Korea (the Republic of); 2Hanyang University, Korea (the Republic of)

Zn-ion batteries (ZIBs) are emerging as a next-generation energy storage solution, characterized by enhanced safety, cost-effectiveness, and a more abundant resource base compared to their flammable, naturally occurring counterparts. Distinctively, ZIBs employ a Zn-metal anode and a Zn-ion (Zn²⁺) storage cathode, resulting in a substantial theoretical capacity (820 mAh g⁻¹ or 5850 mAh cm⁻³) and a low redox potential of ~0.76 V versus the Standard Hydrogen Electrode (SHE). Nevertheless, ZIBs confront several challenges, including limited charge-discharge reversibility attributed to the formation of Zn dendrites via the hydrogen evolution reaction (HER), uneven Zn electrodeposition, and the presence of electrochemically inert by-products such as ZnO, Zn(OH)₂, and ZnS (Zn(OH)₂+H₂O). To resolve these issues, a range of methodologies has been explored, encompassing innovations in Zn electrode design, separator development, and the electrolyte additives.

In this study, the electrochemical characteristics and transformations on the Zn-metal surface were investigated by employing Thioacetamide (TAA) as an electrolyte additive within the aqueous liquid electrolyte of Zn-ion batteries. The primary objective of this research is to reduce the formation of the aforementioned Zn dendrites and byproducts while aiming to achieve a uniform Zn-metal surface deposition. TAA, characterized by primary amine functional groups, is recognized for its electrochemical activity, primarily attributable to the sulfur (S) present in the thioamide species, which tends to actively participate in electrochemical reactions. Furthermore, TAA undergoes hydrolysis within the electrolyte, resulting in the generation of weak acid by-products such as hydrofluoric acid and acetic acid, thereby facilitating the removal of impurities and contributing to a smooth deposition process. Consequently, TAA emerges as a promising functional additive capable of controlling the Zn electrodeposition process.

5:00 PM ES04.07.13 Functional Carbon-Based Zn Host Assisted with Ultra-Thin Hydrophilic ZnO Layer for Practical Aqueous Zn-Metal Batteries Jungs Been Park and Dong-Wan Kim; Korea University, Korea (the Republic of)

Eco-friendly aqueous Zn-metal batteries (AZMBs) is considered a promising candidate for grid-scale energy storage system owing to its high theoretical capacity (5,854 mAh cm⁻³), low standard reduction potential (~0.76 V vs. Standard Hydrogen Electrode), and high compatibility with aqueous electrolyte. However, the inevitable dendritic Zn growth and side-reactions (hydrogen evolution reaction (HER) and Zn corrosion) during continuous cell operation block the practical utilization of AZMBs. Hence, we effectively ameliorate the growth of Zn dendrite and the side reactions of Zn-metal anode by developing the zincphoric porous carbon host (top layer) and ultra-thin ZnO layer (bottom layer) originating from native-oxide of metallic Zn. The functional carbon host provides many zincphoric Zn nucleation/growth sites due to its large specific surface area and oxygen doping effect, which inhibits Zn dendrite growth and volume expansion, as well as inhibits sides reactions due to its low HER properties stemming from hydrophobicity of carbon. Also, the hydrophilic ultra-thin ZnO layer (~10 nm) facilitates hygroscopicity of the aqueous electrolyte to the host to prevent “top accumulation” of Zn deposits on the carbon host, compensating low wettability of hydrophobic carbon host. Thus, the resonance between these two layers layer stably maintains low overpotential (~50 mV) even at ultra-high current density and high capacity (10 mAh cm⁻² and 5 mAh cm⁻², respectively) during repetitive Zn plating/stripping. Furthermore, when combined with a MnO₂ cathode, the full-cell exhibits superior cyclability over 1,000 cycles at a low negative-to-positive electrode capacity ratio (~7.3), approaching practical AZMBs.

ACKNOWLEDGMENTS
This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2022R1A2C3003319).

5:00 PM ES04.07.14 Colloidal Synthesis and Defect Engineering of Vanadium Selenide: A High-Performance Anode Material for Li-Ion Batteries Chiheoong Wee1 and Jae-Young Choi; Sungkyunkwan University, Korea (the Republic of)

Defect engineering is essential for enhancing the performance of lithium-ion batteries (LIBs), particularly in transition metal chalcogenides (TMCs). Vanadium selenide, known for its outstanding electrochemical performance, has been extensively studied. In this study, we successfully synthesized Mo-doped V₂Se₃ at the nano-scale using a liquid-phase process. The resulting Mo-doped V₂Se₃ anode enhances reactive sites, facilitates Li⁺ ion transport, and exhibits high electronic conductivity. With these advantages, a reversible capacity of 1309.45 mAh g⁻¹ at 100 mA g⁻¹ was confirmed even after the 100th cycle. Furthermore, Mo-doped V₂Se₃ exhibits non-anomalous behavior, demonstrating a 30.34% increase in capacity after 100 cycles compared to the initial cycle. Herein, we elucidate the variation in capacity with doping concentration and provide insights into the reasons for the capacity increase. This study presents an expandable strategy for synthesizing doped TMCs, contributing to the enhancement of the lithium-ion battery anode performance in other TMCs.

5:00 PM ES04.07.18 Characterization of Mg0.5Al0.25Cr0.25Ni0.25A0.25 (A=Nb,Ta,Co) Alloys as Anode Materials for NiMH Batteries Gulhan Cakmak1, Hakan Yüce1, Fatih Piskin1, Berke Piskin1 and Eli Grigorova2; 1Mugla University, Turkey; 2Bulgarian Academy of science, Bulgaria

Hydrogen energy is becoming an important part of a viable solution to worldwide climate change and atmospheric pollution. In this regard, hydrogen storage materials direct the research of rechargeable batteries. High entropy alloys containing Mg-constituent of an attractive system because Mg is light, cheap, and abundant, and has a high absorption capacity. Mg-containing alloys are an attractive candidate for solid-state hydrogen storage and can be further applied in electrochemical systems where the hydrogen atoms occupy the interstitial forming metal hydride (MH). The Ni/MH battery is composed of a Ni(OH)₂ positive electrode, a metal MH negative electrode and an alkaline electrolyte (KOH solution). The family of hydrogen storage alloys based on transition metals (TMG) – Mg Ni – has attracted increasing attention in recent years. They can meet the general electrochemical performance requirements by exhibiting high discharge capacity, long durability, good rate capacity, admirable discharge capacity at low temperature and low self-discharge characteristics. In this direction, it is aimed to add these properties to Mg-based alloys by adding transition metals to Mg-based alloys. In this direction, it is aimed to produce Mg0.5Al0.25Cr0.25Ni0.25A0.25 (A=Nb,Ta,Co) alloys. This alloy electrode will be prepared by melting in a vacuum arc melting furnace under argon atmosphere and with the help of SPEX Ball Mill the alloy will be reduced below 45 microns and then The crystallographic properties of the Mg0.5Al0.25Cr0.25Ni0.25A0.25 (A=Nb,Ta,Co) alloy will be examined. The electrochemical results are aimed at performing charge/discharge tests on NiMH batteries using M.
Increasing the Cycle Life of Zinc Metal Anodes and Nickel-Zinc Cells Using Flow-Through Alkaline Electrolytes

The cathode-electrolyte interphase (CEI) is a critical, but not fully understood component of Li-ion batteries (LIBs). Ethylene Carbonate (EC), a commonly used electrolyte in LIBs, starts to decompose at approx. 3.8 V vs Li/Li+ to form this CEI [1]. One of the initial products formed due to this decomposition is vinylene carbonate (VC) which has been experimentally observed by in-situ FT-IR (Fourier Transform Infrared Spectroscopy) measurements at potentials as low as 3.8 V vs Li/Li+ [2]. In this talk, we explore the feasibility of this reaction occurring through a mechanism involving transition metal ions on the cathode surface through density functional theory calculations performed under realistic surface conditions. Previous ab initio studies on the EC decomposition on Ni/MCo surfaces have been performed [3,4,5]. As a prototype for next generation cathode, we study Disordered Rocksalt(DRX) surfaces as cathodes and explore the equilibrium between EC/VC and abstracted hydrogen as a function of the potential. We find that surface adsorbed hydrogen is released as protons at a potential of 3.7 V vs. Li/Li+, which drives the conversion of EC to VC. We study the thermodynamics of proton release from the DRX surface at different lithiation stages from ab initio calculations to understand the potential dependence of proton release and further understand the thermodynamics of EC to VC decomposition. This will allow us to better understand the reactions occurring at the cathode electrolyte interface as well as crosstalk between anode and cathode materials.

Reference list

Metallic iron is an attractive anode material for aqueous batteries, particularly if the full 3-electron redox between Fe and Fe (III) can be accessed reversibly. However, oxidation of Fe (II) to Fe (III) causes drastic changes and irreversible formation of highly resistive phases. Yet, it remains unclear how these phases form at the nanoscale and, crucially, how they might be avoided. To achieve fully reversible Fe anodes, it is critical to obtain a mechanistic understanding of nanoscale morphology and phase evolution during electrode cycling. Here we investigated the electrochemical transformation pathways between Fe (II) and Fe (III) oxides using both ex-situ and operando techniques, including SEM, Raman, AFM, Infrared Nanospectroscopy (nano-FTIR) and Scanning Transmission X-ray Microscopy (STXM). Correlating the morphology evolution during this transformation to local Fe oxidation state and phase would offer fundamental insight into Fe (II)/(III) conversion and inspire novel engineering of the Fe anode to achieve higher capacity and cyclability.

Peptide Gel Electrolytes for Stabilized Zn Metal Anodes

Yeziou Wang and Husam N. Alshareef; KAUST, Saudi Arabia

The rechargeable aqueous Zn ion battery (AZIB) is considered a promising candidate for future long-duration energy storage due to its intrinsic safety features and low cost. However, Zn dendrites and side reactions (e.g., corrosion, hydrogen evolution reaction, and inactive side product, (Zn hydroxide sulfate) formation) at the Zn metal anode have been serious obstacles to realizing satisfactory AZIB performance. The application of gel electrolytes is a common strategy for suppressing these problems, but the normally used highly crosslinked polymer matrix (e.g., polyacrylamide (PAM)) brings additional difficulties for battery electrode assembly and recycling. Herein, we have developed a gel electrolyte for Zn metal anode stabilization, where a peptide matrix is used, a highly bio-compatible material, is used for gel construction. Various experiments and simulations elucidate the gel-involved battery assembly and cycling. Furthermore, the peptide gel electrolyte provides fast Zn ion diffusion (comparable to conventional liquid electrolyte) while suppressing side reactions and dendrite growth, thus achieving highly stable Zn metal anodes as validated in various cell configurations. We believe that our concept of gel electrolyte design will inspire more future directions for Zn metal anode protection based on gel electrolyte design.

Zn-ion batteries show tremendous potential due to their attractive characteristics of having a high theoretical capacity (820 mAh g-1) and a low potential (-0.76 V vs SHE). Furthermore, coupled with its safety and environmental friendliness advantages, this renders it with significant potential for large-scale applications. In this work, we use graphene oxide (GO)/carbon nanotube (CNT)/cellulose nanofibrils (CNF) composite dough as the 3D scaffold for the electrode. The composite dough is a binder-free and self-sustaining structure with moldable features. The characteristic triangular shapes, highly processable and tunable microstructures endow it with significant potential for diversified applications. The composite dough combines the advantages of three different carbon materials. GO possesses a large surface area and, after annealing, maintains structural integrity to prevent collapse. CNT prevents the aggregation of GO after reduction and enhances the hydrophobic property of the composite. CNF improves the mechanical strength of the composite and its abundant hydroxyl groups enable the dough to maintain the viscoelastic state at high water content up to 90 wt%. The composite dough is then transformed into an electrode scaffold characterized by high porosity, excellent conductivity, and a large surface area. The anode features Zn powders (ZPs) integrated into the composite dough-based electrodes, which enhances control over the N/P ratio. However, zinc anodes normally suffer from issues including hydrogen evolution and corrosion. Coating TiO2 nanoparticles onto the surface of the dough not only protects the ZPs from side reactions but also suppress dendrite growth. In addition, TiO2 can also enhance the electrode’s hydrophilicity, zincliphilicity, and facilitate Zn ion diffusion. On the cathode side, α-MnO2 is used as the active material and is incorporated into the composite dough. Our results indicate that the MnO2@composite dough-based electrode has higher gravimetric capacity and cycle stability compared to the MnO2@carbon paper. The improved contact between MnO2 and composite scaffold leads to enhanced performance. The ZPs@TiO2@composite@MnO2@composite dough-based cell exhibits more stable cycle performance and higher discharge capacity than those of ZPs@carbon paper@MnO2@carbon paper cell. This work offers an alternative approach for fabricating 3D and moldable electrodes, broadening the horizons for 3D electrodes in high-performance energy storage devices.
Revitalizing Native Lithium-Metal Electrode Surfaces through Hydrohalic Acid-Assisted Pre-Halogenation Jiyeon Seo, Jaeho Lee and Hongkyung Lee; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

Solid-state lithium batteries have garnered significant attention in recent years as they are a promising technology with immense potential for development with diverse applications. Utilization of solid electrolytes is particularly appealing as it enables the use of lithium metal anodes and thus offer superior energy density with enhanced safety compared to traditional liquid electrolytes. Solid-state lithium batteries have therefore received increasing attention in recent years.

1.30 PM ES04.09.01

Anthraniqune-Based Silicate Covalent Organic Frameworks as Solid Electrolyte Interphase for High-Performance Lithium-Metal Batteries Chen Li; The Hong Kong University of Science and Technology, China

Lithium (Li)-metal batteries (LMBs) possess the highest theoretical energy density among current battery designs and thus have enormous potential for use in energy storage. However, the development of LMBs is severely hindered by safety concerns arising from dendrite growth and unstable interphases on the Li anode. Covalent organic frameworks (COFs) incorporating either redox-active or anionic moieties on their backbones have high Li-ion (Li+) conductivities and mechanical/chemical stabilities, so are promising for solid-electrolyte interphases (SEI) in LMBs.

Here, we synthesized anthraquinone-based silicate COFs (AQ-Si-COFs) that contained both redox-active and anionic sites via condensation of hydrochloric acid with silicon dioxide. The nine Li+ mediated charge/discharge processes enabled the AQ-Si-COF to demonstrate an ionic conductivity of 9.8 mS cm⁻¹ at room temperature and a single-ion-conductive transference number of 0.92. Computational studies also supported the nine Li⁺ mechanism. We used AQ-Si-COF as the solid electrolyte interphase on the Li anode. The LMB cells with LiCoO₂ cathode attained a maximum reversible capacity of 188 mA h g⁻¹ at 0.2 C during high-voltage operation. Moreover, this LMB cell demonstrated suppressed dendrite growth and stable cyclability, with its capacity decreasing by less than 3% up to 100 cycles. These findings demonstrate the effectiveness of our redox-active and anionic COFs and their practical utility as SEI in LMB.

1.45 PM ES04.09.02

Modifying Li+ Transport and Interface Chemistry via Citric Acid-Treated Silica Carrier in Nanoparticle Colloidal Electrolyte toward Stable Li-Metal Batteries Minhong Lim and Hongkyung Lee; DGIST, Korea (the Republic of)

Tailoring the lithium ion (Li⁺) microenvironment is essential for achieving rapid ionic transfer and a mechanically strong solid-electrolyte interphase (SEI). This is key to the stable cycling of lithium-metal batteries (LMBs). Beyond the conventional approach of adjusting salt and solvent compositions, this study introduces a novel method. It involves simultaneous modulation of Li⁺ transport and SEI chemistry through a citric acid (CA)-modified silica-based colloidal electrolyte (C-SCE). The CA-tethered silica (CA-SiO₂) provides more active sites for attracting complex anions. This leads to a greater dissociation of Li⁺ from these anions, resulting in a high Li⁺ transference number (approximately 0.75). The intermolecular hydrogen bonds formed between solvent molecules and CA-SiO₂, along with their migration, serve as nano-carriers. These nano-carriers are responsible for transporting additives and anions to the lithium surface, thereby strengthening the SEI through the co-implantation of SiO₂ and fluorinated components. Notably, C-SCE has shown promise in suppressing lithium dendrite formation and enhancing the cycling stability of LMBs. This is a significant improvement over the CA-free SiO₂ colloidal electrolyte. The study highlights that the surface properties of nanoparticles play a crucial role in the dendrite-inhibiting capabilities of nano colloidal electrolytes.

2.00 PM ES04.09.03

Revitalizing Native Lithium-Metal Electrode Surfaces through Hydrohalic Acid-Assisted Pre-Halogenation Jiyeon Seo, Jaeho Lee and Hongkyung Lee; Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

Lithium metal anodes (LMAs) represent the ultimate choice for advancing beyond traditional Li-ion batteries due to their remarkable attributes, including a high capacity of 3860 mAh g⁻¹ and a low working potential of ~0.3 V vs. SHE. However, the inherent challenges associated with LMA usage, such as their exceedingly high surface reactivity, uncontrollable dendrite plating, and unbounded volume expansion, have long hindered the development of practical lithium-metal batteries (LMBs). The primary culprit behind these issues is the formation of a non-uniform solid-electrolyte interphase (SEI) layer, arising from byproducts within the electrolyte and the inherent surface characteristics of LMAs. In light of these challenges, achieving uniform passivation of LMAs and the formation of a homogeneous SEI layer during the initial stages are imperative. Such uniformity is crucial to enable consistent Li⁺ ion flux.

Here, we synthesized anthraquinone-based silicate COFs (AQ-Si-COFs) that contained both redox-active and anionic sites via condensation of hydrochloric acid with silicon dioxide. The nine Li⁺ mediated charge/discharge processes enabled the AQ-Si-COF to demonstrate an ionic conductivity of 9.8 mS cm⁻¹ at room temperature and a single-ion-conductive transference number of 0.92. Computational studies also supported the nine Li⁺ mechanism. We used AQ-Si-COF as the solid electrolyte interphase on the Li anode. The LMB cells with LiCoO₂ cathode attained a maximum reversible capacity of 188 mA h g⁻¹ at 0.2 C during high-voltage operation. Moreover, this LMB cell demonstrated suppressed dendrite growth and stable cyclability, with its capacity decreasing by less than 3% up to 100 cycles. These findings demonstrate the effectiveness of our redox-active and anionic COFs and their practical utility as SEI in LMB.

2.15 PM ES04.09.04

Tracking Dendrites and Solid Electrolyte Interphase Formation in Composite Electrolyte using Solid State NMR Spectroscopy Ayan Maity, Asya Svirinovsky-Arbel, Yehuda Buganim, Chen Oppenheim, Brijith Thomas, Arava Zohar and Michal Leskes; Weizmann Institute of Science, Israel

Solid-state lithium batteries have garnered significant attention in recent years as they are a promising technology with immense potential for development with diverse applications. Utilization of solid electrolytes is particularly appealing as it enables the use of lithium metal anodes and thus offer superior energy density with enhanced safety compared to traditional liquid electrolytes. Among the different types of solid-state batteries, polymer-based electrolytes are attractive due to their flexibility and non-flammable nature [1]. However, the practical implementation of polymer electrolytes in rechargeable batteries for high-energy applications faces challenges. These include limited room temperature Li-ion conductivity and formation of lithium dendrites at high current densities.

Address these issues, one potential approach is to incorporate solid-state ceramic particles into the polymer matrix. However, there is still a limited understanding as to how ceramics incorporation impacts dendrite formation and propagation, as well as the composition and properties of the solid electrolyte interphase (SEI). The SEI plays a crucial role in the battery chemistry and gaining insights into its atomic-level structure and composition has the potential to transform the development of composites, enhancing their ability to suppress dendrite formation [2]. Unfortunately, there is a shortage of analytical tools capable of precisely identifying the SEI's chemical constituents at the atomic scale, and even more so, of understanding how these constituents affect ionic transport across the SEI. Here we introduce an innovative approach which allows us to (i) quantify dendrites formation, (ii) determine SEI composition and its properties which allows us to (iii) determine the dendrite's propagation path within the composite electrolyte.

Using Li NMR spectroscopy, we successfully quantified the formation of dendrites in the cycled composites. Remarkably, we find a consistent rise in dendrite formation by increasing ceramic content up to 40 wt. %, when using Li₁ₓAlₓO₂GeₓSi₈P₁₆O₄₈ (LAP) and Li₁ₓAlₓGaₓZₓSn₄O₁₂ (LLZO) as ceramic fillers in polyethylene oxide. To determine the effect of ceramic content on dendrites formation, we employed dynamic nuclear polarization (DNP) [3], a method in which the high electron spin polarization is used to increase NMR sensitivity, to selectively enhance the SEI signal [4]. We make use of the inherent conduction electrons of the dendrites for DNP, enabling us to identify the chemical components and structure of the SEI, as well as the SEI permeability to Li-ions. We determined the chemical components of the SEI formed on dendrites in a pure polymer electrolyte and with the addition of varying content of LAP and LLZO. Surprisingly, we found that SEI structures significantly differ not just with varying ceramic types but also with different ceramic contents, suggesting the nature of possible interaction of the dendrites with ceramic and polymer matrix. Furthermore, analysis of the SEI composition allows us to trace the dendrite propagation within the composite. We showed that in composites with 40 wt. % LAP, dendrites chemically react with LAP, hindering their growth towards the opposite electrode and impacting battery lifespan. Conversely, with 40 wt. % LLZO, dendrites are physically blocked without any chemical reaction. In summary, our study offers valuable insights into the SEI's composition, structure, and its correlation with dendrites and ceramic components. The approach can be used to identify the optimal ceramic material to reduce dendrite formation and enhance SEI's Li-ion permeability for improved battery performance.

References


2:30 PM *ES04.09.05
Enhancing Lithium Stripping Efficiency in Anode-Free Solid-State Batteries through Self-Regulated Internal Pressure

Anode-free all-solid-state lithium metal batteries (ASLMBs) promise high energy density and safety but suffer from low initial coulombic efficiency and rapid capacity decay, especially at high cathode loadings. Using operando techniques, we concluded these issues to interfacial contact loss during lithium stripping. To address this, we introduce a conductive carbon felt elastic layer that self-adjusts pressure at the anode side, ensuring consistent lithium-solid electrolyte contact. This layer simultaneously provides electronic conduction and releases plating pressure. Consequently, the first coulombic efficiency dramatically increased from 58.4% to 83.7% along with over tenfold improvement in cycling stability. Overall, this study reveals an approach to enhance anode-free ASLMB performance and longevity by mitigating lithium stripping inefficiency through self-adjusting interfacial pressure control enabled by a conductive elastic interlayer.

Exploring Wet SEI Layer Dynamics and Stability in Lithium-Ion Batteries Through Salt Concentration: An Ab Initio Molecular Dynamics and Machine Learning Study

The Solid-Electrolyte Interphase (SEI) layer plays a key role in the longevity and performance of lithium-ion batteries (LiBs) (1), with its stability being crucial for efficient reversible operation of LiBs. This study focuses on the dynamics of the wet SEI – an inorganic layer in contact with electrolyte solution (2), comprising components such as lithium fluoride (LiF), lithium oxide (Li$_2$O), and lithium carbonate (Li$_2$CO$_3$). A combination of ab initio molecular dynamics (AIMD) simulations and machine learning models is employed to identify a 'goldilocks' salt concentration that optimizes the stability of the SEI layer, a critical factor in enhancing battery performance.

The study provides a comprehensive analysis of the interaction dynamics of LiF, Li$_2$O, and Li$_2$CO$_3$ in various electrolyte environments. The changes in cluster stability, surface area, and bond dynamics are explored, particularly focusing on the effects of varying salt concentrations on these parameters. The goal is to characterize an optimal salt concentration that yields an ideal inorganic SEI layer, enhancing the layer's protective qualities and improving overall battery safety and efficiency.

The findings of this study are significant for advancing the understanding of wet SEI layer formation and its optimization in LiBs. The implications of achieving an optimal SEI layer are profound, potentially leading to batteries with higher energy density, longer cycle life, and improved safety profiles.

References:
(1) A. Wang, S. Kadam, H. Li, S. Shi, Y. Qi, Review on modeling of the anode solid electrolyte interphase (SEI) for lithium-ion batteries, npj Computational Materials, 4 (2018) 15.

Unraveling The Impact of Pectin on Transport and Mechanical Properties of EC-LiTFSI Electrolytes

Biocompatible electrolytes are becoming attractive alternatives for the existing counterpart technology for battery electrolytes, as they are sustainable, renewable, and easily degradable. We used all-atom molecular dynamics simulations to study the transport and mechanical characteristics of a new class of battery electrolytes containing ethylene carbonate (EC), Li-TFSI, and pectin at different weight percentages. Pectin is a polysaccharide exhibiting high ion solvating capability, making it a potential candidate for battery electrolyte applications. Our simulation results demonstrate that pectin reduces the coordination numbers of lithium ions surrounding the counternets (and vice versa) as a result of the strong lithium-pectin interactions in comparison to lithium-TFSI interactions. We observed that smaller ionic clusters are favored over larger ones due to strong ion-polymer interactions, which is different from the trend observed in conventional electrolytes. Moreover, the ion association probability shows an increase in free ions, which indicates an enhancement in the overall ionic conductivity of pectin EC-LiTFSI electrolytes. Interestingly, TFSI ionic diffusivities show a strong correlation with the ion-pair relaxation timescales, with a relationship of $D_T$, $\tau_{ip}^{-0.95}$. On the other hand, the diffusivities of lithium ions follow a different pattern, with $D_L$, $\tau_{ip}^{-3.1}$, suggesting a unique transport mechanism for lithium ions. Consequently, the Nernst-Elctrode interface scales with the ion-pair relaxation timescales as $\sigma_{NE} \sim \tau_{ip}^{1.85}$. Furthermore, the increase in viscosity and ion-pair relaxation timescales show that pectin can also enhance the mechanical stability of the electrolytes.

References:

Organic Electrode Materials for Li-Ion Batteries

Organic materials hold promise as less-scarce materials for electrodes in a range of emerging battery technologies. Despite this, they have significant hurdles to overcome in terms of capacity, stability, and conductivity. Here, we will discuss our efforts in the rational design of organic materials as electrodes, both anodes and cathodes, for Li-ion batteries. First, I will discuss functional groups to maximize theoretical capacitance. Second, I will discuss the arrangement of these functional groups as macromolecules that render them insoluble, which is a requirement for any electrode in both the charged and discharged state. And in both, synthetic strategies for developing the functional group chemistry and macromolecules will be discussed. We consider both linearly and 2D/3D type macromolecular designs for this purpose. Finally, I will share some insight into designs that have afforded very high capacity as anodes, where the lithium intercalation exceds the expected 1 Li per 6 carbon units. Overall, this presentation will describe chemical structures and electrochemical properties and then aim to rationalize performance at the molecular level.

SYMPOSIUM ES05
An increasing amount of renewable energy sources are being integrated into the electric grid in the US and around the world. However, as intermittent wind and solar begin to approach more than a quarter of grid production, significant energy storage technology must be employed as well to mitigate the unbalanced energy production and demand in the grid. To meet the emission targets in an economically viable manner, low-cost grid-scale energy storage technology must be developed. This talk will compare different battery technologies and describe our efforts in development of new generation of inexpensive redox active species for redox flow batteries (RFB) that can offer extraordinary energy density and cycling stability. This involves identification of critical needs for redox couple design in RFB and development of simplest yet effective synthetic routes towards redox active molecules with desired performance.

8:30 AM *ES05.01.01
Molecular Engineering toward Highly Stable Redox Flow Batteries with High Energy Density Dawei Feng; University of Wisconsin–Madison, United States

Organic redox flow batteries (RFBs) have been investigated for future energy storage systems (ESSs). Tailoring organic redox-active molecules tunes solubility, redox potential, and chemical stability, which gives the promise to enhance energy density, cyclability, and calendar life in RFBs. Numerous studies focused on increasing molecular solubility to satisfy economic criteria. In addition, introducing electron-donating and withdrawing groups to the redox-active core modulated redox potentials to negative and positive shifts, respectively. The most effective way to multiply raising energy density is to find a redox-active core undergoing multiple electron-transfer processes. Quinone is the representative one providing a single two electrons transfer in an aqueous electrolyte solution. Fast redox kinetics and chemical stability are achieved by H+ coupling; The reduced form, hydroquinone, promoted the following electron transfer in the acidic solution. A similar approach is applied for non-aqueous electrolyte solutions and using cations of supporting electrolytes. However, such an ion-coupled electron transfer was rarely studied to date.

Here, we demonstrated naphthalene diimide (NDI) and Li+ coupled electron transfer in acetonitrile (MeCN). The NDI is an excellent model for the stepwise two-electron transfer process. Its low solubility by the strong p-stacking interaction was surmounted by introducing ammonium cationic substituents to the NDI via simple condensation and N-alkylation. As a result, two ammonium-tethered NDI and bistri fluoride (TFSI-) as the counter anion showed 0.9 M solubility in MeCN. Two cathodic events made an anionic radical and dianionic NDI core, respectively. The received electron is delocalized over the NDI core and also stabilized by pairing it with the cation. Cyclic voltamnograms showed ~120 mV of potential difference from two cathodic waves with Li+ of LiTFSI electrolyte in MeCN, which was narrower than ~370 mV with K+ of KTFSI. It suggested that the Li+ possessing high charge density was closely coupled with the anionic radical NDI, expediting the second electron-transfer process. The process was also dependent on non-aqueous solvents. High donor number (DN) solvents widened the potential difference with Li+ because a thick solvation shell of Li+ weakened the ion coupling. We applied this system for non-aqueous RFBs. Unlike two distinct galvanostatic plateaus appearing with K+, the ammonium-introduced NDI with Li+ showed almost a single overlaid plateau caused by the rapid reduction of the anionic radical. The ammonium-tethered NDI/Li+ in MeCN cells performed high cyclability and low crossover through an anion exchange membrane, showing a capacity fading rate of 0.0089%/1000 cycles in RFBs.

9:00 AM *ES05.01.02
Ion-Coupled Electron Transfer of Naphthalene Diimide for Organic Redox Flow Batteries Hye Ryung Byon; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Redox-flow batteries employ dissolved active materials separated by a semi-permeable membrane to store energy. Cell life and capacity are maximized when active materials can be sequestered in their respective cell compartments at high concentration. Here, I will investigate how the design of the semi-permeable membrane must be considered alongside that for the active materials, whose infinite miscibility with non-aqueous electrolytes allow for high volumetric capacity. The oligomeric design of these active materials makes them sufficiently large to be excluded by a microporous membrane, while maintaining substantially faster electron transfer kinetics than competing polymeric and colloidal active materials. I will discuss how these design features influence charge transfer with the electrode and other attributes that impact the efficiency of the flow cells as they relate to emerging applications in grid-scale energy storage.

10:15 AM *ES05.01.05
U.S. DOE Initiatives Advancing Flow Battery Manufacturing Innovation Changsewon Suh; U.S. Department of Energy, United States

The Department of Energy’s Advanced Materials and Manufacturing Technology Office (AMMTO) continues to invest in energy storage research, development, demonstration, and deployment (RDD&D) to help stakeholders improve efficiency, cut costs, and make materials, devices, and systems with superior performance. Despite recent promising advances, manufacturing capabilities are still necessary to meet the expected demand for energy storage as we move toward a clean energy economy. Strengthening the domestic manufacturing supply chains is also another important task to pursue in parallel.

AMMTO funded projects through Battery Manufacturing funding opportunity announcement and national laboratory call to address technical and manufacturing challenges in U.S. flow battery production, specifically targeting the optimization of flow batteries across commercial, industrial, and utility applications. These projects aim to and improve the manufacturability of flow batteries and reduce the cost of manufacturing battery components and systems by implementing advanced designs and processes. In this talk, the status and accomplishments of the projects will be highlighted. In addition, there will be a robust discussion of a wide variety of AMMTO’s efforts in the context of technical and manufacturing challenges regarding scale-up and performance that still prevent the flow battery community from achieving cost targets and commercial viability.
Embedded, Micro-Interdigitated Flow Fields for Flow-Based Electrochemical Desalination and Beyond

The delivery of fluids to porous electrodes is essential to the efficient functioning of flow-based electrochemical devices. To date this has been accomplished in flow batteries and fuel cells by hydraulic permeability of flow battery and fuel cell electrodes (~10 µm²). We fabricate these microfluidic patterns using laser engraving. Here, electrode wetting prior to laser engraving is induced perpendicular flow within the electrode material between adjacent microchannels to promote reaction uniformity, despite parallel flow within electrode material being realized for the hydraulic permeability of flow battery and fuel cell electrodes (~10 µm²). We fabricate these microfluidic patterns using laser engraving. Here, electrode wetting prior to laser engraving is shown to produce enhanced microchannel resolution and smoothness while maintaining the chemical and microstructural integrity of electrodes by suppressing the propagation of heat zones via the low thermal diffusivity and high latent heat of water. The resultant patterned electrodes exhibit as much as 100-fold increased apparent permeability relative to unpatterned electrode material, resulting in decreased pumping pressure and energy requirements. Consequently, simulated brackish water (~100 mM NaCl) and simulated seawater (~500 mM NaCl) solutions were desalinated to near-potable water with thermodynamic energy efficiencies (TEEs) of 40% and 7%, respectively. While TEEs show room for significant improvement relative to the thermodynamic limit, brackish TEE is at parity with reverse osmosis neglection energy recovery. Such efficiency also shows the promise of embedded, micro-interdigitated flow fields for flow-based electrochemistry using low-permeability porous electrodes, such as those that contain nanomaterial conductive additives, catalysts, or active materials.

1:15 PM *ES05.02.01

Deep and rapid decarbonisation of the global energy systems require the wholesale replacement of fossil fuels with renewable resources (e.g., wind, solar). However, these resources are intermittent and unpredictable challenging the existing grid infrastructure which is based on the just-in-time dispatchable generation enabled by combustion of fossil fuels. As such, flexible energy management systems, including electrochemical energy storage technologies, are urgently required to enable reliable electricity delivery from the variable assets. Among them, redox flow batteries (RFBs) are excellent candidates for large-scale, long duration energy storage due to their flexible design, long service life, high reliability, and environmental friendliness. Nevertheless, this technology is still in its infancy in terms of optimisation of materials and battery design that can lead to improvement in performance and cost. Our research seeks to improve upon one of their performance-determining components: the electrodes. In my talk, we will present our work on the use of electrospinning to produce self-supporting materials highly conducting and consisting of fibres of 500nm - 1micron diameter. I will also introduce our approach to replace commonly employed petrol-derived materials with biomass-waste carbon electrodes via electrospinning. Electrospinning is a versatile technique that allows the production of freestanding fibrous materials with tailored properties, including fibre diameter, surface chemistry and alignment of fibres. Finally, I will summarise the main challenges and opportunities to the development of efficient electrodes for optimised mass transport and charge transfer for redox flow batteries.

1:45 PM *ES05.02.02

Designing superior redox flow batteries (RFBs) requires advanced electrochemical characterization techniques that elucidate manifold transport, reactivity, stability, and interactive properties of molecules, electrolytes, and other materials present in these systems. The modularity of many RFB designs enables significant flexibility in the choice of experimental conditions, thus making it imperative to swiftly identify those that lead to improved properties. This not only requires the ability to carry out many experiments in a timely fashion, but also to use electroanalytical approaches in a comprehensive and clever way. To accomplish these objectives, our group has recently introduced The Electrolab, an automated electrochemical platform that combines hardware, software, a dispensing robot, and custom-designed e-chips which altogether enable characterization campaigns with minimal supervision while maximizing diagnostic efficiency.

2:15 PM *ES05.02.03

Designing superior redox flow batteries (RFBs) requires advanced electrochemical characterization techniques that elucidate manifold transport, reactivity, stability, and interactive properties of molecules, electrolytes, and other materials present in these systems. The modularity of many RFB designs enables significant flexibility in the choice of experimental conditions, thus making it imperative to swiftly identify those that lead to improved properties. This not only requires the ability to carry out many experiments in a timely fashion, but also to use electroanalytical approaches in a comprehensive and clever way. To accomplish these objectives, our group has recently introduced The Electrolab, an automated electrochemical platform that combines hardware, software, a dispensing robot, and custom-designed e-chips which altogether enable characterization campaigns with minimal supervision while maximizing diagnostic efficiency.
power. The Electrobol is sufficiently versatile to enable both relatively simple but tedious experiments such as determining diffusion coefficients, to systematic experiments incorporating titrations, to more sophisticated measurements of lifetime of redox species using microelectrode e-chips.

In this presentation, we will first describe new opportunities in the use of redox-active polymers for the construction of redox flow batteries. Unlike small molecules, polymeric redox active materials exhibit dynamics that are highly dependent on aspects such as electrolyte concentration and type. I will then explain how the Electrobol incorporates functions to systematically explore these dependencies, including automated robotic titrations which enable to rapidly identify limiting factors. Finally, I will describe how a different type of redox titration experiment based on scanning electrochemical microscopy can be developed and automated to understand charge transfer performance between redox mediators and charge storage media such as redox polymers. Putting together automated electrochemistry, advanced techniques based on microelectrodes, and new concepts for energy storage based on polymeric materials, promises new directions in the identification of RFB systems.

SESSION ES05.03: Poster Session: Flow Based Energy Storage
Session Chairs: Ertan Agar and Raouf Z. Feng
Wednesday Afternoon, April 24, 2024
Flex Hall C, Level 2, Summit

5:00 PM ES05.03.02
Investigation of The Dynamics of Extreme Redox-Active Molecule and Electrolyte Concentrations Relevant for Nonaqueous Redox-Flow Batteries
Anton S. Perov1,2, Nathan Stumme2, Sashen Ruhunage1, Andrew Horvath2, Scott Shaw2 and Chad Risko1,2;1University of Kentucky, United States; 2The University of Iowa, United States

Organic redox-active molecules have been explored for many uses including, acting as the active material in energy-storage systems for redox flow batteries (RFBs) and providing overcharge protection in lithium-ion batteries (LIBs). The concentration of the redox active species and the supporting electrolyte in an RFB play a significant role in determining the energy density of a battery. Nevertheless, at very high concentrations, the physicochemical relationship between the redox active molecule, electrolyte salt, solvent, and the electrochemical performance of an RFB has not yet been well studied. Herein we present a molecular-level understanding of the effect of concentration on physical properties of the redox-active solution to complement experimental observations using molecular dynamic (MD) simulations. To examine this relationship, we explored the redox-active molecule 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and tetrabutylammonium hexafluorophosphate (TBAPF6) electrolyte salts varied across concentrations of 1 mM to over 1000 mM in acetonitrile. We observed relationships between the transport properties of these solutions that were primarily based on solvation and ion-pairing effects. Furthermore, we also provide suggestions on obtaining optimum performance in such systems based on our theoretical insight.

5:00 PM ES05.03.04
Architecting Electrospin Carbon Fibres for Redox Flow Batteries and The Influence of Fibre Size and Alignment
Michael W. Thielske1, Luis M. Murillo Herrera1, Carlos Minguez1, Alexander H. Quinn2, John N. Vergados2, Fikile Brushett2 and Ana Jorge Sobredo1;1Queen Mary University of London, United Kingdom; 2Massachusetts Institute of Technology, United States

As one of the promising uprising technologies in the field of stationary energy storage, redox flow batteries are in focus for the future storage of sustainable energy harvesting. The carbon fibre-based electrodes in these batteries are a crucial component in achieving high efficiency and performance, which is significantly influenced by the composition and morphology of the utilized carbon fibres. Our work is based on the fabrication of carbon fibres by using electrospinning, a potential alternative to replace commercial carbon felts with higher performance based on the outstandingly high surface-to-volume ratio. This also allows the effective fabrication of doped and decorated fibres by an in situ doping of the fabricated fibre with catalytically active metal nanoparticles or through heteroatom-based doping of the fibre material itself.

Electrospinning has been proven to be a highly versatile technique to fabricate submicron carbon fibres and can be performed with alternative polymeric materials to synthesize carbon fibres, including biopolymers from renewable sources, such as lignin, opening the possibility of a fully sustainable future of energy storage, without any dependence on petrol-derived resources. In recent years, different approaches to implementing bideroded carbon into the electrode have been reported, most commonly by using an additive method to enhance the commercial carbon felt with biomass-derived carbon particles, or by using given biobased fibrous materials from fibrous structure.

The versatility of the electrospinning process allows the fabrication of different fibre architectures. By modifying the collector of the electrospinning process to a rotating drum, the fibres can be collected in alignment with the rotation which can then be installed parallel or perpendicular to the flow field of a redox flow battery. The orientation can lower the pressure within the system and significantly influence the current density during the operation of the battery. To optimize the balance between pressure and performance, the degree of orientation of the fibres was gradually controlled through the rotation speed of the drum.

Another important factor that influences the performance of a redox flow battery is the fibre diameter, which can be controlled by changing the parameters of the electrospinning process. While electrospun carbon fibres are generally used due to their electrochemical active surface area compared to commercial felts, the process itself has the potential to form fibres in different sizes, in this case in the magnitude starting from 220 nm and up to 850 nm.

Changing the size of the fibres is a trade-off between the available performance through the higher surface area of the smaller fibres and lowering the pressure of the flow and favouring the mass transport of the larger fibres.

5:00 PM ES05.03.05
Gas Diffusion in Catalyst Layer of Flow Cell for CO2 Electroreduction Toward C2+ Products
Nageh K. Allam; American University in Cairo, Egypt

The use of gas diffusion electrode (GDE) based flow cell can realize industrial-scale CO2 reduction reactions (CO2RRs). Controlling local CO2 and CO intermediate diffusion plays a key role in CO2RR toward multi-carbon (C2+) products. In this work, local CO2 and CO intermediate diffusion through the catalyst layer (CL) was investigated for improving CO2RR toward C2+ products. The gas permeability tests and finite element simulation results indicated CL can balance the CO2 gas diffusion and residence time of the CO intermediate, leading to a sufficient CO concentration with a suitable CO2/H2O supply for high C2+ products. As a result, an excellent selectivity of C2+ products ~ 79% at a high current density of 400 mA.cm−2 was obtained on the optimal 500 nm Cu CL (Cu500). This work provides a new insight into the optimization of CO2/H2O supply and local CO concentration by controlling CL for C2+ products in CO2RR flow cell.

5:00 PM ES05.03.06
1D Borophosphates for Use as Electrolyte Membranes in Solid Acid Fuel Cells
Brian Chaloux; James Ridenour, Michelle Johannes and Albert Ephsteyn; US Naval Research Laboratory, United States

Although they are relatively new players in the field of hydrogen energy conversion, solid acid fuel cells (SAFCs) demonstrate several advantages compared to their more well-developed counterparts: polymer electrolyte membrane fuel cells (PEMFCs) and solid oxide fuel cells (SOFCs). The elimination of water as the proton carrier in solid acid electrolytes allows operation at intermediate temperatures (e.g., 200–350 °C), simultaneously improving catalytic activity and removing the need to manage liquid water while avoiding the high-cost, refractory materials required for operation under SOFC conditions. However, higher operational temperatures necessitate the discovery, design, and manufacture of electrolyte materials with improved thermal stability compared to PEMs.

Cesium hydrogen sulfate (CsHHSO4) and cesium dihydrogen phosphate (CsH2PO3·CDP) are two well-studied examples of solid acids: protic materials which remain solid at operational temperature and exhibiting proton conduction. CDP demonstrates particular promise as a SAFC electrolyte, as a superprotonic transition from a low-temperature monoclinic phase to a high-temperature cubic phase dramatically improves its proton conduction above 225 °C. However, active humidification of the CDP electrolyte is required to prevent thermal decomposition (i.e., dehydration) below the superprotonic transition temperature, limiting the practical operational window of CDP-based SAFCs to 225–260 °C.

We synthesize and explore an isostrotrically family of one-dimensional inorganic polyborophosphates, the “BOB” borophosphates – empirical formula M3+xH3[BOB(PO4)3] where M is a monovalent cation – as alternative proton conducting solid acids to commercially available membrane materials including PEMs and CDP. Comparing the previously described RbH2[BOB(PO4)3], NaH[BOB(PO4)3], and the novel (NH4)H3[BOB(PO4)3]2, we find that the rubidium borophosphate (RbBOB) strikes an attractive balance between temperature- and humidity-dependent ionic conductivity and thermal stability. Exhibiting stability under air, inert atmosphere, and hydrogen up to 400 °C and exhibiting ionic conductivity up to 10−4 S cm−1 under active humidification at elevated temperature, RbBOB is an exciting new solid acid for SAFC electrolyte membranes.
Molecular Design for Redox Flow Batteries featuring Oligomeric Active Materials and Selective Polymer Membranes
Brett A. Helms; Lawrence Berkeley National Lab, United States

Nearly a decade ago, we introduced the concept of pairing microporous polymer membranes and oligomeric active materials for cross-over free redox-flow batteries. Since then, the field has advanced designs of considerable efficacy and rigor. Yet, there is more to do as use-cases evolve from multi-hour to long-duration. Here, I will discuss outstanding challenges with respect to different components in the devices as well as their thoughtfull guided toward meeting technical specifications for these emerging use-cases. Increasingly, synthetic advances are coming from detailed understanding of specific electro-physioproperties of membranes and active materials as well as emergent failure mechanisms, which present differently at different stages of the battery's useful life and and must be taken into account for there to be a credible pathway to commercialization and deployment.

SYMPOSIUM ES06

Sulfur and Sulfide Chemistry in High Performance Electrochemical Energy Storage
April 23 - May 7, 2024

Symposium Chair: Teran Agar and Ruo Zhu Feng

Symposium Organizers
Yoon Seok Jung, Yonsei University
Dongping Lu, Pacific Northwest National Laboratory
Hui Wang, University of Louisville
Yang Zhao, University of Western Ontario

Symposium Support
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Lithium-sulfur (Li-S) batteries are appealing owing to the high specific capacity (1672 mA h g⁻¹) and low cost of sulfur. Lithium-sulfur cells involve a solid-liquid-solid conversion of sulfur species, from S to intermediate lithium polysulfides to the end discharge product Li₂S, which results in a sluggish reaction kinetics due to the insulating nature of S and Li₂S. Furthermore, the dissolution of polysulfides and their migration from the cathode to the anode severely hampers the reversible plating and stripping of lithium-metal anode. These problems impede the practical application of Li-S batteries. Numerous efforts have been devoted to overcoming these challenges, but the intrinsically low stripping and plating efficiency of Li and the corrosion from polysulfides necessitate excess Li and electrolyte.

This presentation will focus on the exploration of the chemistry of tellurium, which lies in the same group as sulfur in the periodic table. The addition of a small amount of tellurium into lithium sulfates helps enhance the cycle life of Li-S cells. However, due to the poor utilization of Te, a significant amount of Te is required to improve cell cycling performance, resulting in an increase in cost. To overcome this challenge, we have adopted two approaches: (i) use of tellurium nanowires (TeNW) synthesized via a hydrothermal method and (ii) incorporation of LiTe₃ synthesized by a one-step process as an additive into the electrolyte.

Coating TeNW onto the separator greatly enhances Te utilization and a significant improvement in cell cycle life. The versatility of TeNW is further demonstrated by utilizing it with carbon nanotubes as the anode substrate. The exceptional performance of TeNW is due to its high surface area nanostructure and excellent conductive network, facilitating efficient electron transfer during cell cycling.

On the other hand, LiTe₃ reacts rapidly with polysulfides and functions as a redox mediator to significantly improve the cathode kinetics and the utilization of active material in the cathode. The formation of a Li₂TeS₃/Li₂Te-enriched interphase layer on the anode surface enhances ionic transport and stabilizes Li deposition. By regulating the chemistry on both the anode and cathode sides, the LiTe₃ additive enables a stable operation of anode-free lithium-sulfur cells with only 0.1 M concentration in conventional ether-based electrolytes. With a high utilization of Te, the additive enables significantly longer cycle life of anode-free pouch full-cells under lean electrolyte conditions.

A Long cycle-life Li-S battery pouch cell with high sulfur loading (5 mg per cm²) is reported with the mitigation of the shuttle-effect. The performance was achieved with a bifunctional carbon material with three unique features. The carbon can catalyze the disproportionation of dissolved long-chain polysulfide ions to elemental sulfur; the carbon can ensure homogenous precipitation of Li sulfide on the host carbon and the carbon has honeycomb porous structure which can store sulfur batter. All the features will be demonstrated experimentally and reported.

Through an ex-situ, postmortem analysis in which a Li-S cell was disassembled after many cycles, few dissolved polysulfides were found in the electrolyte of the Li-S cell made with the bifunctional carbon in comparison with a control Li-S cell. A HPLC was used to determine the distribution of dissolved elemental sulfur and polysulfide ions in the electrolyte of the Li-S batteries during cycling. Only dissolved elemental sulfur was detected in the cell with the bifunctional carbon, while a distribution of polysulfide ions of various -S-S- chain length was observed in the control Li-S cell. A catalytic polysulfide disproportionation reaction mechanism was proposed, in which polysulfide ions can be catalytically disproportionate to elemental sulfur and Li₂S and/or Li₂S precipitates. Since the dissolved polysulfides are the engine driving the shuttle effect, the detrimental shuttling in a Li-S cell can be mitigated through the removal of dissolved polysulfide ions in the electrolyte during the discharge and charge.

The unique porous structure of the bifunctional carbon which was made from a raw silk was revealed by a SEM and a N₂ absorbption isotherm. The pore structure was believed to store sulfur uniformly and ensured the homogeneous deposition of Li₂S and/or Li₂S. The N-containing functionalities that were introduced to carbon from the amino acids of raw silk can catalyze the disproportionation of the dissolved S₂⁻ to solid S0 at the cathode side, thereby mitigating the shuttle effect. In addition, the hierarchical honeycomb porous structures generated by a carbonization process can physically trap high-order lithium polysulfides and sustain the volume change of sulfur. With the synergistic effects of the unique structures and characteristics of the carbon, the sulfur/carbon composite using delivers a high reversible capacity of over 1000 mAh g⁻¹ and over 600 mAh g⁻¹ with a sulfur content of 1.2 mg cm⁻² 2 and 2 mg cm⁻² in a pouch cell, respectively.
Li-S battery is a highly desirable technology featuring high energy density and low-cost materials. However, the challenges with the technology are also well documented. In ether-based electrolytes, the redox of sulfur goes through a soluble polysulfide mechanism, which facilitates the reaction kinetics but greatly impacts the cycle life and practical energy density due to the need for elevated amount of electrolytes. Sulfurized polyacrylonitrile, SPAN, in contrast, does not involve the polysulfide mechanism. Instead, the material goes through a solid-solid conversion process. Coupled with the presence of a robust cathode electrolyte interface (CEI), the material has demonstrated exceptionally long cycle life, well over 1000 cycles.

SPAN’s limitation lies in its limited sulfur content (~43 wt%) and specific capacity (~700 mAh/g). These values put a practical limit for the energy density of Li-S/SPAN battery at around 300 Wh/kg. In order to increase the capacity, we have embarked on understanding the concept and the structure-limiting mechanism. During the first cycle, lithiation leads to a loss of H2S which in turn improves the degree of conjugation and electronic conductivity. Both sulfur and the nitrogen on the pyridine ring are involved in the charge storage during the subsequent cycles. Recent works have focused on further raising sulfur contents in SPAN by introducing sulfur species that resist the formation of long-chain polysulfide in the solid state. Structural analysis reveals the critical roles played by the nitrogen in facilitating the redox reaction of the additional sulfur. More than 20% improvement in capacity is obtained without the introduction of soluble polysulfide. We will discuss in detail the reaction mechanisms of these high-sulfur SPAN materials and the pathway towards their implement in high energy density batteries.

2:30 PM ES06.02.04
Carbon Nanofoam Papers as Electrode Architecture for Allochogens in Lithium- and Sodium-Based Batteries Jeffrey W. Long1, Zachary G. Neale2, Matthew J. Leifer2, Debra R. Rolison1, Megan B. Sassin1 and Rachel E. Carter1; Naval Research Laboratory, United States; U.S. Naval Research Laboratory, United States

Sulfur has emerged as a promising charge-storage material for advanced rechargeable batteries based on the high capacity of the sulfur/sulfide redox reaction and earth-abundance of this element. The main challenge is that the redox transition, but also facilitated Li-ion diffusion, which is confirmed by both cyclic voltammetry (CV) at various scan rates and Randles-Sevcik equation. Anatase and rutile phases of TiO2 nanoparticle and nitrogen doping, respectively. Porous structure of chain polysulfide adsorption was confirmed by direct visualization of Li2S6 migrating from electrolyte to the exterior surface. Despite works applying porous carbons in ASSLSBs, the optimal structure has not been well elucidated. Here, we pioneer discussion on the ideal carbon structure and develop polyacrylonitrile-derives porous carbon fibers (PPCF) with a unique core-shell morphology. A microporous shell on a dense core provides high surface area with accessible pores for the polysulfides and electrolytes. Consequently, ASSLSBs with PPCF show outstanding performance. Furthermore, we grow MoS2 nanosheets on carbon fibers. The chemical and electrochemical compatibility of MoS2 with sulfur and sulfide solid electrolytes greatly improves cathode stability and ion/electron transfer, while the layered structure facilitates Li intercalation. This significantly enhances kinetics and relieves electrolyte composition. Our optimized ASSLSBs delivers an ultrahigh initial capacity of 1456 mAh/g with high coulometric efficiency and 78% retention after 220 cycles. Finally, we reveal the Li-S redox reaction undergoes a two-step transformation, producing polysulfide intermediates. Kinetic limitations can cause incomplete conversions, leaving polysulfides like Li2S2. Our mechanistic insights guide design principles for ASSLSBs.

4:00 PM DISCUSSION TIME

4:15 PM ES06.02.07
Binder-Free Manganese Iron Nitrider-N-Doped CNT Cathode for Lithium-Sulfur Batteries Yi-Jie Wang, Bo-Dong You and Che-Ning Yeh; National Tsing Hua University, Taiwan

Lithium-sulfur (Li-S) batteries hold promise for high energy density and improved safety compared to conventional lithium-sulfur cells using liquid electrolytes. However, low utilization of active sulfur caused by sluggish reaction kinetics has greatly hindered ASSLS development. Achieving efficient sulfur ion accessibility in the cathode structure is critical. Porous carbon hosts, widely used in liquid cells, have been proposed to address these challenges. However, conventional porous carbons with buried pores are ineffective for ASSLSBs, as the non-noble solid electrolyte cannot penetrate the pores to access enclosed sulfur. An ideal porous carbon should maximize surface area for sulfur while restricting pores to only the exterior surface. Despite works applying porous carbons in ASSLSBs, the optimal structure has not been well elucidated. Here, we pioneer discussion on the ideal carbon structure and develop polyacrylonitrile-derived porous carbon fibers (PPCF) with a unique core-shell morphology. A microporous shell on a dense core provides high surface area with accessible pores for electrolytes and sulfur. Consequently, ASSLSBs with PPCF show outstanding performance. Furthermore, we grow MoS2 nanosheets on carbon fibers. The chemical and electrochemical compatibility of MoS2 with sulfur and sulfide solid electrolytes greatly improves cathode stability and ion/electron transfer, while the layered structure facilitates Li intercalation. This significantly enhances kinetics and relieves electrolyte composition. Our optimized ASSLSBs delivers an ultrahigh initial capacity of 1456 mAh/g with high coulometric efficiency and 78% retention after 220 cycles. Finally, we reveal the Li-S redox reaction undergoes a two-step transformation, producing polysulfide intermediates. Kinetic limitations can cause incomplete conversions, leaving polysulfides like Li2S2. Our mechanistic insights guide design principles for ASSLSBs.

4:30 PM ES06.02.08
Synergistic Effect of Anatase/Rutile Nanoparticle and Nitrogen Doping on NH2-MIL-125(Ti)-Derived Porous Carbon as High Performance Lithium-Sulfur Battery Cathodes Sooneah Oh1, Seokhee Lee2 and Jiwon Kim1; 1Yonsei University, Korea (the Republic of); 2Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of)

Lithium-sulfur (Li-S) batteries have garnered significant attention as a future energy storage systems owing to their high theoretical capacity, energy density, and abundance of sulfur in nature. However, their development has been hindered by the polysulfide shuttle effect, which adversely affects the cycling stability of Li-S batteries. Various approaches – such as designing the pore structure of porous carbon, or introducing heteroatoms and/or metal oxides into the porous carbon – have been applied to address these issues. For instance, Yang et al. controlled the polysulfide adsorption on the porous carbon cathodes which depends on the phase of titanium dioxide (TiO2) particles (i.e., anatase or rutile) introduced in the cathodes1). Furthermore, Kim et al. improved the retention of Li-S battery via coupled effects of nitrogen (N) vacancies and the rutile phase of TiO22). However, the synergistic effects from the correlation among these factors (e.g., heteroatom doping and phase type of TiO2 particles) have not yet been systematically studied.

In this work, we present a micro-sized NH2-MIL-125(Ti) metal organic framework (MOF)-derived porous carbon (micro-cNMT) as a host material of sulfur for Li-S battery cathodes. micro-cNMT possesses a hierarchical micro-/meso-porous structure, N heteroatoms, and mixed phases of TiO2 nanoparticles (i.e., both anatase and rutile). These parameters collectively enhance the performance of Li-S batteries through their specific functions. Specifically, micro-cNMT enhanced the polysulfide shuttle effect by the cooperation of physical and chemical adsorptions, facilitated by its hierarchical porous structure and TiO2 nanoparticle doping, respectively. Porous structure of micro-cNMT not only accommodated active sulfur and its volume transition, but also facilitated Li-ion diffusion, which is confirmed by both cyclic voltammetry (CV) at various scan rates and Randles-Sevcik equation. Anatase and rutile phases of TiO2 nanoparticles preferentially adsorbed short-chain polysulfide and long-chain polysulfide, respectively, preventing the loss of active sulfur throughout the entire discharging process. The long-chain polysulfide adsorption was confirmed by direct visualization of Li2S6 migrating from electrolyte to the micro-cNMT. Furthermore, scanning electron microscope (SEM) images of cathodes after 100 cycles of discharge-charge and operand X-ray diffraction (XRD) measurement during the first discharge demonstrated that the micro-cNMT enhances short-chain
polysulfide adsorption, thereby facilitating sulfur reduction reactions from polysulfide to Li$_2$S. As a result, the micro-ENMT cathode improved cycling stability owing to a synergistic effect from N and mixed phases of TiO$_2$ (0.39% decay at 0.1 C for 100 cycles), compared to the control group without N or with a single phase of TiO$_2$ nanoparticles (either anatase or rutile only).

References

4:45 PM ES06.02.09
Synthesis, Electronic Structure and Redox Chemistry of Li$_2$MnP$_2$S$_6$, A Candidate High-Voltage Cathode Material Yi-Ting Cheng,$^1$ Fujii Yuta,$^2$ Yu Nomata,$^2$ Madhulika Mazumder,$^3$ Nataly C. Rosero-Navarro,$^3$ Aichi Yamashita,$^4$ Yoshikazu Mizuguchi,$^5$ Chikako Moriyoshi,$^6$ Takao Mitsudome,$^7$ Kiyoharu Tadanaga,$^8$ Akira Miura$^9$ and Chris Bartel$^1$; $^1$University of Minnesota, United States; $^2$Hokkaido University, Japan; $^3$Tokyo Metropolitan University, Japan; $^4$Hiroshima University, Japan; $^5$Osaka Metropolitan University, Japan; $^6$Osaka University, Japan

While significant efforts have been made to harness the large capacity of sulfide-based cathodes, there has been limited focus on increasing their voltage. Here, by a novel iodide-assisted synthesis route, we successfully synthesized lithium metal thiophosphates Li$_2$MnP$_2$S$_6$ (M = Mn, Fe, and Co), of which Li$_2$MnP$_2$S$_6$ is a new compound. Electrochemical cycling revealed Li$_2$FeP$_2$S$_6$ and Li$_2$MnP$_2$S$_6$ can both be cycled at an equivalent voltage of ~3 V, significantly higher than other sulfide-based cathodes. Despite the similar voltages, these two materials were found to operate despite very different redox mechanisms. Density functional theory calculations show that while Li$_2$FeP$_2$S$_6$ exhibits traditional cationic redox, Li$_2$MnP$_2$S$_6$ involves participation and rehybridization of coupled Mn-S and S-S states. This work reinforces the importance of high-voltage sulfide-based cathodes for Li-ion batteries with the potential for significant capacity by combining both cationic (transition metal) and anionic (sulfur) redox.

SESSION ES06.03: Poster Session: Sulfur and Sulfide Chemistry for Electrochemical Energy Storage
Session Chairs: Dongping Lu and Hui Wang
Tuesday Afternoon, April 23, 2024
Flex Hall C, Level 2, Summit

5:00 PM ES06.03.01
Enhancing Aqueous Zinc Sulfur Battery Performance with a Novel Hybrid Electrolyte Yujie Guo,$^1$ Rodney Y. Chua$^1$, Yingqian Chen$^2$, Yi Cai$^1$, Ernest Tang$^1$, Nicholas J. Lim$^1$, Thu Ha Tran$^1$, Vivek Verma$^1$, Ming Wah Wong$^2$ and Madhavi Sinivasan$^1$; $^1$Nanyang Technological University, Singapore; $^2$National University of Singapore, Singapore

Rechargeable aqueous Zn/S batteries hold significant promise due to their high capacity and energy density. However, their long-term cycling stability is hindered by sulfur side reactions and the growth of Zn anode dendrites in the aqueous electrolyte. In response, this research explores a simultaneous solution to these challenges through the development of a unique hybrid aqueous electrolyte incorporating ethylene glycol as a co-solvent. This innovative electrolyte design strategy facilitates the fabrication of Zn/S batteries with exceptional performance metrics on capacity, energy density and cycling stability under a high current rate. In addition, the investigation of the cathode charge-discharge mechanism reveals a multi-step conversion reaction. During discharge, elemental sulfur undergoes sequential reduction by Zn, ultimately forming ZnS. On charging, ZnS and short-chain polysulfides are oxidized back to elemental sulfur. This mechanism contributes to performance enhancement.

References
Lithium-sulfur batteries, recognized for their high theoretical capacity and plentiful sulfur source, are potential candidates for future energy storage devices. One significant challenge to commercialization is the polysulfide shuttle effect, which reduces the cycling stability and battery lifespan. We solved this issue by incorporating porous nanostructured metal sulfide into the battery's separator. We prepared metal sulfide nanoparticles through a simple hydrothermal synthesis and subsequently developed a porous thin film using the breath figure approach. Variables like substrate choice, temperature, and humidity were adjusted to refine the nanostructures. These modifications helped curb the shuttle effect by trapping the mobile polysulfides, thereby enhancing battery efficiency. The electrochemical attributes of these upgraded devices are elaborated upon in this research.

5:00 PM ES06.03.09 Hafnium Trisulfide Nanoribbons as a Promising Anode for High-Performance Lithium-Ion Storage Wei Shangying; University of Chemistry and Technology, Prague, Czechia

Exploring the electrochemical characteristics of low-dimensional van der Waals materials is crucial for advancing novel rechargeable energy-storage devices, such as lithium-ion batteries (LiBs). Given their diverse band gaps, anisotropic conductivity, and high specific capacity, materials within the extensive family of transition metal trichalcogenides (TMTCs), including hafnium trisulfide (HfS2), have garnered increased attention in recent years. Throughout numerous theoretical and experimental studies focusing on the synthesis and physicochemical attributes of hafnium trisulfide, there remains a scarcity of experiments delving into its lithium-ion storage properties. Hence, HfS2 material with a quasi-1D structure was applied as anode material for lithium-ion batteries. HfS2 micro-belts were produced using a simple solid-state reaction. Upon performing the relevant electrochemical tests, after 100 cycles, the HfS2 electrode exhibits a high reversible capacity of 221.7 mAh g⁻¹ at a current density of 100 mA g⁻¹ and a great rate capability of 157.5 mAh g⁻¹ at the 101st cycle at a high current density of 800 mA g⁻¹. The excellent lithium storage performance can be related to the lithiation amorphization process, surface-controlled pseudocapacitive behavior, and low charge transfer resistance. The promising electrochemical characteristics of HfS2 may shed new light on the design of transition metal trichalcogenides as viable anode materials for lithium storage. Nevertheless, the lithium storage behavior of ZnS flakes is thus largely unexplored due to its low electronic conductivity and the challenges associated with its exfoliation.

5:00 PM ES06.03.10 Lithium-Ion Batteries: Thermal Degradation and Supercapacitors Steve Martin; Madison Olson, Alec Wakefield, Nicholas Oldham and Noah Riley; Iowa State University of Science and Technology, United States

While lithium batteries are currently the most popular battery for grid scale energy storage, the rapidly increasing demands for Lithium to electrify transportation will soon outpace available geological reserves. For this reason, sodium batteries, with their comparable volumetric energy storage density, yet orders of magnitude lower cost, have been of interest for more than 50 years. The lack of a high conductivity, low cost, and electrochemically stable solid electrolyte has been a central reason for the current lack of a commercially available Na battery. In this talk, I will describe our recent efforts in developing new chemistries of Na-based glassy solid electrolytes that can be formed as thin films and in characterizing the many thermal, chemical, electrochemical, and mechanical properties needed of them.

5:00 PM ES06.04.01 Progress Towards New Sodium Mixed Oxy-Sulfide-Nitride Glassy Solid Electrolytes Steve Martin; Madison Olson, Alec Wakefield, Nicholas Oldham and Noah Riley; Iowa State University of Science and Technology, United States

Sulfide-based solid-electrolytes can potentially be employed in conjunction with a lithium metal negative electrode and 5V-class high voltage positive electrode material. Different families of solid electrolyte or the use of oxy-sulfide in the literature. Nevertheless, all these materials are based on the same precursor: Li2S: very expensive and unsafe material. The ideal sulfide material would be one that is stable at high potential and low potential with lithium metal, a strong resistance to humidity allowing the handling of the material as well as its safe use in batteries with a low cost synthesis method in a minimum of steps using the minimum of expensive precursors. In this field and since a few years, Hydro-Quebec has decided to conduct specific research on all-solid ceramic batteries and especially in the field of sulfide-based ceramic electrolytes. A specific study has been carried out to (1) optimize the composition of sulfide solid electrolyte with cheaper precursors to maintain or increase the properties as ionic conductivity and...
Further, the Li2O and Li2S interface layers showed different lithium metal wettability. A combined density functional theory (DFT) and kinetic Monte Carlo (KMC) interface evolution simulation showed that the lithiophilic interface (Li/Li2O) repels vacancies into the bulk Li, so Li atoms can quickly fill the Li vacancies near the interface and maintain a smooth Li surface. In contrast, the more lithiophobe interface (Li/Li2S) shows no such behavior. This is consistent with the observed trend and morphology of Li dendrite growth in different solid electrolyte materials. For decades, the pursuit of solidifying electrolytes using inorganic solid electrolytes (SEs) that display high mechanical strength has been regarded as a "Holy Grail" in the quest to enable Li metal batteries. However, these materials encounter a critical limitation: their electrochemical instability in contact with Li metal. This instability leads to the reductive decomposition of sulfur SEs, which substantially escalate interfacial impedance. More critically, Li metal tends to grow through the SE layers, inducing catastrophic short circuits. To address these challenges, various sulfur modification techniques have been explored. Inorganic materials (e.g., LiF) and alloying elements (e.g., Ag) have received considerable attention. However, despite advances in enhancing the performance of Li metal ASSBs, there is a noticeable gap in our understanding of the interfacial evolution, particularly concerning factors associated with cell fabrication methods and operating conditions.

In this presentation, we report our strategies for stabilizing Li metal anodes in ASSBs that use Li6PS5Cl, specifically through the incorporation of electroless-plated In or MgF2 interlayers. Our findings indicate that neither intermetallic nor simple inorganic interlayers maintain stability throughout cell fabrication or operation. In contrast, MgF2 interlayers exhibit substantial enhancements in these aspects. Furthermore, comprehensive analytical techniques, including operando electrochemical pressiometry, to probe the interfacial evolution in ASSBs are also presented.
Lithium-sulfur (Li-S) batteries have been widely emphasized as alternatives to commercial lithium-ion batteries not only for their higher theoretical capacity (1,675 mAh/g) but also for abundance of sulfur in nature and being highly. However, the shuttle effect of lithium polysulfide limits long cycle life of batteries, and separators have been modified to effectively control reaction intermediates. For example, polymer-based separators have been coated with oxide or carbon in order to enhance filtration via por or electrical attraction/repulsion. In particular, metal-organic frameworks (MOFs) as coating materials have advantages of porosity and electrochemical property which can be easily adjusted by the composition of metal clusters and ligands. However, most traditional coating techniques such as chemical vapor deposition (CVD) and vacuum filtration coating methods require heating process and produce relatively thick layer (at least micrascale), thereby limiting its applicability. Herein, we synthesized two types of MOF (i.e. MOF-5 and IRMOF-3) nanosheets using Langmuir-Blodgett (LB) technique to functionalize Li-S battery separator. A modified separator was uniformly formed (1.27 Å for P2) by depositing five monolayer films (total thickness of ~47.5 Å) at room temperature, while zinc acetate dihydrate and (2-aminophenyl)acetone were used as MOF precursors. To note, polysulfide permeation test in H-cell revealed that a LB-coated MOF separator had comparable degree of filtration to a slurry-coated MOF separator despite of its thin thickness (~4.000 times thinner than slurry-coated one). Moreover, Li-S battery with a IRMOF-3 coated separator exhibited 1.13 times higher cycle stability (retention of 45.2% after 100 cycles) compared to one with non-coated separator (retention of 48.8% after 100 cycles). This suggests that heteroatom (i.e. nitrogen in IRMOF-3) and pore structure of MOF coating layer contribute to enhanced filtration ability of separators. Consequently, we can improve the cycle stability of Li-S batteries by applying a nanoscale MOF modification layer to separators via LB, which can further pave a way for commercialization of Li-S batteries.

1:45 PM ES06.05.02
Towards a Sealed Rechargeable Li-SO2 Battery: Overcoming Slow Diffusion Kinetics and Side Reactions

Rechargeable lithium-sulfur dioxide (Li-SO2) batteries are potentially of low-cost and high-energy density. The high SO2 solubility in organic solvents has enabled cell operation under non-pressurized conditions. For example, electrochemical behavior of this system has been observed in carbonate-based electrolytes. However, most of the reports so far employ an “open cell configuration”, where continuous SO2 supply is provided. The needed accessories, such as gas diffusion layers and Swagelok-type cell construction with heavy steel frames, and gas handling systems, greatly impede the development of practical high-energy-density batteries. Herein, we report our progress on the understanding of behavior of electrolytes containing SO2 within a closed system and to maximize the utilization of the active material. In comparison to other redox-active gases, SO2 molecules, with their relatively high molecular weight (twice as heavy as O2) and polarity, not only suffer from slow diffusion (~0.7 times lower diffusion coefficient compared to that of O2) within the electrolyte but also exhibit a peculiar reverse osmotic behavior. When SO2 is consumed in the electrolyte volume between the two electrodes, dissolved SO2 in electrolyte outside the current path does not diffuse in. Instead, organic solvents are driven into the current path, leading to an evolution of SO2 gas outside a cell stack. Our investigation confirmed that this behavior is driven by the molecular interactions between SO2 and the organic solvents. Based on the above insights, we have designed electrochemical cells to strategically place all SO2 containing electrolyte within the current path, leading to maximize utilization. Our optimized bobbin-type battery, in which the electrolyte containing SO2 is entirely contained within the cell stack, has proven highly effective in maximizing discharge capacity. This configuration allowed us to achieve exceptional utilization (~73%) of SO2 along with an acceptable E/C ratio (~13 g/Ah, with discharge capacities of 2639 mA h/gKB and 7.9 mA h/cm2). To further enhance the performance, we have developed a nanoporous lithium protective layer made of a composite of Nafion and alumina nanopowder, capable of retaining SO2 reactant within the cell stack while minimizing continuous reactant loss from undesirable reactions with Li metal anode. In addition, we have achieved remarkable cycling stability by identifying catalysts to reduce side reactions and polarization on the cathode. This research sheds new light on the working mechanisms of the Li-SO2 chemistry and points to its potential as a low-cost, sustainable battery.

2:00 PM ES06.05.03
Alloy Anodes in Sulfide-Based Solid-State Batteries

Alloy anodes offer high theoretical capacity, but they typically exhibit fast capacity decay in lithium-ion batteries because of excessive solid-electrolyte interphase growth. Here, we investigate a variety of alloy anodes in sulfide solid-state batteries, and we show that they can exhibit significantly improved interfacial stability and enhanced cyclability when engineered effectively. In-situ measurement of stack pressure evolution during cycling shows that the volume changes of alloy anodes can lead to large pressure swings within the solid-state battery cell, giving insight into electrode composite evolution. We further investigate the fundamental electrochemical behavior of 12 different foil-based alloy anode materials in solid-state batteries, and we find that lithium trapping by the delithiated phase can play a key role in limiting performance. Based on these insights, we present a new design for dense foil aluminum-based alloy anodes with multiphase microstructure that offers significantly improved performance due to retained transport pathways within the foil. This design offers a paradigm that does away with slurry coating, potentially reducing manufacturing costs. In addition, we investigate solid-state dealloying of foil anodes to understand the interplay between densification and interfacial contact evolution at different stack pressures. Taken together, these findings show the importance of controlling chemo-mechanics and interfaces in alloy anodes for sulfide-based solid-state batteries for improved energy storage capabilities.

2:30 PM ES06.05.04
Tuned Reactivity at The Lithium Metal – Argyrodite Solid State Electrolyte Interphase

Tuned Reactivity at The Lithium Metal – Argyrodite Solid State Electrolyte Interphase

Thin intermetallic Li2Te–LiTe3 bilayer (0.75 mm) derived from 2D tellurene stabilizes solid electrolyte interphase (SEI) of lithium metal and argyrodite (LPSCl, Li6PS5Cl) solid-state electrolyte (SSE). Tellurene is loaded onto standard battery separator and reacted with lithium through single-pass mechanical rolling, or transferred directly to SSE surface by pressing. State-of-the-art electrochemical performance is achieved, e.g. symmetric cell stable for 300 cycles (1800 hours) at 1 mA cm−2 and 3 mA cm−2 (25% DOD, 60 mm foil). Cryo-FIB sectioning and Raman mapping demonstrate that Li2Te–LiTe3 bilayer impedes SSE decomposition. The modified Li–LPSCl interphase is electrochemically unstable with geometrically heterogeneous reduction decomposition reaction front that extends deep into the SSE. Decomposition drives voiding in Li metal due to its high flux to the reaction front, as well as voiding in the SSE due to the associated volume changes. Analysis of cycled SSEs found no evidence for pristine (unreacted) lithium metal filaments/dendrites, implying failure driven by decomposition phases with sufficient electrical conductivity that span electrolyte thickness. Density Functional Theory (DFT) calculations clarify thermodynamic stability, interfacial adhesion, and electronic transport properties of interphases, while mesoscale modeling examines interrelations between reaction front heterogeneity (SSE heterogeneity), current distribution and localized chemo-mechanical stresses.

SESSION ES06.06: Sulfide-Based Solid-State Batteries—Cathode and Devices

Thursday Morning, April 25, 2024
Room 432, Level 4, Summit

8:30 AM ES06.06.01
Hot-Pressed FeS2 Cathodes with Oxy sulfide Solid-State Electrolyte for All-Solid-State Batteries

The performance of all-solid-state batteries (ASSBs) is limited by poor interfacial contact between active material (AM) and solid-state electrolyte (SSE) particles. At the cell level, poor interfacial contact manifests as difficult operating specifications (e.g. high stack pressure, elevated temperature, or slow charge rate), or poor cell durability. This seminar investigates how an advanced processing technique can better consolidate electrode composites. It will be shown that the electrochemical performance of FeS2/InLi ASSBs was improved when the cells were hot-pressed at a temperature > 200 °C. When cycled at 25 °C, a cold-pressed (CP) FeS2/InLi ASSB delivered negligible capacity whereas a hot-pressed (HP) FeS2/InLi ASSB delivered a 15% increase in cycle charge and a two-fold improvement in excess of 600 mAh g−1. The improved performance is attributed to better interfacial contact between AM and SSE. This result was achieved by selecting thermally stable FeS2 active material and highly processable Li1P3S9.75O1.25 (LPSO) SSE.
Bulk-type solid-state batteries hold promise as an enabling technology for high density electrochemical energy storage. Especially layered (Ni-rich, low-Co or Co-free) oxide cathode materials (e.g., LiNi0.5Co0.2Mn0.3O2) and Li1xPS4-xCl2 and Li1xPS4-xClx phosphate solid electrolytes are both considered for high energy density solid-state batteries. However, electro-chemo-mechanical degradation occurring during cycling is a major obstacle towards development of stable and long-lived cells. In this presentation, I will highlight the importance of tailoring Ni-rich cathodes for increasing performance of pellet-type and slurry-cast electrodes. In addition, I will show recent findings on the effect that protective surface coatings have on interfacial side reactions and mechanical degradation in thiophosphate-based cells.

In this presentation, we propose a comprehensive strategy that addresses not only the poor electrochemical stability of sulfide SEs but also the detrimental phase transition of Ni-rich CAMs. To address the structural stability issues inherent in Ni-rich CAMs, multi-doping techniques were employed. Concurrently, functional compositional coatings were designed and evaluated. In this talk, I will introduce a novel binder design based on protection-deprotection chemistry, which resolves the tricky issue of polarity compatibility among the three electrode components (solvent, binder, and SE) in the slurry solution. Protection by the tert-butyl group allows for homogeneous dispersion of the binder in the slurry based on a relatively low polar solvent, with subsequent heat-treatment during the drying process to cleave the tert-butyl group. Upon deprotection, the polar carboxylic acid group is exposed, which enables hydrogen bonding interaction with the high-nickel layered oxide active material. Deprotection strengthens the electrode adhesion drastically, even beyond the levels of commercial LIB electrodes, and the key electrochemical performance parameters are improved markedly in both half-cell and full-cell settings. This study highlights the potential of sulfide-based ASSBs for scalable manufacturing and also provides insights that protection-deprotection chemistry could generally be useful for various battery cells that suffer from polarity incompatibility among multiple electrode components.

Sulfurized polymers are an attractive cathode active material, promising to overcome the intransigent polysulfide shuttle effect sulfur cathodes face via the anchoring of sulfur by a carbon-sulfur bond (C-S bond). Both sulfur-dispersed polypyrrole/copolymers (SDSP) and sulfurized polycrystallite (SPAN) contain C-S bonds which should function in this way, however, their performance in ether electrolytes still exhibit capacity fade associated with the polysulfide shuttle. We investigate this anchoring effect using in-operando ATR-FTIR spectroscopy to develop a molecular level understanding of the polysulfide speciation reaction in sulfurized polymers and cathode level molecular changes. We find that in SDSP copolymers with sulfur wt% of 80 and 30 wt%, the C-S bond is not active in the voltage window of Li-S batteries (1.8-2.6 V vs Li/Li+). In SPAN, however, we found that the C-S bond is active in the typical voltage window (-1 V vs Li/Li+) contributing to the evolution of polysulfide species in electrolyte with low concentrations of lithium nitrate (LiN03), however this effect is mitigated when higher concentrations of LiN03 are used. We attributed the mitigation of the polysulfide shuttle to the formation of a cathode electrolyte interface (CEI), composed of lithium fluoride, established via ex-situ XPS studies on cycled cathodes. Additionally, we observed the reversible behavior of the C-S bond in IR at ~680 cm-1 in electrolytes with high concentration of LiN03, as opposed to the irreversible behavior of the bond in electrolyte with low concentrations of LiN03. Moreover, we observed the lithiation of the cyclized PAN backbone, identified by the elimination of the aromatic region of the IR spectrum after the first cycle.

For ASSBs to meet the practical demands of high energy density, the use of Ni-rich layered oxide active materials (CAMs), denoted as LiMO2 (M = Ni, Co, Mn, and/or Al), which are prevalent in LIBs, is essential. However, a significant change arises with sulfide SEs, known for their high ionic conductivity but poor electrochemical stability. This instability necessitates the application of an insulating buffer layer on Ni-rich CAMs. Furthermore, Ni-rich CAMs are prone to structural instability, leading to internal cracking and significant degradation, notably an irreversible H2-H3 phase transition when in high states of charge. To address the structural stability issues inherent in Ni-rich CAMs, multi-doping techniques were employed. Concurrently, functional compositional coatings were designed and evaluated. In this talk, I will introduce a novel binder design based on protection-deprotection chemistry, which resolves the tricky issue of polarity compatibility among the three electrode components (solvent, binder, and SE) in the slurry solution. Protection by the tert-butyl group allows for homogeneous dispersion of the binder in the slurry based on a relatively low polar solvent, with subsequent heat-treatment during the drying process to cleave the tert-butyl group. Upon deprotection, the polar carboxylic acid group is exposed, which enables hydrogen bonding interaction with the high-nickel layered oxide active material. Deprotection strengthens the electrode adhesion drastically, even beyond the levels of commercial LIB electrodes, and the key electrochemical performance parameters are improved markedly in both half-cell and full-cell settings. This study highlights the potential of sulfide-based ASSBs for scalable manufacturing and also provides insights that protection-deprotection chemistry could generally be useful for various battery cells that suffer from polarity incompatibility among multiple electrode components.

Self-templated 3D porous sulfide solid electrolytes for solid-state sodium metal batteries Xiaolin Guo, Yang Li and Hui Wang; University of Louisville, United States

Rechargeable solid-state sodium (Na) batteries have gained great attention for their high-safety, high energy density and low cost. However, due to the high reactive Na anode, poor electrolyte/electrode interfaces compatibility is the biggest obstacle for inorganic sulfide solid electrolytes (e.g., Na2MS4, M=P, Sb) to achieve high performance batteries. Thus, it is necessary to design the nanostucture of sulfide solid electrolyte (SE) and modify interface to address that challenge on the electrochemical instability. In this talk, we will introduce a facile and simple synthesis to prepare Na2Sb2S4 (NSS) sulfide solid electrolyte with 3D porous framework, which can be further infiltrated with a phase transition polymer to form a composite solid electrolyte. The Na2Sb2S4-based composite (NSSC) experts enhanced interface stability towards Na metal compared with pristine NSS. The fabricated cells with structure of Na/NSSC/TiS2 shows excellent cycling stability for 200 cycles with decent capacity retention. This result demonstrates great promise of achieving high-energy sodium metal batteries with sulfide solid electrolytes.

11:05 AM ES06.06.07

Investigating the Electro-Mechano-Chemical Coupling Phenomena of an Electrolyte in All Solid-State Battery Kethsooem Var1,2, Christel Labetty Robert1, Sofiane Maiza2, David Sicic2 and Damien Bregiroux1; 1Sorbonne Universite - Laboratoire Chimie de la Matiere Condensee de Paris, France; 2Renault Group, France

Lithium-ion technology's energy density is constrained by negative electrode intercalation. The integration of lithium metal into solid-state batteries shows promise for a substantial enhancement of energy density. It would increase energy density from 372 mAh/g to 3862 mAh/g. However, several challenges persist, including cycling pressure, dendrite growth, and volumetric electrode variations that can lead to detachment and cracks in the electrodes, ultimately causing premature battery degradation. This study primarily focuses on understanding the intricate relationships between electrochemical and mechanical properties within solid-state batteries. The chosen material is the argyrodite (Li1xPS4-xCl), which exhibits high ionic conductivity (10^-3 cm/s), comparable to that of liquid electrolytes. This material can be easily compacted through cold pressing due to its favorable mechanical properties. According to literature results, the material has a relatively low Young's modulus [E] 25-40 GPa [1,2], classifying it as a soft material, in contrast to oxide families. The material's intrinsic properties (such as Young's modulus, hardness, viscosity and elasticity, etc.) were investigated using nanoindentation. In order to overcome the reactivity issues related to air and humidity, we have designed a specific device, inspired by Hikima [2] to conduct nanoindentation tests in ambient atmosphere. Young's modulus values for the pure material were around 16 GPa, which is lower than literature. The inconsistency in these results is attributed to the shaping process which introduces factors like porosity and surface inhomogeneity, necessitating refinement. On the other hand we showed that the material has small elastic range, corresponding to its reversible deformation. It becomes evident that expanding the material's elastic range is imperative to accommodate electrolyte volume changes. We studied mechanical properties of argyrodite by a) modifying the particle size to manipulate macrostructural defects, and b) modifying the material's stoichiometry by introducing elements like F, Cl, Br, I. This modification is intended to affect the strength of chemical bonds, consequently influencing the Young's modulus. Simultaneously, on a macroscopic scale, a testing cell is developed to monitor pressure variations during cycling. The Li1xPS4-xCl/LiPS4-xCl/LiPS4-xCl/NMC811 (single or polycrystalline) system is the primary focus. The nearly negligible volumetric variation of LTO allows for the examination of pressure changes specifically at the positive electrode. Using this system, we were able to monitor the impact of electrolyte particle size on the pressure variation. Moreover, a composite with polymer is studied to accommodate volume variation and reduce pressure variation at macroscale.

The ultimate goal of this research is to enhance our understanding of the intricate mechanisms involved in the electro-mechano-chemical coupling and the degradation processes within solid-
Bioinspired Multifunctional Nanocomposites for Energy Storage Applications

Ahmet Emre, Emine Turali-Emre and Nicholas A. Kotov; University of Michigan, United States

8:00 AM *ES06.07.01

Characteristic Analysis of Single Particle Cathode Materials for Sulfide-Based All Solid State Batteries

Jiwon Jeong1,2, Kyounghun Kim1,3, Mingony Kim1,3, Sang Ok Kim1,3, Woo Young Yoon1, Ji-Young Kim1 and Kyung Yoon Chung1,3, 1Korea Institute of Science and Technology, Korea (the Republic of); 2Korea University, Korea (the Republic of); 3KIST School, Korea University of Science and Technology, Korea (the Republic of)

All Solid State Batteries (ASSBs) have great attraction as next generation energy storage technology due to their nonflammable solid electrolytes (SE) and high energy density compared to commercial Li-ion batteries. However, there are still some issues that need to be addressed to move beyond lithium-ion batteries (LIB).

One of the troublesome challenges is the unstable contact between active material and SE. A typical case of unstable interface contact is unwanted side reactions between active material and SE. In particular, among solid particles, sulfide-based solid electrolytes with high reactivity and a narrow operating voltage accumulate ions and electrons at the interface in contact with the cathode active material, causing many side reactions. In order to prevent such a side reaction, there have been efforts to coat the surface of the cathode material with stable polymer, metal oxide, and lithium metal oxide. Another cause of interfacial contact loss is volume change. Whether ASSB or LIB, volume changes occur due to intercalation and deintercalation of lithium in the active material. In particular, materials that achieve higher capacities have larger volume changes because more lithium is accommodated. For this reason, composite anodes containing high-nickel NCMs in ASSB exhibit rapid capacity decline because it is difficult to restore contact between the cathode and the electrolyte once separated. To suppress volume changes, various methods are used, such as controlling the shape of active materials, surface coating using hard materials, and improving the physical properties of solid electrolytes.

Here, we adopt a method of strengthening physical properties of a material and suppress volume changes by growing a cathode active material as a single particle. The single particle cathode material was synthesized by growing the primary particles of the polycrystalline cathode precursor into large sizes. For performance comparison based on physical properties, poly and single particle cathode material is applied to a sulfide based ASSBs. The details will be discussed at the meeting.

8:30 AM *ES06.07.02

Sulfide Solid Electrolyte for Lithium/Sulfide All-Solid-State Batteries

Xiaxin Yao1,2, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China; 2Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, China

All-solid-state lithium batteries are considered as the most promising next generation electrochemical energy storage devices because of their high safety and energy density. Among all solid electrolytes, sulfide solid electrolytes have attracted increasing attention due to their high ionic conductivities and favorable interface compatibility with sulfur-based cathodes.

In the past decade, different sulfide solid electrolytes with room temperature ionic conductivity of $10^{-3} - 10^{-2}\, \text{Scm}^{-1}$ have been successfully synthesized. The moisture stability can be improved with oxide or halogen doping. Besides, according to new water molecule adsorption and dissociation reactions, LiF-coated core-shell solid electrolyte can reduce the adsorption site, thus resulting in superior moisture stability when exposing in moist air. Meanwhile, the ionic conductivity of sulfide solid electrolyte is also enhanced. In order to reduce the sulfide solid electrolyte particle size, a liquid/solid fusion technology is used to synthesize high ionic conductivity sulfide solid electrolyte with reduced particle size.

Based on the high ionic conductive sulfide solid electrolyte powder, thin film can be obtained by cold press solid electrolyte with surface modification and wet coating approaches. The obtained Li$_2$S$_{4}$P$_{4}$S$_{11}$ sulfide solid electrolyte membrane possesses a high ionic conductivity of 8.4 mSm$^{-1}$ with a thickness of 30 μm. The thickness of sulfide solid electrolyte film can be further reduced with relative high ionic conductivity above 1 mSm$^{-1}$.

Due to similar chemical potential, sulfide cathodes show excellent interface compatibility with sulfide solid electrolytes. A series of transition metal sulfides or sulfur-based materials are employed as electrodes for all-solid-state rechargeable batteries based on intercalation/deintercalation and conversion reaction mechanisms. Nevertheless, transition metal polysulfides, such as FeS$_2$, VS$_2$, and MoS$_2$, exhibit typical anionic redox driven electrochemical processes. Combination of electroconductive carbonaceous materials and sulfide solid electrolyte coating can realize three-dimensional electronic/ionic conduction networks at the triple solid-solid contact interface. The well-designed transition metal polysulfide MoS$_2$ nanocomposite delivers a high reversible energy density of $1640\, \text{Wh kg}^{-1}$ based on the active material at 0.1 A g$^{-1}$.

Although bright prospect of all-solid-state lithium batteries, there are still many challenges for their practical application. More attentions should be concerned on the high ionic conductivity and high chemical stable sulfide solid electrolytes, reducing the solid electrolyte thickness, electronic/ionic conduction network construction in the electrode layer, high specific area capacity as well as alleviating stress/strain and volume changes.

References:

Conversion-type cathodes for lithium metal batteries are considered long-term goals due to their low cost and high energy density. However, they suffer from poor cycling life. In this talk, we present various interface engineering strategies, such as designing topotactic reactions and constructing a 3D ionic-electronic network to overcome this challenge. We demonstrate that micro-sized FeSx cathode achieves an long cycling life at a high areal capacity (~4 mAh/cm²) at high current rates. Meanwhile, we also demonstrate Li-FeSx pouch cell prototype with an energy density up to 390 Wh/kg at room temperature without adding external pressure. It reveals the potential of conversion cathodes, even in micro-size, for practical applications.

Related works:
Liping Wang, Zhenrui Wu, Jian Zou, Peng Gao, Xiaobin Niu, Hong Li*, Li-free cathode materials for high energy density lithium batteries, Joule, 3(2019) 2086-2012.
Zhendong Li, Ge Zhou, Shuai Li, Hongyu Liu, Liping Wang*, Hong Li*, Unlocking cycling longevity in micro-sized conversion-type FeS2 cathodes, Joule, just-accepted, 2023.
Jian Zou, Jun Zhao, Bojun Wang, Shulin Chen, Pengyu Chen, Qiwen Ran, Li Li, Xin Wang, Jingming Yao, Hong Li, Jianyu Huang*, Xiaobin Niu*, Liping Wang*, Unraveling the Reaction Mechanism of FeSx as a Li-ion Battery Cathode, ACS Applied Materials & Interfaces, 2020, 12, 40, 44850-44857.

9:15 AM
ES06.07.04
Irreversibility and Structural Distortion in Organic and Inorganic Fullerenes Arising from Electrochemical Cycling of Alkali-Metal-Ions. Arijit Roy, Sonjoy Dey, Shakir Bin Mujib and Garpurjeet Singh, Kansas State University, United States

While large interlayer spacing allows for Na+ and K+ ion storage in transition metal dichalcogenide (TMD) based electrodes, side reactions, and volume change leading to pulverization of crystalline structure are persistent challenges for employing these materials in next-generation devices. Here in this study, we first investigate if irreversibility due to structural distortion resulting in poor cycling stability is also apparent in the case of quantum confined organic and inorganic (TMDs; such as MoS2) fullerenes. To address these problems, we propose upper and lower voltage cut-off experiments to limit specific reactions. Differential capacity curves and derived surface plots highlight the continuation of reactions when a high upper cut-off technique is applied, indirectly suggesting the restriction of structural dissolution. Furthermore, structural preservation in half-cell electrodes during Li+, Na+, or K+ storage delivered better capacity retention with stable performance and higher coulombic efficiency, laying the ground for future works.
Multimaterial Actinic Spatial Control (MASC) 3D Printing

10:30 AM #MF01.02.01
Multimaterial Actinic Spatial Control (MASC) 3D Printing
Andrew Bovdelet
University of Wisconsin–Madison, United States

Creation of multimaterial parts with complete 3-dimensional geometric freedom is a considerable challenge with potentially game-changing potential for manufacturing capabilities. Various approaches within the additive manufacturing and 3D printing communities have relied on equipment modifications that enable segregation of build materials and then selective deposition of different materials (from separate reservoirs) during printing. We propose a chemical approach to multimaterial parts fabrication that allows for a breadth of compositional diversity through orthogonal reaction mechanisms that can be mediated by different wavelengths of light. In this way, we are able to create multimaterial parts from single resin reservoirs (or vats) and control compositional gradients, heterogeneity, feature sizes, and colour without requiring complex crosstalk in a single resin composition.

11:00 AM #MF01.02.02
Multi-Material Volumetric Additive Manufacturing of Hydrogels Using Gelatin as a Sacrificial Network and 3D Suspension Bath
Morgan Riffe1, Matthew Davidson2, Gabriel Seymour1, Abhishek Dhand3, Megan Cooke2, Hannah Zlotnick2, Robert McLeod1,1 and Jason Burdick1,2,3; 1University of Colorado Boulder, United States; 2University of Colorado-Boulder, United States; 3University of Pennsylvania, United States

Volumetric additive manufacturing (VAM) is an emerging layer-by-layer method for the rapid processing of reactive resins into 3D structures, where printing is much faster (seconds) than other lithography and direct ink writing methods (minutes to hours). As a via of resin roteates in the VAM process, patterned light exposure defines a 3D object and then resin that has not undergone gelation can be washed away. Despite the promise of VAM, there are challenges with the printing of soft hydrogel materials from non-viscous precursors, including its fast maturation, and difficulties in controlling the composition and properties of the final structure. To address this, we have introduced a sacrificial gelatin matrix to modulate resin viscosity to support the cyto-compatible VAM printing of macromers based on poly(ethylene glycol), hyaluronic acid (HA), and polycrylamide. After printing, gelatin and unreacted resin are removed by washing at an elevated temperature (37°C). These constructs are soft due to the low polymer concentration and would be difficult to print in other types of additive manufacturing. In this work, we will discuss how we can use this process to enable volumetric 3D printing, including the chemical, material, and optical designs required to do so and recent progress in pushing towards exciting applications.

11:15 AM #MF01.02.03
Upconversion-Enabled Volumetric 3D Printing
Dan Congreve1,2, Tracy Schloemer1,2, Sam Sanders3, Qi Zhou1, Aryn Gallegos1, Hao-Chi Yen1, Mahesh Gangishetty2, Daniel Anderson2, Michael Seitz1,2 and Chris Stokes2; 1Stanford University, United States; 2Rowland Institute at Harvard University, United States

Triplet fusion upconversion, the manipulation of excited states in molecules to convert low energy photons into one higher energy photon, has shown tremendous potential for a wide range of applications. Here, we will discuss how we can use this process to enable volumetric 3D printing, including the chemical, material, and optical designs required to do so and recent progress in pushing towards exciting applications.
The next step in rapid additive manufacturing is represented by volumetric 3D printing, such as xolography. Unlike traditional layer-by-layer approaches, volumetric printing directly polymerizes a defined resin volume, allowing for arbitrary geometries while maintaining high resolution at rapid printing speeds. Xolography is a linear volumetric 3D printing method that utilizes dual-color polymerization for precise volumetric curing. A photostimulable photodetector switches from a dormant to a latent state by illumination with the first wavelength in the UV-light spectrum. Upon illumination with the second wavelength, polymerization is initiated. Based on this principle, the polymerized volume can be set by projecting an image of the second wavelength onto the UV-light sheet. By moving the resin through the UV-light sheet and synchronizing a sequence of images with this movement, complex 3D geometries can be produced in seconds to minutes.

Xolography emerges as a possible choice for medical applications like tissue engineering, owing to its ability to achieve high printing speeds while maintaining high resolution, even with marginal photoinitiator concentrations (0.01wt%) - which can be a safety concern in biomedical contexts - and the use of high-viscosity resins, making it compatible with biodegradable high-molecular-weight polymers. In this study, Xolography is transformed from a batch process into a continuous fabrication method by vertically flowing resin through the UV-light sheet. The sequence of the projected images is synchronized to the resin velocity at the area of both intersecting wavelengths. The flow profile is visualized by computational fluid dynamic simulations. By designing a symmetrical flow cell with four inlets, the flow profile can be adjusted by the ratio of the volume flow through each inlet and is subsequently flattened in the intersecting area of both wavelengths for an enhanced printing resolution.

A second prerequisite for continuously printing objects via xolography is the circumvention of unwanted polymerization by the UV-light only. At increased radiant fluxes, polymerization occurs without the second wavelength. This is particularly the case at the glass-resin boundary where the resin velocity is reduced, and the radiant flux received by the resin is maximized. By integrating oxygen-permeable side windows to the flow cell, oxygen can diffuse into the resin, quench the photoinitiator in the boundary layers and thus prevent unwanted curing. With these modifications, the continuous xolography process achieves recognizable feature sizes of up to 10 μm in x/y and 25 µm in z-direction. Objects can be printed in parallel at a minimum object distance of 80 μm to utilize the entire printing area with constant resolution and print speed, showcasing the flexibility and potential for upsampling continuous volumetric 3D printing via xolography. This innovative approach closes the gap between high volume generation rate at high resolutions and holds great promise for biomedical applications.

SESSION MF01.03: Bioapplications
Session Chairs: Emily Davidson and Emily Pentzer
Tuesday, April 23, 2024
Room 325, Level 3, Summit

1:30 PM *MF01.03.01
A Molecular Approach to Additive Manufacturing Medical Devices for Use in The Clinic
Matthew L. Becker, Duke University, United States

The emergence of additive manufacturing has afforded the ability to fabricate intricate, high resolution, and patient-specific polymeric implants. However, the availability of biocompatible resins with tunable resorption profiles remains a significant hurdle to clinical translation. In this presentation, I will outline our strategies for synthesizing highly functional oligomeric resins that can be photochemically printed into a variety of structures possessing unique mechanical, chemical and degradation properties. I will also describe their use in a number of pre-clinical applications.

2:00 PM MF01.03.02
Materials Development for Additive Manufacture of Magnetic Resonance Imaging (MRI) Phantoms
Brian Derby, University of Manchester, United Kingdom

Magnetic resonance imaging (MRI) is an important non-invasive probe used extensively for medical diagnostics. Phantoms are manufactured devices of controlled specific composition, dimensions and shape that are used for: instrument calibration, to provide common reference samples to allow the calibration of multisite research collaborations, they can act as replacements for human volunteers or live animal models during operator training or technique development. Additive manufacture is an attractive method for the production of phantoms with better physiologic shape reproduction, if appropriate printable materials can be developed that provide the appropriate imaging contrast to mimic healthy and diseased tissue. Phantoms are more difficult to develop for MRI applications than other medical imaging techniques, such as X-ray or ultrasonic imaging, because the imaging contrast is provided by the relaxation times, T1 and T2, of the nuclear magnetic resonance excitations of protons in biological systems. These relaxation times (T1 and T2) in biological tissue are much longer than in conventional polymeric materials because of the presence of water and the soft matter gel nature of biological tissue. Hence, conventional MRI phantom materials are either aqueous solutions or weak gels of biologically extracted hydrogels such as agarose gels, carageens and alginates, possibly doped with paramagnetic ions to further tune the relaxation times. These phantoms have a very limited shelf-life and are normally formulated prior to use and disposed of afterwards. They are not particularly stable and the relaxation may be affected by the local environment, e.g. humidity, ambient temperature or oxygen pressure (altitude of the site).

Here we demonstrate a family of printable materials that have been developed using formulations of silicone resins that can access the T1 and T2 parameter space that encompasses most medically important organs and tissues. This tunability can be achieved using conventional silicone formulations and commercially available resin using simple variation of polymer and oligomer molecular weight and cross-linking density. A second strategy is also presented that uses a multiphase or composite approach with blends of immiscible materials. These formulations are shown to have the rheologic properties appropriate for extrusion additive manufacturing methods. Simple demonstrator structures have been produced that show good imaging quality and stability.

2:15 PM MF01.03.03
3D Printed Core-Shell Structured Scaffolds with NIR-Triggered Dual Release for Cancer Therapy and Uterine Tissue Regeneration
Shangsi Chen, Zhaobei Xu and Min Wang, The University of Hong Kong, Hong Kong

Gynecologic cancers and uterine fibroids can cause dysfunction of the uterus and hence result in female infertility. Various treatment options, including surgical resection, radiation therapy, chemotherapy and hormone therapy, are available for treating gynecologic cancers and uterine fibroids, aiming to restore fertility for women of the child-bearing age. Surgical resection is one of the most used treatments for cancerous tissues and uterine fibroids. However, insufficient clinical intervention can result in tumor recurrence, and the residual defective tissue after surgery can cause intrauterine adhesion (IUA) and further affect women’s reproductive ability. Therefore, new and novel treatments that can effectively kill residual tumor cells and at the same time, regenerate new and healthy uterine tissues should be developed. In the current study, a dual drug/biomolecule release system, with the release being triggered by a near-infrared (NIR) laser that would deliver anticancer drug and biomolecules for promoting uterine tissue regeneration in a chronological manner, was designed and fabricated. In this study, gelatin (Gel) hydrogel/poly(L-lactide-co-trimethylene carbonate) (PLLA-co-TMC, “PTMC” in short) core-shell structured scaffolds with NIR-triggered dual releases of anticancer drug doxorubicin hydrochloride (DOX) and hormone estradiol (E2) were constructed via 3D printing for providing cancer therapy and for promoting uterine regeneration for postoperative females. DOX is a commonly used antineoplastic agent for treating many cancers and has been clinically used for uterine cancers. E2 is an estrogen steroid hormone extensively used to facilitate uterine regeneration. In our fabrication, Gel and DOX were homogeneously mixed first and 3D printed to form Gel-DOX scaffolds. E2-containing polydopamine (PDA@E2) microspheres were synthesized and homogeneously dispersed in PTMC-dichloromethane (DCM) solution. Gel-DOX scaffolds were then soaked in the PDA@E2 solution for fabricating Gel-DOX/PTMC-PDA@E2 core-shell structured scaffolds. It was observed that the PTMC-PDA@E2 coating layer significantly enhanced mechanical properties of the scaffolds, making them comparable strong with the native uterine tissue. Furthermore, the coating layer protected the Gel-DOX core from rapid biodegradation and thus inhibited the burst release of DOX. Moreover, Gel-DOX/PTMC-PDA@E2 scaffolds could release DOX and E2 in a chronological manner, firstly delivering DOX together with photothermal therapy (PTT) to effectively kill Hela cells used in the in vitro experiments and then sustainably releasing E2 over 28 days of the experiment duration to promote uterine tissue regeneration. The in vitro experiments showed that DOX could be quickly released in 3 days and that the core-shell scaffolds exhibited excellent anticancer ability through the synergy of DOX release and hyperthermia cell ablation. E2 via controlled release over the 28 days promoted the proliferation of bone marrow-derived mesenchymal stem cells (BMSCs) and induced their differentiation. The novel Gel-DOX/PTMC-PDA@E2 core-shell scaffolds have shown their high potential for postoperative management for female patients.

3:00 PM BREAK

SESSION MF01.04: Bioapplications / Soft Polymers
Session Chairs: Emily Davidson and Emily Pentzer
Tuesday, April 23, 2024
Room 325, Level 3, Summit
3:30 PM *MF01.04.01
Solvent-Cast 3D Printing with Multi-Material Inks to Independently Control Biochemical and Physical Properties
Lesley W. Chow; Lehigh University, United States

The biochemical and physical properties of a polymer-based biomaterial are commonly tailored to drive desired cellular responses for specific applications. However, modifying one property can lead to unwanted changes to another that make it difficult to fine-tune cell-material interactions. For example, surface chemistry can be controlled by changing composition, but this also impacts mechanical properties. Scaffold stiffness can be tuned without changing polymer type by changing porosity, but pore size and shape also affects cellular infiltration and nutrient and oxygen exchange. To address these challenges, we developed a versatile solvent-cast 3D printing platform using inks containing different polymer MW ratios and/or end-functionalized polymer conjugates to independently control surface chemistry, stiffness, and architecture. Blending different MW ratios of the same polymer allow us to change scaffold stiffness while the end groups of the conjugate become displayed on the surface during fabrication. In addition, using multiple printer heads enable us to spatially deposit different inks to organize biochemical and physical cues within the same construct. This talk will describe our platform and how we are 3D printing heterogeneously organized scaffolds to regenerate complex tissues like the osteochondral interface.

4:00 PM MF01.04.02
3D-Nanomaterials Printing for Tailorable Sensing and Flexible Electronics
Rahim Esfandyarpour and Xiaochang Pei; University of California, Irvine, United States

Over the past decade, three-dimensional (3D) printing technology has fundamentally transformed traditional fabrication and manufacturing, particularly for micro-scale structures, models, and devices. Recent advancements in 3D printing, especially in the domain of nanomaterials, offer benefits such as ease of operation, cost-effectiveness, rapid prototyping, high resolution, and the capability to tailor designs and fabricate sensors customized to specific model requirements, individual needs, or disease diagnostics. Notably, with the rising emphasis on in-situ real-time health monitoring, the demand for wearable sensors is surging. However, to achieve widespread adoption of wearable biosensors for large-scale population monitoring, there’s a need for swift, reliable, cost-effective, and high-throughput integration of these platforms.

In this study, we demonstrate our innovative approach to 3D printing of nanomaterials, successfully producing multiplexed, cost-effective, and mechanically flexible wearable bioelectronic sensing patches. These patches comprise 3D-printed nanomaterial-based flexible sensors and flexible wearable microfluidic sample-handling units, all integrated within just a few hours.

Further, we demonstrated the mechanical and electrical robustness of these patches under repeated bending cycles. We characterized the performance of the sensing units ex situ with various target ion samples across a spectrum of concentrations. Negative control experiments further showcased the patches’ capability for selective ion detection. Additionally, we highlighted the potential of our 3D-printed nanomaterial patches for continuous health monitoring. This was evidenced by the simultaneous in situ monitoring of multiple ions (e.g., H+, Na+, K+, and Ca2+) present in sweat.

Our work represents a significant stride towards enabling personalized health monitoring practices, deploying 3D nanomaterial printing technology for the facile and affordable development of tailored, integrated wearable, and flexible biosensing platforms, optimized for the noninvasive and continuous monitoring of individual health parameters.

4:15 PM *MF01.04.03
Room-Temperature 3D Printing of Super-Soft and Solvent-Free Elastomers
Christopher Bates; University of California, Santa Barbara, United States

This talk will discuss versatile strategies for designing new 3D-printable resins to efficiently access materials with unique properties.

4:45 PM MF01.04.04
Directed Self-Assembly of Thermoplastic Elastomers via 3D Printing for Mechanically Tailored Soft Architectures
Alice Ferguson; Ben H. Gorse and Emily C. Davidson; Princeton University, United States

Many biological systems utilize self-assembled hierarchically ordered structures to achieve complex functional properties. However, current methods cannot scalably achieve this level of control over structure and function across multiple length scales in synthetic systems. Here, we make progress towards bridging this gap by demonstrating the use of material extrusion 3D printing to induce tunable alignment of a cylindrical-forming polystyrene-β-poly(ethylene-co-butylene)-β-polystyrene (SEBS) thermoplastic elastomer along a controlled print path. We demonstrate that the extent of nanostructure alignment and resulting anisotropy can be tuned via the shear and extensional forces applied to the material during 3D printing. In addition, we show that post-printing thermal annealing plays a critical role in maximizing domain alignment via relaxation of trapped stresses. Ultimately, we have demonstrated the ability to induce up to 85% greater tensile modulus along the print direction compared to perpendicular to the print direction. By designing custom print paths for these soft and mechanically anisotropic materials, we enable fabrication of soft architectures with tailored macroscopic mechanical behavior such as controlled localization of strain upon deformation.

5:00 PM MF01.05.01
Development of Binding System for Metal Fused Filament Fabrication of AlSi10Mg Alloy
Gustavo M. Delfino1,2, Kaue R. dos Santos1,2, Leandro J. de Camargo3, Haroldo C. Pinto2 and Tamires d. Nossa1; University of São Paulo, Brazil; 1Federal Institute of Education, Science and Technology - IFSP, Brazil; 2University of São Paulo, Brazil; 3Federal Institute of Education, Science and Technology of São Paulo - IFSP, Brazil

Additive manufacturing technology through 3D printing can efficiently produce parts with complex geometries using smaller, portable equipment. 3D printing plays a significant role in manufacturing polymer prototypes and products in various areas. One promising area of research involves incorporating metallic powder into polymer filaments for 3D printing, aiming to expand the versatility of the technique and provide an alternative to conventional approaches such as Fused Filament Manufacturing (FFF). The binder polymer formulation plays a crucial role in the success of the 3D printing process. This study presents the development of a specific binding system for the 3D printing of AlSi10Mg filaments. The binder includes low-density polyethylene (LDPE) and thermoplastic starch (TPS). LDPE contributes to structural integrity during binder dissolution, reduces viscosity, and increases strength and stiffness. Meanwhile, TPS, besides being biodegradable, provides flexibility to the filaments. The study included an analysis of the shape and size distribution of metallic powder particles before their incorporation into the polymeric matrix. The composite filaments were produced using reactive extrusion (REX), being mechanically characterized and evaluated for their homogeneity. The reactive extrusion method demonstrated effectiveness in the production of homogeneous composite filaments in relation to the metallic filler incorporated into the thermoplastic polymer blend. Although extruded filaments exhibit inferior mechanical properties compared to thermoplastics generally used in FFF additive manufacturing, the method has potential for application in the manufacture of new composite filament compositions using LDPE and TPS blend matrix as a binding for application in 3D printing.

5:00 PM MF01.05.02
Different Strategies for Developing an Electrically Conductive and Flexible Composite by DLP 3D Printing
Luca Montainà1, Rocco Carcione2, Francesca Pescosolido1,3, Silvia Orlanducci1, Silvia Battistoni1 and Emanuela Tamburri1,3; 1University of Tor Vergata, Italy; 2ENEA, Italy; 3University of Tor Vergata, Italy; National Research Council, Italy

Additive manufacturing (AM), or 3D printing, is one of the main elements in the development of Industry 4.0, which can increase plant productivity and improve product quality. Indeed, thanks to the layer-by-layer manufacturing approach, AM opens up the possibility of mass customization of products by achieving complex designs, with minimal material waste. However, despite several advantages of AM, the widespread usage of this technology is still limited by several factors, such as surface finish, standardization, and lack of materials. In this context, the primary contribution of this work involves the design and synthesis of a flexible and electroconductive composite, being the flexibility and conductivity essential properties in various industries, spanning from electronics, to sensors, and wearable technology. In particular, we are focusing our research on different strategies for including a conductive polymer, i.e. polyaniline (PANI), into a polyethylene glycol) diacrylate (PEGDA) matrix by using a Digital Light Processing (DLP) [e1] 3D printer. Such printing technique typically makes use of a light to selectively cure a thin layer of a photosensitive ink. However, the 3D printing technology for CPs is still in its early stages and faces many challenges, mainly related to poor solubility and printability of CP systems. In this context, we report two different protocols for producing PEGDA-PANI items by means of a DLP 3D printer. In the first, an in-situ approach is exploited to synthesize PANI inside a printed PEGDA substrate, by combining 3D printing with a subsequent chemical oxidation process. Conversely, the second approach exploits the printer UV light to start the photopolymerization of aniline monomers directly during a PEGDA printing process. The PEGDA-PANI systems produced by both the methods show suitable morphological and structural
features, as well as electrical and electrochemical performances, making them potentially useful for various soft electronics applications. The two distinct production methods developed highlight the versatility and adaptability of 3D printing in producing electrodecoative materials. Moreover, the possibility to produce flexible and customizable electronics provides broader implications for various industries, as an expanded list of available materials for AM opens doors to novel product designs and functionalities.

5:00 PM MF01.05.03
Material-Process-Property Relationships for Direct-Ink-Writing of Ceramic Matrix Composites

Caitlin Grover1, Imnak Sargin2, Scott Beckman1 and Arda Gozen1; 1Washington State University, United States; 2Middle East Technical University, Turkey

Ceramic matrix composites (CMCs) consist of a reinforcing secondary material phase within a ceramic matrix. These material systems can resist corrosive/oxygenizing environments and have high hardness even at high temperatures. Among the two types of CMCs, ones featuring chopped fiber reinforcements offer simpler processing compared to the ones continuous fiber reinforcement systems. However, chopped fiber CMCs remain inferior to their continuous fiber counterparts in terms of mechanical and thermal properties [1]. This is primarily because the conventional processing methods generally lack control over the part microstructure and produce a randomly distributed reinforcement phase, limiting the achievable property enhancement. Emerging material extrusion-based additive manufacturing methods such as Direct-ink-writing (DIW) offer an exciting potential to address this issue. In DIW, highly viscous inks including ceramic matrix powders and reinforcing fibers are deposited layer-by-layer as they are extruded out of small capillaries. It has been shown that the high shear and extensional stresses experienced by the inks during this process can align the reinforcing particles along the printing direction [2,3], providing means to control final part microstructure.

This study aims to understand the material-process-property relationships for DIW of CMCs including aluminum oxide matrix and chopped silicon carbide fiber reinforcements. Here, we formulate inks by combing aluminum oxide powder and silicon carbide fibers with a liquid phase polymer which is a precursor to silicon carbide. Through a custom DIW print head with integrated capillary rheometry [4] capability, we characterize the shear rates experienced by the inks during the printing process. We then examine the density, microstructure and mechanical properties of the printed and sintered CMCs to understand the influence of the DIW process on these outcomes. We expand the analysis to cover various ink compositions and nozzle sizes to explore the key material and process parameters to achieve microstructural control.

References:

5:00 PM MF01.05.06
Temperature Dependent Hygro-mechanical Behavior of Additively Manufactured Nylon (polyamide 6) and ULTEM (polyetherimide) Continuous Carbon Fiber Composites

Madeline A. Morales, Bradley D. Lawrence and Todd C. Henry; DEVCOM Army Research Laboratory, United States

Fused deposition modeling (FDM) is used extensively for rapid prototyping with 3D printed thermoplastic materials. Nylon (polyamide 6) is a popular filament material; however, the mechanical properties are known to degrade in the presence of moisture and/or elevated temperature. In contrast, ULTEM (polyetherimide) has higher strength/stiffness and resistance to moisture/temperature but is more expensive. This work compares the impact of hygrothermal conditioning on the flexural strength and modulus of Markforged Onyx (Nylon + chopped carbon fiber) and ULTEM 9085 samples with and without the addition of continuous carbon fibers printed using a Markforged FX20 3D printer. Samples for bend testing were conditioned at 90% RH at 22°C for 26 days, and mass/dimension increase was recorded. 3-point bend testing according to ASTM D7264 was conducted while varying temperature from 22°C (room temperature) to 50°C using an Instron load frame with an environmental testing chamber. The rate of flexural strength/modulus decrease with increasing temperature was compared for the four different materials (Onyx, Onyx + continuous carbon fiber, ULTEM, ULTEM + continuous carbon fiber) in the as-printed and conditioned state. Ductile vs. brittle failure mechanisms are discussed considering the polymer moisture content and microstructure. Fiber-polymer interfacial bonding is also discussed. The results will help inform end users of the optimal material to use given the operating load, moisture, and temperature conditions for their specific application.

SESSION MF01.06: Poster Session II: Biomaterials/Bioapplications
Session Chairs: Alice Ferguson and Daryl Yee
Tuesday Afternoon, April 23, 2024
Flex Hall C, Level 2, Summit

5:00 PM MF01.06.01
Additive Manufacturing of 3D Microchannels for Cell Culture

Aman Singhal1, Tejas Y. Suryawanshi1, Arun Jaiswal2, Shobha Shukla1 and Sumit Saxena1; 1Indian Institute of Technology Bombay, India; 2The University of Sydney, Australia

Two-photon polymerization (TPP) has been developed as a direct laser writing technique for the preparation of complex 3D structures with resolution beyond the diffraction limit. Its remarkable characteristics, such as precise 3D fabrication, sub-diffraction resolution, material flexibility, and mild processing conditions, have made it suitable for several applications in biosciences. One such application is the fabrication of microchannel scaffolds for cell culture, which are three-dimensional structures that provide mechanical support and a three-dimensional environment for cells growth and differentiation. Here, we report the fabrication of 3D square microchannels scaffold using TPP technique. Fabricated scaffolds are made up of microchannels and microchannels interconnected to create a porous structure that mimics the extracellular matrix (ECM) of natural tissues that can provide a suitable environment for cell growth and differentiation. These scaffolds can be used in tissue engineering and regenerative medicine applications.

5:00 PM MF01.06.02
Carboxymethylation of Silk Fibroin and Injectable Microgel Assembly Prepared from Thereof

Yoonwoo Yu, Seonghyeon Jo, Yehee Lee and Ki Hoon Lee; Seoul National University, Korea (the Republic of)

Silk fibroin (SF) from silkworm cocoons is a fibrous protein and found its application in various fields such as tissue engineering, drug delivery, soft electronics, etc., owing to its biocompatibility. SF can be fabricated into various different forms, such as films, macro-to-nano fibers, scaffolds, and hydrogels. Among these forms, SF hydrogel can be made by physical and chemical crosslinking. Physical crosslinking of SF is based on the formation of β-sheet structure, which results in a brittle mechanical behavior of the hydrogel. On the other hand, chemical crosslinking of SF through enzymatic crosslink or photo-crosslink results in elastic SF hydrogel. In 3D printing, various kinds of natural polymers are used as ink, and in many cases, 3D constructs are formed upon the gelation of the polymer right after its extrusion. SF was also considered as a candidate natural polymer in 3D printing. In this study, we explore the key material and process parameters to achieve microstructural control.

The aim of this study is to prepare a suitable SF microgel assembly for 3D printing. Many previous studies have been reported on preparing SF microgels, but they had to dissolve the SF fiber. However, large amounts of chemicals are required during this dissolution, and time-consuming dialysis should be followed. We have skipped this step by conducting direct modification of SF. The negative charges of carboxymethyl groups allowed high water uptake and swelling by the repulsive forces, but the dissolution was prevented by the intact β-sheet structure working as a physical crosslinker. By controlling the concentration and the degree of carboxymethylation of SF microgel, optimum conditions for microgel assembly formation were established. Rheological studies confirmed the injectability of SF microgel assembly, in which gel-like behavior under a low shear rate but flowability under a high shear rate. Finally, we have successfully built a standalone 3D construct of SF microgel assembly by extrusion 3D printer. The prepared SF microgel would have high potential in tissue engineering, and enhancing the structural stability of the 3D construct of SF microgel is currently underway.
As the main structural protein found in connective tissues, type I collagen constitutes approximately 70-80% of the dry weight in ligaments and tendons.[1] Ligaments and tendons coordinate and stabilize our body’s movement, but damage to these soft tissues accounts for 30% of musculoskeletal clinical cases every year.[2] While athletes who play contact sports are most commonly prone to sprains or ruptures of the anterior cruciate ligament (ACL), people can experience ligament and tendon injuries through falls, twists, or overuse. The patient’s body, which often requires months of recovery and fails to achieve enthesis healing or true regenerative capabilities. Promisingly, the development of synthetic biomaterials that mimic the native hierarchical structure of ligaments/tendons can facilitate tissue repair.[3]

The overarching goal of our work is to elucidate the relationship between printing parameters and mechanical behavior of collagen bioinks to fabricate tunable scaffolds for biocompatible implants. With an eye towards translation and ease-of-use, we utilize the commercially-available CellInk BiO bioprinter and two different concentration collagen bioinks to control the infill density and heating duration for extruded 5x5x3mm³ cubes. Scanning electron microscopy (SEM) is first used to visualize the collagen bioink’s surface morphology, and uniaxial compressive loading is performed post-crosslinking to evaluate the material’s strength and stiffness. Secondly, we aim to create a stiffness gradient by varying incubation time across layer height so that the printed collagen can achieve enhanced integration as a connective tissue. Preliminary results indicate that the higher collagen concentration (70mg/mL) hydrogels require at least 35 minutes of heating time for sufficient crosslinking compared to the recommended 30 minutes for the low collagen concentration (35 mg/mL) samples. Meanwhile, longer heating durations have a greater effect on producing higher strength and stiffness prints compared to changes in infill density alone. Ultimately, optimizing the printing parameters that determine resultant mechanical behavior of collagen bioinks will inform customizable, on-demand printing of ligaments and tendons for regenerative medicine.


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**5:00 PM MF01.07.01**

Stimuli-Responsive Microscale Mechanical Logic Abhinav Parakh, Caitlyn C. Krikorian (Cook), Elaine Lee and Widianto P. Moestopo; Lawrence Livermore National Laboratory, United States

To overcome the operational limitations of conventional electronics, equivalent logic circuits composed of precisely fabricated mechanical systems have shown promise as a viable alternative here. We develop microscale, battery-free mechanical sensors in which stimuli-responsive materials are paired with micro-scale mechanical circuits to enable high mechanical computing power within a sensor system. We utilize additive manufacturing with micro-scale precision to fabricate structures that respond to thermal and chemical changes, and we perform computation by applying these stimuli. By integrating multiple stimuli-responsive actuators to mechanical logic gates, we demonstrate proof-of-concept computation of environmental cues in the microscale without electrical power. Our exploration of signal propagation dynamics in microscale mechanical logic circuits actuated by materials with different stimuli responsiveness will accelerate the development of smart, active, and sentient materials that can interface with extreme environments and respond to external changes without needing batteries. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 (LLNL-ABS-850674). Support from LDRD Exploratory Research 22-ERD-030 and LDRD Feasibility Study 24-FS-018 are gratefully acknowledged.

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**5:00 PM MF01.07.02**

Investigation of Mechanical Performance of Composites Based on ‘Hat’ Aperiodic Monotile Structures Hyung June Jung, Ailin Chen and Grace Gu; UC Berkeley, United States

Disordered structures, as oftentimes found in nature, have the potential to have unique behaviors and higher mechanical performance in terms of stiffness, strength, and toughness compared to ordered structures. However, such a disordered structure increases the complexity of design and fabrication process, which can be resolved if the infinite plane can be aperiodically covered with a single unit cell (i.e. aperiodic monotile). With the long efforts of the mathematics community, a hat-shaped aperiodic monotile structure was recently discovered. This study proposes new composite designs using an aperiodic monotile structure and investigates mechanical performance and mechanisms. For tensile loading, aperiodic monotile composites consisting of stiffer material for core areas and softer material for boundaries are considered varying volume fractions of each phase. On the other hand, for compressive loading, the composites composed of stiffer material forming boundaries and softer material as filling are examined with different size of unit cells. The specimens are fabricated using multimaterial polyjet additive manufacturing processes. To probe further into the mechanisms, phase field modeling based fracture simulations are conducted for tensile loading cases and explicit dynamic fracture simulations are conducted for compressive loading cases. Simulations show that aperiodic monotile structure enables high strength and toughness compared to a honeycomb structure under tensile loading. In addition, the aperiodicity of the aperiodic monotile structure allows superior performance under compression compared to the periodic structure. This study shows that the aperiodic monotile composite structure can be next generation of composite structure showing superiority to other conventional composite structures in terms of stiffness, strength, and toughness.

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**5:00 PM MF01.07.03**

Xerographic 3D Printing with Periodic Patterns Hyung Ju Ryu, Hadi Moein Mia, Omar Nemir, Sami Khan and Woo Soo Kim; Simon Fraser University, Canada

3D Printing, a form of additive manufacturing (AM) has gained widespread popularity for the fabrication of intricate structures. It is recognized as an innovative solution to overcome the limitations associated with traditional subtractive manufacturing methods. It also offers cost efficiency, design flexibility, rapid prototyping, and environmentally friendly attributes. In this research, we explore the Xerographic 3D printing method. The objective is to fully harness the potential of AM, capitalizing on the high productivity of the well-established Xerographic 2D digital printing techniques. In addition to the core electrostatic interactions underpinning the Xerographic dry copying process, our work introduces hydrophobic interactions between fluoro- polymer particles and interin and Xerographic substrates, thus contributing to the formation of 3D structures through a transfer method. To implement this approach, we use a surface micro-texturing technique to create periodic structures on metal substrates followed by surface functionalization, which subsequently impacts hydrophobic properties. Thus, our research reveals that the supplementary hydrophobic effects substantially improve the fidelity and precision of 3D structures produced through Xerographic 3D printing. Our study is poised to advance the utilization of Xerographic 3D printing by providing a more efficient avenue for 3D structure fabrication while also deepening our understanding of the interaction mechanisms within the Xerographic setup.

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**5:00 PM MF01.07.04**

Materials Design guided by Defects in Liquid Crystals Jeremy R. Money¹, Fakhreddin Emami¹, Andrew Gross¹, Jose A. Martinez-Gonzalez² and Monirasadat Sadatî¹; ¹University of South Carolina, United States; ²Universidad Autónoma de San Luis Potosí, Mexico

Architected cellular materials represent a growing body of materials research encompassing a broad classification of materials, from open celled foams to sheet-based lattices. Comprised of unit cells of varying geometries and tessellation patterns, these material systems give rise to unique properties attributed primarily to their unit cell geometry as opposed to their bulk material chemistry. Enabled by additive manufacturing technologies, architectured cellular materials are increasingly making their way into commercial design and production, offering solutions to many challenges faced by industries such as biomedicine and personal protective equipment and energy. However, additional barriers to ubiquity such as the stiffness/toughness tradeoff of lattice based architectured cellular materials present opportunities for the development of novel unit cell geometries with tunable topological features. Current areas of design inspiration are drawn from the intricate patterns displayed by nature or solid atomic crystals. However, the opportunity for novel approaches to unit cell design presents a frontier ripe for exploration.
Nowadays, micro-scale light-emitting diodes (LEDs) are widely used in applications requiring high light emission and efficiency. To achieve the maximum chucking force, the development of efficient LED encapsulating materials is critical. Conventional encapsulating materials, such as Polydimethylsiloxane (PDMS) and Polyethylene Glycol, face challenges in terms of high thermal stability and refractive index, which limit their performance in LED applications. To overcome these limitations, novel encapsulating materials have been developed, such as Polyethylene Terephthalate (PET) and Polyamide (PA), which exhibit improved thermal stability and refractive index properties.

To further enhance the performance of LED encapsulating materials, a combination of distinct materials was selected for the body and dielectric layer of the Electrostatic Chuck (ESC). This ESC design, fabricated using Ceramic 3D Printing technology, aimed to create a highly efficient and durable device that can be used in various applications, including semiconductor wafer and LCD panel adsorption. The ESC consists of an insulating layer (body), a dielectric layer, and an electrode in which the electrode is formed in a bi-polar type and interdigitated pattern. The chucking force is known to be enhanced by optimizing the dielectric constant and breakdown voltage of the dielectric materials. However, it is difficult to find a single material that can simultaneously exhibit both required characteristics. In this study, two distinct materials were selected for the body and dielectric layer of the ESC.

Two different ceramic composite resins were formulated by varying the content of BaTiO3 (BTO) and Al2O3 (Alumina) between 0 to 30 vol% within a photocurable resin. BTO, which has a relatively high dielectric constant (εr ~ 23) but a lower breakdown voltage (7 kV/mm), was used for the dielectric layer. In contrast, Alumina, with a lower dielectric constant (εr ~ 6) but a higher breakdown voltage (43 kV/mm), was chosen for the body. Using the DLP (Digital Light Processing) 3D printing technology, a body comprising alumina with an interdigitated electrode pattern was created. Subsequently, the body was coated with a dielectric layer composed of BTO. The structural dimensions of the ESC were optimized through the finite element simulation (COMSOL). The simulation results indicate that the measured chucking force of the fabricated ESC was compared and analyzed. The ESC made of a combination of Alumina (body) and BTO (dielectric layer) exhibited superior performance compared to ESCs made solely of Alumina or BTO for both body and dielectric layer. Additionally, these findings were consistent with the simulation results. In this study, by utilizing ceramic composite resin to photopolymerized 3D printing technology, it was possible to achieve electrostatic chucking performance through 3D ceramic printing.

Controlling Dielectric Constant and Breakdown Voltage for Optimizing Chucking Force in 3D-Printed Electrostatic Chucks: A Combined Simulation and Experimental Investigation

Yujin Kim, Jihoon Kim and Suken Yoong; Korea National University, Korea (the Republic of)

Electrostatic chuck (ESC) is used to adsorb objects such as semiconductor wafers and LCD panels using electrostatic force and is attracting great attention as a device that can compensate for the shortcomings caused by mechanical clamps or vacuum chuck. The ESC is composed of an insulating layer (body), a dielectric layer, and an electrode in which the electrode is formed in a bi-polar type and interdigitated pattern. The chucking force is known to be enhanced by optimizing the dielectric constant and breakdown voltage of the dielectric materials. However, it is difficult to find a single material that simultaneously exhibits both required characteristics. In this study, two distinct materials were selected for the body and dielectric layer of the ESC.

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5:00 PM - 5:00 PM

Dual-Function Hydrogel-Based Smart Wearables: AI-Driven Temperature Responsiveness & UV Index-Indicative Color Monitoring

Munseong Kim, Jihoon Kim and Suken Yoong; Korea National University, Korea (the Republic of)

These transformative hydrogel wearables challenge existing perceptions of material capabilities. With direct colorimetric feedback for UV protection and AI-assisted temperature monitoring, this novel approach leverages the unique properties of hydrogel composites to create a smart wearable that not only serves as a protective barrier against harmful UV rays but also offers real-time temperature monitoring. The wearable design is created using Digital Light Processing (DLP) technology, which allows for the fabrication of durable and precise components through the precise control of light exposure during the 3D printing process. The use of a combination of hydrogel composites and high-performing optical materials ensures that the wearable is not only functional but also provides a comfortable and versatile user experience.

While this technology stands out for its exceptional precision and rapid production speeds, it also highlights the importance of balancing form, function, and comfort. The wearable’s design prioritizes the integration of advanced technology with a user-friendly interface, ensuring that the device is not only effective in monitoring personal thermal environments but also visually appealing. The inclusion of AI-assisted temperature monitoring further enhances the device’s utility, providing users with real-time insights into their thermal environment. This combination of features not only meets the needs of consumers seeking protection from UV exposure but also caters to individuals interested in maintaining optimal body temperature, offering a multi-functional wearable solution.

5:00 PM - 5:00 PM

Controlling Dielectric Constant and Breakdown Voltage for Optimizing Chucking Force in 3D-Printed Electrostatic Chucks: A Combined Simulation and Experimental Investigation

Yujin Kim, Jihoon Kim and Suken Yoong; Korea National University, Korea (the Republic of)

Electrostatic chuck (ESC) is used to adsorb objects such as semiconductor wafers and LCD panels using electrostatic force and is attracting great attention as a device that can compensate for the shortcomings caused by mechanical clamps or vacuum chuck. The ESC is composed of an insulating layer (body), a dielectric layer, and an electrode in which the electrode is formed in a bi-polar type and interdigitated pattern. The chucking force is known to be enhanced by optimizing the dielectric constant and breakdown voltage of the dielectric materials. However, it is difficult to find a single material that simultaneously exhibits both required characteristics. In this study, two distinct materials were selected for the body and dielectric layer of the ESC.

Two different ceramic composite resins were formulated by varying the content of BaTiO3 (BTO) and Al2O3 (Alumina) between 0 to 30 vol% within a photocurable resin. BTO, which has a relatively high dielectric constant (εr ~ 23) but a lower breakdown voltage (7 kV/mm), was used for the dielectric layer. In contrast, Alumina, with a lower dielectric constant (εr ~ 6) but a higher breakdown voltage (43 kV/mm), was chosen for the body. Using the DLP (Digital Light Processing) 3D printing technology, a body comprising alumina with an interdigitated electrode pattern was created. Subsequently, the body was coated with a dielectric layer composed of BTO. The structural dimensions of the ESC were optimized through the finite element simulation (COMSOL). The simulation results indicate that the measured chucking force of the fabricated ESC was compared and analyzed. The ESC made of a combination of Alumina (body) and BTO (dielectric layer) exhibited superior performance compared to ESCs made solely of Alumina or BTO for both body and dielectric layer. Additionally, these findings were consistent with the simulation results. In this study, by utilizing ceramic composite resin to photopolymerized 3D printing technology, it was possible to achieve electrostatic chucking performance through 3D ceramic printing.

5:00 PM - 5:00 PM

Dual-Function Hydrogel-Based Smart Wearables: AI-Driven Temperature Responsiveness & UV Index-Indicative Color Monitoring

Munseong Kim, Jihoon Kim and Suken Yoong; Korea National University, Korea (the Republic of)

These transformative hydrogel wearables challenge existing perceptions of material capabilities. With direct colorimetric feedback for UV protection and AI-assisted temperature monitoring, this novel approach leverages the unique properties of hydrogel composites to create a smart wearable that not only serves as a protective barrier against harmful UV rays but also offers real-time temperature monitoring. The wearable design is created using Digital Light Processing (DLP) technology, which allows for the fabrication of durable and precise components through the precise control of light exposure during the 3D printing process. The use of a combination of hydrogel composites and high-performing optical materials ensures that the wearable is not only functional but also provides a comfortable and versatile user experience.

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3D Printed Stretchable Soft Electronics with Metamaterials-Inspired Electromagnetic Architecture
LeiHua Li, Dwipak Sahu, Jared Anklam, Samuel H. Hales, Samannoy Ghosh and Yong Lin Kong; University of Utah, United States

The integration of electronics with soft and stretchable materials can enable active functionalities on the otherwise passive constructs. Previous works have demonstrated exciting success in imparting stretchability with geometrical designs but often require challenging microfabrication processes. Here, we propose a 3D printing approach that can create freeform electronics by selectively annealing metal-extruded nanomaterials in situ using a metamaterials-inspired electromagnetic architecture. This enables the creation of microscale three-dimensional interconnects and electronics with a desktop-sized platform that can resist strain and flexing – allowing the integration of stretchable active components on a soft substrate. We are also studying the integration of printed electronics into a broad range of soft materials by leveraging soft matter physics phenomena. Overall, we envision that this approach can enable new fabrication methodologies that lead to strategies that not only improve device compatibility and durability but also enable new classes of 3D-printed soft electronics.

3D Printing of Polyvinyl Alcohol Hydrogels (PVA) Enabled by Aqueous Two-Phase System (ATPS) — Michihiro Hashimoto; Singapore University of Technology and Design, Singapore

The synthesis of PVA hydrogels (PVA-Hy) requires a high-concentration alkali solution (e.g., sodium hydroxide, NaOH, 4.2 M), and the rapid physical crosslinking of PVA makes it challenging to ensure layer-to-layer adhesion for 3D printing. This work demonstrated the three-dimensional (3D) printing of PVA hydrogels in benign conditions (NaOH, 0.3 M) using a two-phase system (ATPS). Salting out of PVA to form ATPS allowed temporal stabilization of 3D-printed PVA structures while it was physically crosslinked by moderate alkaline conditions. Crucially, the layer-by-layer printing of PVA was enabled by delayed reaction at low alkaline concentrations. To verify this principle, we studied the feasibility of direct ink write (DIW) 3D printing of PVA inks (5 – 25% w/w, m = 0.1 – 20 Pa s, and MW = 22000 and 74800) in aqueous embedding media offering three distinct chemical environments: (1) salts for salting out (e.g., Na2SO4), (2) alkali hydroxides for physical crosslinking (e.g., NaOH), and (3) mixture of salt and alkali hydroxide. The presence of the salt did not compromise the stretchability and durability of PVA-Hy. Overall, our method demonstrated a unique concept of embedded 3D printing enabled by ATPS for temporary stabilization of the printed structures to facilitate 3D fabrication.

A Digital Exploration of The Mechanical Property Space of Self-Stabilizing Dynamic Printable Foams — Brett A. Emery1, Daniel Revier2, Kelsey Snap3, Jeff Lipton1 and Keith Brown3; 1Northeastern University, United States; 2University of Washington, United States; 3Boston University, United States

Foams are versatile by nature, and are used ubiquitously in applications ranging from padding and insulation to acoustic dampening. Previous work established that foams additively manufactured via Viscous Thread Printing (VTP) are capable of enabling a greater degree of control over many of the key mechanical properties of conventional foams such as Young’s modulus, fracture characteristics, and toughness while eliminating the need for chemical foaming agents. However, the relationship between input parameters and output properties is currently only accomplished via iterative empirical testing which limits generalizability and predictive control of desired output properties. Our work addresses this by combining high-throughput automated experimentation with machine learning to identify a subspace able to predict material behavior down to the stress-strain curve level. We identify a self-stabilizing microstructure trend in the VTP process, amplifying confidence in achieving desired output properties. Evidence for this self-stabilization is demonstrated by introducing various print height perturbations during the print process and measuring layer thickness as a function of the number of layers before restitution. This predictive mapping was developed utilizing data collected from thermoplastic polyurethane (TPU) specimens before being generalized by applying assumptions inherent to filament-based additive manufacturing to VTP's core physical models. This generalization was then validated using polylactic acid (PLA) and Nylon suggesting inherent compatibility with any material suitable for filament-based 3D printing.

Temperature-Responsive Dynamic Granular Hydrogels for 4D Printing Applications — Keisuke Nakamura, Nikolas Di Caprio and Jason Burdick; CU Boulder, United States

4D printing is an emerging technology to fabricate dynamic objects that can change their shape and properties in response to external stimuli (e.g., temperature). Such 4D printed materials have a wide range of potential applications, including soft robotics, active drug delivery systems, and pharmaceutical models. Granular hydrogels, comprised of jammed microparticles, are promising as 3D printable materials due to their shear-thinning and self-healing properties, as well as unique micropore structure. By introducing stimul responsive materials (e.g., volume transitions) into individual microparticles, we anticipated that printed granular hydrogels would exhibit dynamic macroscopic and microstructure properties; such dynamic granular hydrogels remain largely unexplored. To investigate this, we developed temperature-responsive microparticles and assembled them into granular hydrogels to explore their application for 4D printing. Specifically, temperature responsiveness was achieved by crosslinking norbornene-modified hyaluronic acid (NorHA) with dithiol-terminated poly(N-isopropyl acrylamide) (DTPN) via a thiol-ene reaction, which showed a low critical solution temperature (LCST) transition. To form microparticles, an emulsion of NorHA, DTPN, and photoinitiator was formed in stirring mineral oil and crosslinked via UV irradiation, which produced microparticles with an average diameter of ~155 µm at room temperature (rt) after washing from the oil. Microparticles diameters decreased by ~29% when heated (41°C), which was reversible when cooled back to rt. Granular hydrogels were prepared from microparticles, with structures exhibiting porosity and pore sizes of ~18 % and ~5360 µm², respectively, at rt. The porosity and the pore sizes significantly increased (~28 % and ~10300 µm², respectively) when heated (41°C), presumably due to micropore shrinkage and disconnection. To enhance the stability of granular hydrogels, we utilized an inter-printer photocrosslinking process that was integrated into a multi-material 3D printing system. Post-print crosslinking of printed granular hydrogels was achieved by using a 3D printer equipped with a UV light module, which allowed arbitrary post-print crosslinking. By adjusting the post-print crosslinking time, we were able to control the degree of crosslinking. The resulting hydrogels were able to undergo multiple shape changes upon heating and cooling, demonstrating the potential for dynamic hydrogels in 4D printing applications.

3D Printing-Assisted Casting of Soft Electronic Materials — Yue (Jessica) Wang; University of California, Merced, United States

It is challenging to balance architectural complexity, electrical conductance, and material generality for the 3D printing of soft electronic materials. In this talk, I will discuss our efforts on 3D printing-assisted casting to alleviate this trade-off. Light-based 3D printing is used to create hollow molds, providing structural complexity and design freedom, whereas the casting nature imparts material versatility. The casting molds are made of superabsorbent polymers and printed in a partially hydrated state. Their dehydration provides significantly enhanced feature resolution and excellent thermal and mechanical properties, making them versatile for casting. After casting and curing desired materials within the mold cavity, over-hydration of the molds facilitate their energy-efficient removal. Using a polymeric conductor, poly(3,4-ethylendioxythiophene) (PEDOT), as a model system, complex architectures such as octet and truncated octahedron can be achieved. Composing silver flakes with PEDOT through a thermal injection process leads to prints with conductivity over 6000 S/cm. This method can also be applied to other hard-to-print soft materials and composites, and potentially enable multi-material structures through sequential casting.

SESSION MF01.10: High Performance Polymers
Session Chairs: Emily Pentzer and Daryl Yee
Wednesday Morning, April 24, 2024
Room 325, Level 3, Summit

8:30 AM MF01.09.01
3D Printed Stretchable Soft Electronics with Metamaterials-Inspired Electromagnetic Architecture — LeiHua Li, Dwipak Sahu, Jared Anklam, Samuel H. Hales, Samannoy Ghosh and Yong Lin Kong; University of Utah, United States

8:45 AM MF01.09.02
3D Printing of Polyvinyl Alcohol Hydrogels (PVA) Enabled by Aqueous Two-Phase System (ATPS) — Michihiro Hashimoto; Singapore University of Technology and Design, Singapore

9:00 AM MF01.09.03
A Digital Exploration of The Mechanical Property Space of Self-Stabilizing Dynamic Printable Foams — Brett A. Emery1, Daniel Revier2, Kelsey Snap3, Jeff Lipton1 and Keith Brown3; 1Northeastern University, United States; 2University of Washington, United States; 3Boston University, United States

9:15 AM MF01.09.04
Temperature-Responsive Dynamic Granular Hydrogels for 4D Printing Applications — Keisuke Nakamura, Nikolas Di Caprio and Jason Burdick; CU Boulder, United States

9:30 AM MF01.09.05
3D Printing-Assisted Casting of Soft Electronic Materials — Yue (Jessica) Wang; University of California, Merced, United States

10:00 AM BREAK
The Practical Application of Additive Manufacturing for Extreme Environments

Melissa A. Smith and Bradley Duncan; MIT Lincoln Laboratory, United States

In the automotive, aerospace, and defense industries, there is need for additively manufactured components that cannot only withstand extreme environments but also be capable of multiple functions or enhanced capabilities. Existing material sets for additively manufactured components are often unsuitable for extreme environments, which limit their practical use and implementation. For example, organic or polymeric components are not rugged or suitable for temperature extremes. More rugged materials (metals and ceramics) can be difficult and expensive to process and are constrained in their compatibility to make composites or blends, hindering the fabrication of multifunctional structures. At MIT Lincoln Laboratory, our mission being technology in support of national security, we develop new materials sets to address shortcomings of the existing, well-established material sets. Success in this mission will facilitate not only the adoption of additive manufacturing for demanding or extreme applications, but also to provide a more far-reaching technological advantage. Specifically, this talk will highlight three distinct cases where new materials are implemented for (1) thermal, mechanical, and chemical stability extreme environments by using inorganic glass-based structures, (2) shielding of high energy particles or radiation for the localized protection of electronic components in space systems by designing composite materials consisting of materials with high and low atomic numbers, and (3) for obscuring transmission line designs in radio frequency systems using graded dielectrics. In all cases, the materials and composites were processed using direct write additive manufacturing, which features low processing temperatures and active mixing. Further, we expect the wide adoption of these materials and methods and also the increased acceptance of additively manufactured components for real applications (beyond prototyping and structural modelling), especially those in extreme environments.

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This material is based upon work supported by the Under Secretary of Defense for Research and Engineering under Air Force Contract No. FA8702-15-D-0001. Any opinions, findings, conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Under Secretary of Defense for Research and Engineering.

11:00 AM MF01.10.02
3D Printed Electromagnetic Wave Absorber based on Carbon Black-Based Load-Bearing Metastructure Jeongwoo Lee1, Daniel D. Lim2, Jaemin Lee1, Dowon Noh1, Sujin Park1, Grace Gu2 and Wonjoon Choi1; 1Korea University, Korea (the Republic of); 2University of California, Berkeley, United States

As electronic equipment becomes more diverse and miniaturized due to advances in science and technology, addressing the issues of interference shielding and electromagnetic (EM) radiation absorption becomes increasingly important. Carbon-based composites combined with porous metastructures are lightweight, flexible and their EM properties can be modified in a desired frequency band, making them suitable for a variety of applications. However, the low density of these structures intrinsically limits their mechanical properties.

In this study, we report a multifunctional broadband metamaterial absorber (MBMA) with EM wave absorption, energy absorption, and constant relative stiffness using a bending-dominated lattice structure based on Kelvin Foam comprising carbon-black composite polyacrylate acid (PLA). Using computational simulation, EM wave characteristics are optimized by adjusting structural parameters such as beam diameter and unit cell size, and intrinsic material properties like dielectric constant according to carbon black filler concentration. Then, the optimized structure is additively manufactured for experimental validation to demonstrate the feasibility of actual implementation. The results demonstrate that MBMA achieves an outstanding broadband (C-Ka band) EM wave absorption rate (>90%, average 95.9%) even at densities as low as cork (200 kg/m³), with a maximum absorption of 99.1% at 15.8 GHz. Regardless of the layer stacking direction, the relative density-to-relative stiffness ratio is close to 2.0, maintaining the theoretical stiffness of Kelvin Foam. The experimentally measured performances using 3D-printed MBMA are almost identical to the theoretically confirmed simulation results, validating the design and fabrication of the developed structure. This rational design strategy using 3D lattice structures can inspire multifunctionality of mechanical metamaterials including EM wave absorption, enabled by developing various polymer-based materials and unit cell structures.

11:15 AM MF01.10.03
Responsive 3D Printed Composites for Protective Applications Miaojian Zou and Sebastian Pattison; University of Cambridge, United Kingdom

Responsive materials that change their properties depending on their environment could enable diverse new medical, wearable, and other devices with exceptional function and compact form factors. Shear-stiffening gels (SSG) can be flexible but harden in response to rapid impact. This could enable protective devices amongst other applications. However, SSG can be easily deformed under external force and cannot recover its original shape, which limits its potential applications. In this work, we develop a 3D-printed elastic shear-stiffening composite to achieve shear-stiffening behavior alongside shape recovery. We find that the composite displays good anti-impact properties better than pure SSG, as well as shape recoverability. We also describe initial results describing further applications for these structures enabled by complex 3D printed geometries.

11:30 AM MF01.10.04
Digital Light Processing of Stiff yet Tough Single Network Hydrogels Abhishek Dhand1, Matthew Davidson2, Hannah Zlotnick2 and Jason Burdick1,2; 1University of Pennsylvania/Ivania, United States; 2University of Colorado Boulder, United States

Wide applicability of hydrogels towards tissue repair, drug delivery, or biomedical devices is often restricted due to weak mechanical properties and an inability to process them into structures compatible with native tissue architecture. Conventional strategies to enhance stiffness through increased number of crosslinks often result in embrittlement.

To process highly entangled hydrogels into complex shapes with open, interconnected pores (e.g., trabecular structure), hollow channels, and knotted topologies with high print fidelity and resolution. These 3D printed structures can sustain cyclic (tensile or compressive) loading and recover their original shape with minimal hysteresis. Further, we show that CLEAR can be applied to other monomer systems through changing the type of monomer (e.g., N-isopropylacrylamide, acrylic acid) or the type of crosslinker (e.g., polyethylene glycol PEG diacrylate, gelatin methacrylamide) to obtain 3D printed, swollen single network hydrogels with modulus and toughness values as high as 300 kPa and 1.8 MJ m⁻³.

As a potential biomedical application, we demonstrate the use of 3D printed, cytocompatible highly entangled hydrogels towards the localized protection of electronic components in space systems by designing composite materials consisting of materials with high and low atomic numbers, and for obscuring transmission line designs in radio frequency systems using graded dielectrics. In all cases, the materials and composites were processed using direct write additive manufacturing, which features low processing temperatures and active mixing. Further, we expect the wide adoption of these materials and methods and also the increased acceptance of additively manufactured components for real applications (beyond prototyping and structural modelling), especially those in extreme environments.

11:45 AM MF01.10.05
Fracture Resistant Architectured Polymers Using Material and Structural Size Effects Zainab S. Patel, Abdulaziz Alrashed and Lucas Meza; University of Washington, United States

Strength and toughness are both highly desirable properties of structural materials, but they are often thought of as mutually exclusive, i.e., it is difficult to increase one without decreasing the other. Much work has gone toward developing materials that are both strong and tough using different composite architectures and material processing techniques.
but they generally ignore the role of length scale and structural size-effects on toughness. In this role, we develop nanoarchitected polymeric materials that utilize heterogeneity and size-affected ductility to enhance their toughness without sacrificing strength. We create specimens with layered architectures in a micro-single edge notch bend configuration using two-photon lithography and various post-processing techniques. Gradually reducing the layer thickness results in an increased fracture energy and slower, stable crack propagation, a phenomenon that became pronounced as the layer thickness approached or was smaller than the material fracture process zone (D = FPZ). This energetic size effect is quantified using Bazant’s Size Effect Law. The thinness of these layered structures demonstrated an increase in toughness by 5x from 60 J/m² to 300 J/m² as interlayer spacing was increased from 0 to 4 μm, a value that is augmented by the creation of heterogeneity along the crack path. Cracks are observed to rapidly propagate in specimens with no interlayer spacing, but then show increasing blunting and deflection in structures with moderately spaced interlayers (~ 3 μm). For larger interlayer spacings (>3 μm), cracks do not propagate through; rather, deflect along the interlayer even at very large displacements. Notably, these materials do not show an appreciable loss in strength and stiffness up to an intermediate layer spacing despite a ~40% reduction in density. The results of this study not only demonstrate the large degree of tunability in these architectures but also show how to fundamentally utilize size effects to create architectured materials with unprecedented properties.

SESSION MF01.11: Intelligent Polymers / Stimuli Responsive
Session Chairs: Emily Pentzer and Daryl Yee
Wednesday Afternoon, April 24, 2024
Room 325, Level 3, Summit

1:30 PM MF01.11.01
Molecular Control via Dynamic Bonding Enables Material Responsiveness in Additively Manufactured Metallo-Polyelectrolytes Seeda Lee, Pierre Walker, Seneca Velling, Amylynn Chen, Zhen-Gang Wang and Julia R. Greer; California Institute of Technology, United States

Metallo-polyelectrolyte Complexes (MPEC) are a class of soft materials that exhibit unique mechanical and physical properties through reversible electrostatic interactions between dynamic crosslinkers (multivalent metal ions) and charged polymer chains. These molecular-level processes give rise to a wide range of material dynamic responses, for example, stimuli-responsive, self-healing, and high toughness through enhanced energy dissipation. The current state-of-the-art fabrication method based on the multistep nature of solution-based metallo-polyelectrolyte synthesis produces materials that suffer from poor long-term stability and inhomogeneity or relies on covalent crosslinking as a backstop for indirect synthesis. The range of scales involved in determining the behavior of MPECs (local bond liability, polymer configurations, and macroscale behavior) further presents computational challenges, which limits the broader application of models to guide experimental methods.

In this work, we demonstrate a facile, single-step fabrication method for MPECs via stereolithography, which produces homogeneous, stable, and high-longevity materials using a straightforward synthesis route. Then, aided by the robust fabrication platform, we present a theory-guided, physically-informed multi-scale study of MPECs. We have developed a roadmap that outlines the effect of different chemical species on the additively manufactured MPEC properties which can be used to tailor its functionality and responsiveness at material level. Our fabrication method enables easy compositional tuning by a simple swap of metal salt precursors during the resin formulation, which allows the wide selection of metal ions and produces a variety of metal-coordinated polymers.

We demonstrate the tunability of mechanical response by adjusting metal ion valency and polymer charge sparsity. We find that mono-, di-, and trivalent metal ions affect control of the coordination environment and bond strength, which propagate to the macroscale properties where higher valency ions result in stiffer and tougher materials. Polyanion charge sparsity, regulated by the pH of the precursor photoresin, also impacts the phase behavior of the gels, leading to changes in the mechanical response. Molecular Dynamic (MD) simulations and diverse polymer characterization methods (morphology, thermal and mechanical) demonstrate that the combination of these parameters controls the extent of dynamic crosslinking present in the system and the emerging polymer configurational distribution governing material properties of MPEC gels. We believe the development of a simple synthesis pathway via additive manufacturing, informed and guided by experimental investigation and molecular modeling, provides a comprehensive understanding of the parameter space and enables the selective design of advanced compliant and functional metallo-polyelectrolytes.

1:45 PM MF01.11.02
Functional Polymers for 4D Additive Manufacturing with High Precision Eva Blasco; Universität Heidelberg, Germany

4D printing has gained much attention during the last years and become a promising tool for the fabrication of dynamic and adaptive structures with potential application in different fields ranging from biomedicine to optics to soft-robotics. The additional fourth dimension refers to the ability of a 3D printed object to change its properties over time. We can imagine it as the addition of “life-like” behavior. While great progress has been made at the macroscale, the continuous miniaturization of today’s devices has tremendously increased the demand for manufacturing at the smaller scales. Emerging technologies such as two-photon 3D laser printing have enabled the precise printing of structures at the micro and nanoscale level.

Our group has recently succeeded in the development of new functional materials for laser micro- and nanoprinting. In particular, we have focused on the incorporation of new features such as conductivity, subtractive manufacturing (inks allowing printing and erasing), supersolution and more recently, stimuli response for complex actuation. In this lecture, special attention will be paid to the design of inks based on functional polymers for 3D/4D microprinting. The challenges as well as the potential and perspectives of the field will be highlighted, too.

2:15 PM MF01.11.03
Free-Form Printing and Deformation Control Strategies for Liquid Crystal Elastomers Devin Roach1,2, Timothy White3, Jeremy Herman3 and Bryan Kaehr2; 1Oregon State University, United States; 2Sandia National Laboratories, United States; 3University of Colorado Boulder, United States

Fabrication pathways for liquid crystal elastomer (LCE) have remained a topic of intensive research interest in recent years. Photopatterning and two-stage reaction techniques were pioneering methods which enabled molecular patterning and fabrication of LCE networks in few, relatively simple steps. Recently, additive manufacturing (AM), or 3D printing, has become another promising approach for facile production of LCE networks. The combination of 3D printing with responsive materials, such as LCE, has led to a new generation of smart structures that not only possess a static shape but also can change their shape over time. This process is termed 4D printing, with the fourth dimension being time. The focus of this talk will be on the development of new 4D printing techniques to couple the printing process with the LCE alignment step. This occurs due to the shear forces generated during extrusion through the DIW nozzle. By combining this approach with multiple materials, novel shape transformations can be achieved. For example, by combining LCE with the unique properties of another smart material called shape memory polymers (SMP), the shape transformation can be locked in place. Furthermore, LCE/SMP composites offer superior mechanical properties in both the deformed and undeformed state for functional engineering applications. The structures produced using this method, however, can only perform 2D to 3D shape transformations. Many smart structures applications require more complex 3D shapes to be fabricated. For this reason, we will discuss a recently developed printing method called embedded 4D printing. Here, LCE is extruded into a gel matrix to create complex 3D architectures which can generate unique 3D to 3D shape transformations. This approach enables LCE molecular programming in any 3D cardinal direction. The ability to 4D print complex 3D LCE structures without the need for supports opens new avenues for the design and development of functional and responsive systems such as soft robotics, biomedical devices, and advanced materials engineering.

2:30 PM BREAK

3:30 PM MF01.11.04
Architected Soft Matter and The 4th Dimension Howon Lee; Seoul National University, Korea (the Republic of)

Stimuli-responsive soft matter promises great potential for autonomous and intelligent engineering systems when precisely manufactured in specific architectures with programmed responses. Emerging pathway to create such dynamic systems involves additive manufacturing of stimuli-responsive and programmable soft matter. This approach has been termed “4D printing”, with the 4th dimension being time. In this talk, additive manufacturing of various soft matter using projection micro-stereolithography (PySL) is presented. PySL is a micro 3D printing technique that turns light into a complex 3D structure by utilizing digital light processing (DLP) technology. Combining rapid, versatile, and scalable micro 3D printing technique with various functional soft material, design principles and mechanics inspired by exquisite motions and morphologies in nature are physically realized. Micro-architectures that can transform and move are demonstrated by programming of dynamic response of various responsive hydrogels. Reconfigurable, deployable, and mechanically tunable lightweight material is created by employing shape memory polymers in mechanical metamaterials. Also presented is printing of liquid crystal elastomers with encoded molecular orientations for programming reversible shape change and soft robotic locomotion.
Polyelectrolytes have a unique property of complexation when oppositely charged paired polymers form films or coacervates. They have found applications in diverse fields, including drug delivery, wastewater treatment, and tissue engineering. With 3D printing, using polyelectrolytes presents an exciting opportunity for precisely fabricating functional materials and devices. However, the strong electrostatic interactions and the complex formation as coacervates are unstable as viscoelastic materials hinder the flow and processability of inks during the direct ink writing (DIW) process. They have been mostly demonstrated by 3D printing in support media. This talk will focus on the use of polyelectrolyte complexes (PECs) suitable for DIW, in air to form complex shapes and objects. To make PEC-based inks amenable to 3D printing in air, a wash-out deplasticizing procedure was developed. Studies on different formulations were developed that meet the printability of polyelectrolyte complexes and their rheological requirements based on the use of polyelectrolytes, water-soluble polymers, and ampholytes. Our investigation entailed systematically exploring solvent composition, pH conditions, and the incorporation of specific additives. Furthermore, we evaluate how these ink formulations impact the final printed structures’ fidelity, mechanical properties, and complexation behavior. The findings have the potential to enlarge the way we design and manufacture PEC functional materials across diverse applications, from biomedicine to electronics by harnessing the properties of polyelectrolyte complexes.

**4:15 PM MF01.11.06 Multi-Axis Magnetic 3D Printing of Magnetically-Responsive Architecture**  
Brian Elder, Taylor Greenwood, Samanany Ghosh and Yong Lin Kong; University of Utah, United States

The ability to program magnetic remanence in situ during extrusion-based 3D printing can enable the creation of soft, magnetically responsive architecture. Indeed, in comparison with other methods, such as folding or assembly, this freeform fabrication approach can create highly complex responsive architecture and actuators. Here, towards this goal, we developed a multi-directional magnetic 3D printing process that allows in situ programming of the magnetic domains during 3D printing. The multi-axis magnetic field enables the variance of magnetic remanence within a continuous filament, achieving complex deformation even in a single printed filament. This capability increases the range of possible motions, including bending, twisting, and contraction. As a proof of concept, we demonstrated the fabrication of a tunable propeller, magnetic-responsive textiles, and a magnetically-activated ingestible device. We also demonstrated eight fundamental remanence pairs that produce deformation units, which we envision could enable the future design of tunable soft actuators and robots.

**4:30 PM MF01.11.07 Intelligentia of Additively Manufactured Polymers**  
Julia R. Greer, Soela Lee, Seneca Velling, Wexin Zhang and Cyrus Fiori; California Institute of Technology, United States

Creation of reconfigurable and multi-functional materials can be achieved by incorporating architecture into material design. In our research, we design and fabricate three-dimensional (3D) nano-architected materials that can exhibit superior and often tunable thermal, photonic, electrochemical, biochemical, and mechanical properties at extremely low mass densities (lighter than aerogels), which renders them useful and enabling in technological applications. Dominant properties of such meta-materials are driven by their multi-scale hierarchy: from characteristic material nanostructure (atoms) to individual constituents (nanometers) to structural components (microns) to overall architectures (millimeters and above).

Our research is focused on fabrication and synthesis of nano- and micro-architected materials using 3D lithography, nanofabrication, and additive manufacturing (AM) techniques, as well as on investigating their mechanical, biochemical, electrochemical, electromechanical, and thermal properties as a function of architecture, constituent materials, and microstructural detail. Additive manufacturing (AM) represents a set of processes that fabricate complex 3D structures using a layer-by-layer approach, with some advanced methods attaining nanometer resolution and the creation of unique, multifunctional materials and shapes derived from a photoinitiation-based chemical reaction of custom synthesized resins and thermal post-processing. A type of AM, vat polymerization, has allowed for using hydrogels as precursors, and exploiting novel material properties, especially those that arise at the nano-scale and do not occur in conventional materials. The focus of this talk is on additive manufacturing via vat polymerization and function-containing chemical syntheses to create 3D nano- and micro-architected metals, ceramics, multifunctional metal oxides (nano-photonics, photocatalytic, piezoelectric, etc.), and metal-containing polymer complexes, etc., as well as demonstrate their potential in some real-use biomedical, protective, and sensing applications. I will describe how the choice of architecture, material, and external stimulus can elicit stimulus-responsive, reconfigurable, and multifunctional response.

**SESSION MF01.12: Sustainable Polymers**

**Session Chairs:** Michinao Hashimoto and Daryl Yee

Thursday Morning, April 25, 2024
Room 325, Level 3, Summit

**8:15 AM MF01.12.01**

**Bacterial Cellulose-Based Inks: Enabling Mechanical Property Control in Sustainable 3D Printing**  
Kuotian Liao, Mallory Parker, Haresh Iyer, Aban Mandal, Taylor A. Hilton, Rebekah I. Brain and Eleftheria Roumelis; University of Washington, United States

Advancements in sustainable materials are needed to combat pressing challenges posed by synthetic plastics, such as non-renewable sourcing, environmentally detrimental manufacturing processes, and end-of-life fates. Biopolymers are attractive alternatives to petroleum-derived polymers, offering a reduction in environmental impact across their entire lifecycle. In parallel, additive manufacturing has revolutionized the production of polymer-based materials for numerous applications, particularly those challenging to manufacture using conventional techniques, utilizing sustainability practices such as minimal material usage and limited waste generation. Currently, the materials used in 3D printing applications are rather limited and majority of them are synthetic polymers. There is a clear need to provide more sustainable materials for the ever-increasing 3D printing applications. In this study, we present an entirely biobased material platform designed for direct ink writing (DIW), with the aim of enabling precise control over the mechanical properties of 3D-printed structures, both at the hydrogel and solid foam states. Utilizing polymer network principles, we use lab-cultured bacterial cellulose (BC) as our primary, load bearing network element. We investigate the effects of chemical treatment with deep eutectic solvents on the BC fiber charge and degree of defibrillation, which ultimately exert a profound influence on ink rheology and hydrogel properties. BC holds particular promise due to its combination of high aspect ratio, molecular weight, and degree of crystallinity, and its capacity for scalable and tunable biosynthesis. Additionally, we explore the impact of introducing other biopolymers (e.g. proteins) and organic small molecules (e.g. lipids) on the rheological properties and mechanical integrity of the printed structures. By incorporating spatially modulated compositions, we open avenues for further fine-tuning of material properties. This comprehensive investigation aims not only to deepen our understanding of the structure-property relationships within BC-based networks but also to pave the way for tailoring the properties of resulting gels and foams for a diverse range of applications. These insights are poised to significantly advance our fundamental understanding of polymer physics and offer innovative solutions for sustainable material development.

**8:45 AM MF01.12.02**

**Additive Manufacturing of Vitrimers with Circularity**  
Sungjin Kim1,2, Md Anisur Rahman1, Karen C. Guzman2, Zoriana Demchuk1, Jeff Foster1 and Tomonori Saito1,3; 1Oak Ridge National Laboratory, United States; 2The University of New Mexico, United States; 3The University of Tennessee, Knoxville, United States

Over 400 million tons of solid plastics are globally produced annually and only ~9% of those are currently recycled in U.S.. Establishing closed-loop circularity of plastics with a facile manufacturing path is critical for global circular economy. When commodity plastics are upcycled into higher-performance materials with facile processability, a sustainable closed-loop manufacturing would become reality. Additive manufacturing (AM) of such upcycled plastics to custom-designed structures accomplishes energy and resource efficient low-carbon closed-loop manufacturing. We hereby open a circular upcycling of a commodity plastic into a higher-performance vitrimer with fused deposition modeling or direct ink writing, resulting in robust printout properties comparable to crosslinked thermostets. Vitrimer exhibits mechanical robustness and chemical resistance because of its covalent network formation, but it can also be malleable by reconfiguring reversibly via crosslinks through the associative bond exchange at elevated temperature, making it recyclable. Due to its crosslinked nature, the upcycled vitrimers provide stronger, tougher, solvent-resistant 3D objects and separatable from unsorted plastic waste. Tailoring the vitrimer composition overcomes the major challenge of (re)printing crosslinked materials, allowing multi-cycle printing. This presentation updates our efforts on AM of upcycled commodity plastics, especially upcycled vitrimers.

**9:00 AM MF01.12.03**

**Sustainability, Biodegradability and Circularity in Photopolymer Resins for 3D Printing**  
Andrew P. Dove; University of Birmingham, United Kingdom

One of the unresolved consequences of the massive global production of plastic is the lack of proper waste management. As a consequence of technological limitations as well as inefficient collection and sorting methods, current recycling schemes are underperforming. In part this is a result of the inherent linear design of our polymer systems, and lack of consideration of waste management and environmental impact of the waste that does escape into the environment, at the polymer design stage. We, among others, are focussing on creating tools that could be applied
A 3D Printable Thermally Conductive yet Electrically Insulating Polymer Nanocomposite based on Ag@SiO₂ Nanowires

Bi-source, and biodegradable polymers for additive manufacturing could enable the rapid fabrication of parts for a broad spectrum of applications ranging from healthcare to aerospace. However, a limited number of these materials are suitable for vat photopolymerization processes. Herein, we report a process to fabricate protein-based constructs using commercially available vat photopolymerization printers. Bovine serum albumin (BSA) is a single-chain nanoparticle that can be chemically derivatized with acrylate and methacrylate functionalities. Aqueous resins were formulated from these materials to produce complex 3D geometrical constructs with a resolution comparable to commercial resins. While BSA is often used in cell culture protocols and diagnostic assays, we demonstrate that BSA can serve as junctions within polymer networks to afford stiff hydrogels and bioplastics with unique physical properties. Protein-based shape-memory objects and engineered living materials were 3D printed and will be highlighted as opportunities for future applications.

What do high density batteries and up-to-date electronic chips have in common? The problem of heat dissipation.

With the emergence of fast charging technologies, high energy density batteries and new generation microprocessors, the heat generation in such systems while in operation becomes significantly more intense. If this heat is not efficiently dissipated: a) the risk of thermal runaway in batteries increases and thus threatens the users safety, b) the performance, lifetime and reliability of electronic systems weaken. Improvement of batteries and electronic devices performances is therefore closely linked to the effectiveness of the thermal dissipation of such systems. Besides high thermal conductivity, very good electrical insulation of these structural materials is also expected to avoid issues such as short circuits or higher power consumption. The use of thermoplastic polymers seems relevant due their intrinsic electrical insulation behavior and simple processability. However, such materials generally present low thermal conductivity (< 0.4 Wm⁻¹K⁻¹). An appropriate strategy for improving thermal conductivity while simultaneously preserving electrical insulation of polymer-based materials is to incorporate thermally conductive yet electrically insulating fillers to the polymer matrix.

In this presentation, we will show that the development of one-dimensional silver-silica core-shell nanowires (AgNW@SiO₂) is a relevant route to very efficient heat dissipative nanocomposites. We will present how the fine tuning of the silica nanolayer on silver nanowires is of utmost importance to reach optimized performances.

By adjusting the rheology of the nanocomposite, i.e. limiting the content of the nanofillers to 3 vo%, a proof of concept was 3D printed by FDM (Fused Deposition Modelling). Thanks to the alignment of the 1D nanofillers during the FDM printing process, as observed under various printing patterns, the thermal conductivity of the PC nanocomposite reaches an unprecedented value of 3.48 ± 0.06 Wm⁻¹K⁻¹ in the printing direction, i.e. a fifteen-fold increase over the thermal conductivity of neat PC.

Due to the significant differences in physical and chemical properties of polymers and metals, their additive manufacturing is conducted using very different and incompatible methods or conditions. Such incompatibility is a significant limitation for multi-material 3D printing and fabrication of 3D functional composites. We address this issue by creating functional composites composed of thermoplastic elastomers, Field’s metal, and graphene; and their 3D printability by fused filament fabrication is achieved. The 3D printable composites have widely tunable internal structures, mechanical, thermal, electrical properties, and full recyclability. Multiphysics modeling was developed to predict and elucidate the structure and properties. The 3D structures can be transformed from insulating to conductive based on the melting and coalescence of Field’s metal nanoparticles. The incorporation of graphene bridges the adjacent Field’s metal particles and significantly enhances the conductivity. Such 3D-printable polymer-metal hybrid platform will enable new advancements in soft electronics and robotics, and energy storage.


Interface-Modified Liquid Metal Elastomer Composites for Printing Stretchable Conductors

Liquid metal alloys of gallium, such as eutectic gallium-indium (EGaIn), have garnered attention for their distinctive metallic and fluidic properties. These materials have been utilized in a variety of forms and device architectures, ranging from fluidic microchannels to polymer nanocomposites. Additionally, liquid metal can be embedded in the elastomer matrix to synthesize liquid metal elastomer composites (LMEC) which can augment various functional properties. These composites, with tailored material compositions, can also show high electrical conductivity while having excellent plasticity. However, creating a percolating network of liquid metal (LM) in low modulus elastomers, such as Ecoflex 00-30, is quite challenging. This is because the ultrasound polymer matrix cannot deliver sufficient mechanical forces to the gallium oxide on the surface of the LM droplets. Since the oxide shell causes separation between the micro-sized LM particles, an innovative strategy for breaking this solid barrier is required to achieve conductive LM pathways in the low elastic modulus LMECs.

In this presentation, we will demonstrate how embedded EGaIn microdroplets in Ecoflex can be “mechanically sintered”, or called “activated”, to become electrically conductive. Surface modification of LM particles is a key for weakening the particle-matrix interface in LMEC, which results in the formation of a percolation network by strain-activation. Furthermore, we will discuss how the formulated composite can be used for printing stretchable conductors. The printed traces can be stretched over 900% tensile strain, and electromechanical testing results indicate minimal changes in electrical resistance under substantial deformations and strain rates. Finally, we will demonstrate the practical application of the formulated printable EGaIn- Ecoflex 00-30 inks in stretchable electronics circuits. Overall, this work highlights the potential of liquid metal elastomer composites for use in functional electronics and provides a promising approach for achieving high electrical conductivity in ultrathin polymer matrices.

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Advancing Semiconducting Polymer Printing: Photothermal Approach for Sub-Micron Feature Fabrication for Electronic NIR Photodetectors Meghna Jha, Joaquin Mogollon Santiana, Megan L. Hong, Harishankar Manikantan and Adam J. Moule; University of California, Davis, United States

The industrial development of Semiconducting Polymers (SPs) faces a significant hurdle in the absence of an inexpensive, rapid, and viable patterning technology capable of producing sub-micron features. In this study, we explore Photothermal Patterning as a promising technique that leverages the solubility characteristics of SPs to address this challenge. The Photothermal Patterning process involves exposing an SP film to a pre-defined thermal profile, allowing the polymer to dissolve at a specific temperature, resulting in a defined pattern. We have demonstrated the feasibility of this approach, and we are currently expanding this method to manipulate SPs by printing patterns with a tailored pH value, allowing the material to dissolve at a specific temperature, resulting in a defined pattern. These patterns can be utilized for a variety of applications, including electronic devices, optical sensors, and medical diagnostics.

In summary, this work presents an AM approach that allows for the precise control of SPs at sub-micron scales. The rheological properties of these pastes are critical for achieving the desired dissolution behavior in these materials. A high yield point and shear thinning behavior are highly desirable for a 3D printing process. These properties can be achieved by combining sodium alginate and ZnO particles in the shape of micrometer-sized crystals (t-ZnO) with a tetrapod geometry. While the sodium alginate adjusts the paste's rheological properties, the individual ZnO particles act as a route to obtain ordering of a material in both an extrinsic and intrinsic manner mimicking that seen in biology.[5,6]

Colour and colour changes play a crucial role in the development of functional materials, as they can be used to convey information, modulate light, and mimic natural phenomena. In this study, we combine the use of SPs, sodium alginate, and ZnO particles to create responsive photonic materials. The use of t-ZnO particles allows for the formation of patterns with a high degree of structural complexity and tunable optical properties. These materials can be utilized in various applications, including electronic devices, optical sensors, and medical diagnostics.

In conclusion, this work presents an AM approach that allows for the precise control of SPs at sub-micron scales. The rheological properties of these pastes are critical for achieving the desired dissolution behavior in these materials. A high yield point and shear thinning behavior are highly desirable for a 3D printing process. These properties can be achieved by combining sodium alginate and ZnO particles in the shape of micrometer-sized crystals (t-ZnO) with a tetrapod geometry. While the sodium alginate adjusts the paste's rheological properties, the individual ZnO particles act as a route to obtain ordering of a material in both an extrinsic and intrinsic manner mimicking that seen in biology.[5,6]
to manufacture soft hydrogels and polymers in combination with hard ceramic particles enabling the versatility of DIW and showing their great potential for biomedical applications.

2:15 PM MF01.14.04
Tuning Aging, Mechanical and Electrical Properties of Liquid Metal Polymer Composites for Improved Stretchable, Deformable and Robust Electronics and Robotics Amanda Koh, Anh Hoang, Chanyeop Park and Omar Faruque; 1University of Alabama, United States; 2University of Wisconsin–Madison, United States

Soft, stretchable electronics are a promising platform for wearable devices for monitoring health, movement, infrastructure damage, robotic environments, among many varied applications. While the literature demonstrates a wide range of strategies for achieving soft electronics, the incorporation of electronically active elements into a soft polymer (typically an elastomer for stretchability) is one of the most successful. To get the most utility out of the elastomer composite, the electronic element must also be able to withstand repeated strain and not degrade the elasticity of the host. Room temperature liquid metal polymer composites (LMPCs) are composites of the metal alloy gallium-indium-tin (galinstan) and an elastomer matrix (most commonly polydimethylsiloxane, PDMS). As galinstan is liquid at room temperature, if inherently has no strain fatigue, and the research in Koh Lab has shown that galinstan can be casted into the matrix at concentrations greater than 70vol% without a dramatic increase in polymer modulus. Simultaneously, the LMPC exhibits dielectric properties with tunable relative permittivity up to and exceeding 160 based on liquid metal loading and polymer molecular weight. To realize the potential of this polymer composite material, it is necessary to fully explore its rheological, electrical, and sensing properties in order to transition it to a functional manufacturing platform. Additionally, it is necessary to understand the dielectric aging and fatigue properties of the composite as made in order to validate the long term utility of the composite as a sensor, wearable, or robotic component. The work presented will show recent data demonstrating how dielectric aging is impacted by LMPC formulation, and how these properties can be simultaneously tuned with mechanical/rheological properties to optimize the system for additive manufacturing or molding. Furthermore, this presentation will include new results related to the spatial homogeneity of the LMPC, which is a property that is both critical to manufacturing (the density of galinstan is greater than six times that of the host polymer) and largely unexplored in the literature. The data presented will demonstrate the boundaries within which spatial homogeneity does or does not impact mechanical, electrical, aging, and sensing properties as well as methods of improving homogeneity if necessary. The work discussed and presented here directly enables ongoing work in the Koh Laboratory to create components for wearable devices, robotic locomotion, and infrastructure hardening that rival and exceed the capabilities of ceramic and thermoplastic polymer dielectrics, expanding the possibilities for such systems.

2:30 PM MF01.14.05
Aggregation-Induced Emission to Visualize and Monitor Progression of Photopolymerization Xiaoxing Xia, Sijia Huang, Elena Belk, Martin De Beer, Abhinav Parakh, Magi Yassa and Johanna Schwartz; Lawrence Livermore National Laboratory, United States

Light-induced polymerization is widely used in high-resolution fabrication such as additive manufacturing and photolithography as well as low-cost industrial processes such as UV curable coating and adhesives. Polymer parts made from acrylate-based resins exhibit a large variation in materials properties due to differences and inhomogeneities in the degree of conversion within each part and thus suffer from quality control challenges for high-precision applications. As new photochemistry are being actively developed, it is increasingly important to examine the uniformity of polymerization with high spatial resolution and monitor its progression kinetics with detailed temporal information. In this work, we introduced a class of fluorophores based on aggregation-induced emission (AIE) as an additive in the photo-resin formulation; their fluorescence intensity increases as the local rigidity of the cross-linked polymer increases. We conducted systematic ex-situ photo-rheology and FTIR measurements to establish the calibrated relation between fluorescence intensity and polymerization conversion for representative resin formulations. We used fluorescence microscopy and confocal microscopy to demonstrate high resolution grayscale mapping of polymerization conversion in 3D printed parts made by various photopolymerization methods including Digital Light Processing (DLP), Two-Photon Polymerization (2PP), and tomographic Volumetric Additive Manufacturing (VAM). With this unique visualization method, we observed the periodic variation of higher and lower conversion across each printed layer in DLP-printed dog-bone samples, which led to large differences in tensile strength as a function of the printing orientation with respect to the loading direction. Finally, we implemented a fluorescence monitoring setup to a VAM system that actively tracks the conversion of the 3D printed parts as tomographic printing progresses, which offers vast opportunities for real-time in-process metrology and feedback control to improve printing quality.

2:45 PM BREAK

SESSION MF01.15: Composites
Session Chairs: Michinao Hashimoto and Devin Roach
Thursday Afternoon, April 25, 2024
Room 325, Level 3, Summit

3:15 PM *MF01.15.01
Bioinspired Hierarchical Composite Hydrogels via Shear-Assembled Direct Ink Writing Technology Wei Zhai, Tian Li and Quyang Liu; National University of Singapore, Singapore

Soft materials, such as hydrogels, have garnered significant attention in fields like wearable electronics, soft robotics, biomedicine, and energy technology, thanks to their unique combination of high electrical conductivity, stretchability, biocompatibility, and self-healing capabilities. Nevertheless, the inherent brittleness of hydrogels has presented a challenge to their practical application. Biological soft tissues, like tendons and cartilage, exhibit remarkable strength, flexibility, and message transmission capabilities due to their composite composition and intricate hierarchical structures. Drawing inspiration from nature, we have developed a promising approach—shear-assembled direct ink writing—to strengthen and toughen hydrogels by incorporating secondary-phase fillers and creating bioinspired hierarchical structures. This process involves applying shear-force-induced self-assembly extrusion printing of nanoceramic platelets enhanced hydrogel inks, providing control over nano- to sub-micro scale structures. Additionally, the filaments can be 3D printed into free-form bioinspired architectures, ranging from micro- to macro-scale, such as unidirectionally aligned, Bouligand, and crossed lamellar configurations. By tailoring the composition, nanoceramic alignment, and printing patterns, the composite hydrogel exhibits multiple strengthening and toughening mechanisms across different scales. Through the application of this technology, we have successfully produced flexible and robust nanoceramic-hydrogel composites with high ceramic compositions for creating reconfigurable structures. Furthermore, we have developed a new form of bioceramic-hydrogel composites with potential applications in bone tissue engineering, as well as strong and tough conductive composite hydrogels for use in flexible electronics.

3:45 PM MF01.15.03
Accurate Rheological Characterization of Highly-Filled Direct-Ink Write Pastes Jessica Kopatz, James Griebler, Jonathan Leonard, Alexander T. Tappan and Anne M. Grillet; Sandia National Laboratories, United States

Direct-ink write is an additive manufacturing technique that enables the creation of reproducible and complex hardware by depositing a viscous, shear-thinning liquid onto a substrate in a custom-pattern via extrusion through a syringe. The rheology of these inks is tailored through the addition of various filler materials. To successfully print highly-filled inks, we need to understand the effect of filler morphology, size, loading, and packing fraction on the ink rheology and corresponding printability. More importantly, characterization methods that accurately capture the ink’s rheological properties that correlate to resin printability is imperative. Various filler particles and volume loadings of particles were dispersed in Polydimethylsiloxane (PDMS, Sylgard® 182) to investigate the change in zero-shear viscosity, shear-thinning behavior, and plateau modulus. Comparisons between capillary rheometer measurements versus parallel plate rheometer measurements were made. The extrusion force was measured at several volume loadings determine the highest attainable volume loading for printable resins as a function of different filler morphologies. The goal of this work is to understand effects of filler morphology on ink printability while determining adequate characterization techniques that accurately capture the rheological behavior.

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4:00 PM MF01.15.04
3D Printed Soft Composites with Tunable Mechanical Properties Kimberlee Hughes and Arda Gozen; Washington State University, United States

The use of soft engineering materials such as silicones has been gaining more traction due to the emergence of technologies such as soft robotics, pre-surgical organ models, and wearable electronics. Where compatibility with soft biological systems and the ability to mimic their functionalities are essential. For the continued advancement and broad utilization of these technologies, there is a need for further development of soft engineering materials with properties required in relevant applications. Particularly, the ability to precisely control the mechanical properties, as well as their spatial distribution towards development of functionally graded biomimetic compliant structures is a significant research interest. Additive manufacturing with multi-polymer systems have proven to be an effective method to achieve this goal, however, the commonly used Polyjet approach is highly expensive and limited in material capabilities. Towards
addressing this challenge, this work presents novel soft composites, consisting of a silicone matrix and thermoplastic elastomer reinforcements, fabricated through low-cost extrusion-based additive manufacturing. Mechanical properties of these composites are functions of the reinforcement geometry that can be precisely controlled. We use a customized 3D printer with direct ink write (DIW) and fused filament fabrication (FFF) capabilities to print composites with a sinusoidal reinforcement pattern. We demonstrate that changes in the amplitude and frequency of these sinus waves lead to significant differences in the hyperelastic behavior of the composites. Specifically, decreases in amplitude and frequency led to an overall stiffening of the composite, while increasing these parameters led to a softer stress-strain response that approached that of a non-reinforced silicone sample. Additionally, changing these parameters independently led to differences in strain-hardening behavior. Finally, we demonstrate the ability of this approach to precisely control the spatially varying distribution of composites, by printing parts with sinusoidal reinforcements of spatially varying amplitude and frequency.

4:15 PM MF01.15.05
Freeform Additive Manufacturing of Carbon Fiber Reinforced Composites Using Dielectric Barrier Discharge-Assisted Joule Heating

Smita Shivraj Dasari1, Aniela Wright1, Amabhab Sarmah1, Jacob Carroll1, Thang Quyet Tran1 and Micah Green1; 1Texas A & M University, United States; 2University of Minnesota, United States; 3Singapore Institute of Manufacturing Technology (SIMTech), Agency for Science, Technology and Research (A*STAR), Singapore

In this work, a novel out-of-oven additive manufacturing (AM) technique to rapidly print and cure thermostetting carbon fiber reinforced composites (CFRCs) using dielectric barrier discharge (DBD)-assisted Joule heating was developed. Conventionally, CFRCs are produced by automated fiber placement machines (AFPs) that use large, cumbersome molds and time-consuming oven/autoclave treatments to cure CFRCs in the desired shapes. Recently, out-of-oven AM has garnered attention as a method to manufacture CFRCs without the use of molds. AM allows for on-the-fly printing and curing of thermostetting CFRCs; however, current out-of-oven AM techniques are limited to UV-curable, low viscosity, or rapid-curing resins. Here, the DBD was used for in-situ heating and curing during AM of continuous CFRCs; this method is resin-agnostic, applying to most commercially available thermostetting resins. As the partially cured composite (prepreg) is deposited, Joule heating induced via a DBD applicator allows the part to cure in the desired shape; this is possible because of the conductive carbon fiber susceptors inside the part. Composites manufactured by this method show properties similar to those manufactured in conventional ovens. With the help of this technique, one can print composites in free space or on stationary and mobile substrates. 2D structures, and 3D multilayered structures can be printed. Automation of this process is also demonstrated. This technology leverages the advantages of AM techniques to enable the printing of high-performance and lightweight materials in any desired shape.

SeMM01.16.01
Squeeze Flow Induced Fiber Alignment in Fused Filament Fabrication of Carbon Fiber and PDMS Mixture

Hoang Minh Khoa Nguyen and Dong-Wook Oh; Chosun University, Korea (the Republic of)

Fused Filament Fabrication (FFF) represents a significant segment of additive manufacturing processes, mainly known for its ability to fabricate complex structures using various materials. Among these, polymer composites integrated with short carbon fibers have gained immense attention due to their potential to exhibit augmented mechanical and thermal properties, positioning them as ideal candidates for high-performance applications in the aerospace and automotive industries. The optimization of these enhanced properties is intrinsically connected to the alignment of carbon fibers within the extruded filament. As current research indicates, this alignment is not a mere consequence of the filament extrusion but is significantly influenced by many factors. Primary among these are the configuration of the printing nozzle and the interactions occurring at the deposition bed. Despite widespread recognition of the merits of these composites, a conspicuous knowledge gap persists regarding the dynamics of fiber rotation during deposition. This paper seeks to bridge this aspect by incorporating experimental and computational methodologies.

Through flow visualization experiments, we observed fiber orientation in multiple focal planes during the extrusion process. This facilitated an in-depth assessment of the alignment axis, indicative of fiber rotations during extrusion. Initially, we examined the fiber rotations as exiting the nozzle, capturing their trajectory and orientation. This was followed by mapping the alignment angles as the extruded filament after the solidification, offering insights into the end-state orientation of the fibers. To foster a comparative analysis, we further performed a numerical flow simulation inside the nozzle and on the deposition bed. The computational calculation was done in a 2-dimensional incompressible Newtonian flow model, which provided velocity information within the filament. The flow field calculation paired with the Advani-Tucker orientation tensors was compared to the fiber orientation obtained from the flow visualization experiment. We also varied configurations of the nozzle and the deposition bed design specifications. Specifically, by adjusting the gap between the nozzle tip and deposition bed, we introduced different squeeze flows, allowing us to delineate their impact on fiber rotation. Additionally, we varied in-nozzle flow geometries. By comparing the "straight channel" against the "orifice-embedded" nozzles, we manipulated flow fields, and each impacted fiber alignment. This study provides insights into the mechanics of fiber alignment in FFF and highlights advancements in customizing polymer composite materials, signaling a significant shift in additive manufacturing material science.

8:15 AM MF01.16.02
Customizable Flexible Pressure Sensors with Enhanced Performance via Ink Optimization and Microdevice Integration

Sina Hassanpour, Kalyiah Shearod and Taeil Kim; Baylor University, United States

This research presents an extensive exploration of the development of customrollable flexible pressure sensors through the application of Direct-Ink-Writing 3D printing technology. It places a primary focus on the optimization of ink formulations, varying filler ratios of carbon nanotubes (CNT) and silicon dioxide (SiO2) in polydimethylsiloxane (PDMS) matrix. The research systematically examines how these optimized ink formulations offer precise control over the electrical and hyperelastic properties of the printed sensors and explains their influence on key sensor characteristics such as conductivity and sensitivity. The optimization process of ink formulation is at the core of this research. By adjusting the proportions of CNT, SiO2, and PDMS, the printability of inks and the electrical properties of sensors could be effectively manipulated. This fine-tuning is essential for ensuring that the sensor operates efficiently in a wide range of environments and applications. Concurrently, the hyperelastic properties of the sensor, which encompasses flexibility and elasticity, can be tailored to meet specific requirements. A crucial aspect of this research is the effect of these controlled modifications on the sensors' performance characteristics. The paper delves into how these adjustments can significantly impact the linearity and sensitivity of pressure sensors. Examining these attributes provides a comprehensive understanding of how customizability can enhance the sensors' precision and suitability for various applications. The integration of microdevices with various sizes and differing ink ratios as printed structures atop a flat printed layer introduces a dynamic dimension to the pressure sensor design. These microdevices are meticulously tailored to function as responsive elements, each uniquely tuned for specific applications. When subjected to varying levels of pressure, these microdevices exhibit an array of behaviors, allowing the sensor to capture detailed data. This multifaceted approach enhances the adaptability of the sensor, making it well-suited for a wide range of applications where precise pressure sensing is imperative, such as touch-sensitive screens, medical devices, or robotic grippers. This adaptability and sensitivity are particularly relevant in healthcare and biomedical applications. Pressure sensors with these attributes can have a meaningful impact on patient care, providing accurate data for diagnosis and treatment.

In conclusion, integrating microdevices onto the sensor surface, each designed for specific functions, enhances the sensing capability to meet real-world healthcare needs. This integration enables tailored performance for practical applications like continuous blood pressure monitoring, prosthetic limb control, and minimally invasive surgical instruments that rely on precise pressure feedback. The comprehensive discussion in this research spans the methodology used in ink optimization, detailed results from experimental work, and the broad implications of this innovative technology for the domain of flexible pressure sensing. With a focus on precise control over sensor properties, this research aims to contribute to the ongoing advancements of sensor technology and its applications across various fields.

8:30 AM MF01.16.03
Adaptive 3D Printing of Resonant-Enhanced Microsensors

Jared Anklaam1, Samuel H. Hales1, LeBin Li1, Sanghoek Kim2, John S. Ho1, Yong Lin Kong1 and Samanov Ghosh1; 1University of Utah, United States; 2Kyung Hee University, Korea (the Republic of); 3National University of Singapore, Singapore

The ability to integrate wireless microelectronics on the surfaces of existing biomedical devices can functionize an otherwise passive construct with advanced sensing capability. The digital fabrication approach directly integrates sensors on a clinically proven device without requiring significant structural modification, lowering the clinical barrier for electronic integration. However, achieving microelectronics integration on biomedical devices (e.g., joint replacement implants) with microextrusion-based 3D printing remains challenging. Biomedical

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devices are typically geometrically complex three-dimensional constructs requiring extensive surface topological scanning, electronic design and calibration. Here, we develop a microscale closed-loop format that aids with a laser displacement sensor capable of printing 3D resonant-enhanced microsensors with trace widths as small as 30 μm on a broad range of 3D constructs. The system adapts to the 3D surfaces, achieving conformal printing without requiring extensive alignment of the target substrate with the generated print path. As a proof of concept, we will demonstrate the ability to integrate sensors on biomedical devices such as joint-replacement implants and biological constructs such as bone. Finally, the sensors can be robustly and reversibly interrogated with high sensitivity using readout techniques that leverage the enhanced sensitivity of systems at special degeneracies, enabling a fundamentally new approach to integrating electronics on existing biomedical devices.

8:45 AM MF01.16.04
Rapid Additive Manufacturing of Thermosetting Resins enabled via Radio Frequency Curing Ethan Harkin1, Anubhav Sarmah2, Thang Quyet Tran3, Matthew Cupich1 and Micah Green1; 1Texas A&M University, United States; 2University of Minnesota, United States

Direct Ink Writing (DIW) is an extrusion-based additive manufacturing method where the print medium is a liquid-phase ‘ink’ dispensed out of small nozzles and deposited along digitally defined paths. Conventional DIW methods for thermosetting resins rely on the use of viscosity modifying agents, novel crosslinking chemistries, and/or long curing schedules in an oven. Here we demonstrate the use of a co-planar radio frequency applicator to generate an electric field, which can be used to rapidly heat and cure nano-filled composite resins as they are printed. This method avoids the need for an oven or post-curing step. This process consists of a sequential print-and-cure cycle which allows for printing of high-resolution, multi-layered structures. Every extruded layer is partially cured using RF before depositing the next layer; this allows the printed part to maintain structural integrity without buckling under its own weight. The process enables both increased throughput and decreased time relative to traditional part manufacturing. Commercial epoxy resin with various carbon-nanotube loadings was examined as the primary DIW candidates. Rheological characterization was used to assess curing kinetics, extrusion behavior, and printability. After printing, the thermo-mechanical properties, surface finish, and shape retention of RF-cured samples were evaluated and found to be comparable against samples conventionally cured in an oven. This method of manufacturing establishes RF heating as a suitable alternative to conventional methods, facilitating rapid, free-form processing of thermosetting resins without a mold.

9:00 AM MF01.16.05
3D-Printing Liquid Crystal Polymers to Replicate The Anisotropic Complexity of Wood Kunal Masani, TU Delft, Netherlands

Anisotropic materials formed by living organisms such as cellulose fibres in wood grain and fibre bundles in osteons of bone can readily be found in Nature. Their microstructures can be shaped into any direction, with spatially tuneable gradients and sharp orientation changes. In contrast, engineered materials such as composite materials cannot be shaped with similar levels of anisotropy and directionality freedom. While the latter can be achieved with 3D printing, compatible anisotropic materials are typically fiber-filled. Paradoxically, these fibers restrict directionality freedom due to their intrinsic stiffness. Problems such as fiber breakage have been reported and often result in setting curvature constraints in the design space. Here, we present a new approach to replicate complex microstructures such as wood using 3D printing of self-assembling thermotropic liquid crystal polymers (LCPs). The LCPs can be reliably extruded to produce lines whose widths vary from half to three times the nozzle diameter, with stiffness ranging from 5 GPa to 35 GPa. This method allows shaping of anisotropic microstructures with tuneable stiffness and failure modes within a single material. By using a distance-aware toolpath generation algorithm, we can generate print lines of varying widths and curvatures that cover the shape domain homogeneously. We successfully 3D-print infills with no curvature constraint. By increasing allowed curvature, our method offers new design possibilities for composites, such as preventing crack propagation, or spatially distributing stress. Furthermore, this method creates the opportunity to study mechanical responses of natural anisotropic materials of intricate microstructures such as wood or bone.

9:15 AM MF01.16.06
Bridging the Gap to Higher Performance Silicone Elastomers for Direct Ink Write Spencer Schmidt1, Jake Grotch2,3, Michael Ford1 and Jeremy Lenhardt1; 1Lawrence Livermore National Laboratory, United States; 2Case Western Reserve University, United States

Additive manufacturing via direct ink write (DIW) offers several advantages over traditional manufacturing processes, such as the ability to fabricate polymeric components of complex geometry with spatially dependent properties and reduced time relative to traditional production methods. Formulation science is critical to new DIW feedstock development as typical inks must exhibit low yield stress thixotropy while avoiding nozzle swell and post-extrusion flow. These ink properties result from the intertwined effects of reinforcing filler, thixotropic additives, polymer molecular weight, catalyst type, and target mechanical response. For DIW silicones, some standard systems that retain ultimate tensile strength (UTS) of ca. 5MPa and 150 - 350% elongation with varying hardness (ca. 20 - 60 ShoreA) set a baseline from which higher performance feedstocks can be developed.

One approach to enhance silicone mechanical response is to chemically graft functional groups to the fumed silica surface, such as vinyl groups that enable covalent silica bonding to the polymer crosslink network. Systematic variations of polymeric components and in-house surface functionalized silica enable both control over cured mechanical properties in a new set of silicones (achieving ca. 8MPa UTS, 400 - 1200% elongation, and 20 - 50 ShoreA hardness) and direct comparisons across treatment type systems. When aggregated, these comparisons begin a detailed, empirical detangling of the reinforcing filler's role in silicone performance from other formulation components that will aid more streamlined development of future generations of printable silicones.

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

SYMPOSIUM MF02

Laser-Induced Nanomaterials—Synthesis, Properties and Applications
April 23 - May 7, 2024

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Matrix assisted Pulsed Laser Evaporation for Layer-By-Layer processing of Thin Films containing Biological Materials
Andrew Sachan1 and Roger Narayan2; 1University of North Carolina at Chapel Hill, United States; 2North Carolina State University, United States

Matrix assisted pulsed laser evaporation has several advantages over dip coating, spin coating, and Langmuir-Blodgett coating for processing thin films that contain pharmaceutical agents and other biological materials. For example, matrix assisted pulsed laser evaporation allows for tight control of thin film thickness. Matrix assisted pulsed laser evaporation also allows for good control of thin film roughness. In addition, matrix assisted pulsed laser evaporation is a “cold” process that does not heat biological material. Matrix assisted pulsed laser evaporation has been used to deposit coatings of many types of biological materials; for example, it has been used to deposit thin films of the antiproliferative drug rapamycin on glass surfaces. Alamar Blue and Pico Green assays were used to evaluate the viability and proliferation rates of L929 fibroblast-like cells on the rapamycin coatings, respectively. The cells on the rapamycin thin films exhibited 70.6% viability (p = 0.0097) and 53.7% proliferation (p = 0.0120) compared to cells on the control material (borosilicate glass), respectively [1]. This result indicates that the rapamycin thin films deposited by matrix assisted pulsed laser evaporation successfully reduced cell viability and proliferation. Matrix assisted pulsed laser evaporation offers many potential opportunities to impart biological functionality to the surfaces of medical devices and other medically-relevant structures.

References:

Comparing The Effect of Single and Dual Sintering Methods Using Silver and Copper Nanoparticle Patterns for Flexible Electronics Applications
Raiba Chowdhury and Seonhee Jung; University of Louisiana at Lafayette, United States

The utilization of metallic nanoparticle (NP) ink has gained significant attention in the fabrication of cost-effective and mechanically flexible printed electronic devices, including wearables, displays, sensors, and solar cells. The choice of metallic NPs is a crucial determinant of the electrical, material, and mechanical properties of the printed patterns. Commonly used NPs for ink formulation include silver (Ag), gold (Au), and copper (Cu). Ag NP ink is highly favored for its exceptional oxidation stability and electrical conductivity. Although Au NPs offer good electrical conductivity and oxidation resistance, their high cost makes them less desirable. Cu NPs have good electrical conductivity and cost-effectiveness, but they have lower oxidation stability. The metallic NP ink is not electrically conductive after the printing process due to steric repulsion forces acting between the particles. These repulsion forces are caused by the introduction of organic additives and stabilizing agents to the ink, preventing the NPs from agglomerating due to Van Der Waals interactions between them. To achieve electrical conductivity, a post-processing step, known as the sintering process, is necessary to decompose the additives and stabilizing agents.

In this study, Ag NP ink (PSI-211, NovaCentrix) and Cu NP ink (CP-008, NovaCentrix) were chosen for printing and characterizing the conductive patterns. Flexible Kapton polyimide (PI) sheets with a thickness of 0.102 mm were used as the substrate. The experiment explored the single and dual sintering methods on the printed Ag and Cu NP patterns. In the single sintering methods, the printed NP patterns were exposed to either laser irradiation (LO) or thermal treatment (TO). For the LO sintering condition, the Ag and Cu NP patterns underwent Nd: YAG laser irradiation at 600 mJ for 15 s and 800 mJ for 30 s, respectively. For the TO sintering condition, the Ag and Cu NP patterns were placed in a formic acid (FA) environment at 140 °C for 1.5 min and 260 °C for 15 min, respectively. In the case of the dual sintering methods, one approach is to subject the printed metal patterns to thermal treatment followed by laser irradiation (TL), while the other method involves exposing the patterns to laser irradiation followed by thermal treatment (LT). The sintering parameters for TL and LT followed the same sintering conditions as LO and TO.

After analyzing the microstructure using the scanning electron microscope, the Ag NP patterns sintered using LT showed enhanced agglomeration and increased networking of particles through necking compared to the Ag NP patterns sintered using the other conditions. This pattern also displayed the highest roughness of 48 nm from atomic force microscopy (AFM) analysis, indicative of superior grain growth. Due to this fact, the Ag NP pattern sintered using LT demonstrated the lowest electrical sheet resistance with a value of 0.0031 Ω·Sq and the lowest resistance ratio (R/R0) of 1.75 after the folding test. The highest hardness was found for the Ag NP pattern sintered using LT with a value of 4.28 N/mm², which contributed to a better result in the adhesion test. On the other hand, the Cu NP pattern sintered using TO showed the most uniform grain growth through agglomeration and coalescence. Additionally, due to increased connectivity between the patterns, the Ag NP pattern sintered under TO showed the highest electrical hardness of 55.36 N/mm² and the lowest R/R0 value of 10.58 after the folding test. The lowest electrical sheet resistance was observed for the Cu NP pattern sintered using LT with a value of 0.0117 Ω·Sq, which thermogravimetric analysis (TGA) showed to be due to the complete removal of organic residue from the pattern. Additionally, the Cu NP pattern sintered under LT showed the highest roughness value of 51.36 nm.

References:

Laser-Induced Graphene (LIG) from Different Polymeric Precursors Predicted Using Machine Learning
Pranav Gupta1, Dazhong Wu2 and Gerd Grau1; 1York University, Canada; 2University of Central Florida, United States

The conversion of polymers to laser-induced graphene (LIG) is a facile and low-cost process to create a patterned conductive nanomaterial for applications such as sensing and energy storage. However, the complexity of the laser conversion process means that it is difficult to predict the effect of different laser parameters, especially for different polymeric precursors. This research...
leverages advanced machine learning models to optimize and predict the laser parameters necessary for polymer conversion into LIG. Data to train the models was collected experimentally and extracted from the academic literature, after which preprocessing techniques were applied. A major input parameter studied in this work is the type of polymer precursor. To this end, we transformed the molecular structures of different polymers from their Simplified Molecular-Input Line-Entry System (SMILES) representation into molecular fingerprints, descriptors, and tokenized representations using RDKit and a pre-trained BERT model. A variety of predictive models including fully connected neural networks, random forest, gradient boosting, and XGBoost were trained, evaluated, and optimized. The cornerstone of the analysis was a specialized testing of feature importance across three distinct SMILES representations, illuminating the complex interplay between molecular structures and polymer properties. The superior performance of the random forest model highlights the vital importance of feature selection and optimization. This creates a comprehensive understanding of influential features in predictions including both laser parameters and different molecular representations. By integrating molecular descriptors and advanced machine learning techniques, this research offers a robust framework for predicting LIG properties, potentially reducing extensive experimental needs. The results have broad implications in material science and flexible electronics.

2:25 PM MF01/MF02/MF03/MT03.05
Flexible Carbon Dioxide Sensors Based on Polyethyleneimine – A Study on Their Aging and Potential Solutions
Tianyu Liu, Daniel Padilla, Kening Lang, Nickolas Boeser, Rishi Patel, Qihua Wu, Marriana Nelson, Christopher Landorf and Jiadeng Zhu; Brewer Science, United States

CO2 sensors, being widely utilized in indoor air quality monitoring, ventilation systems, automotive emission control, and healthcare, can be constructed using various materials and technologies. In recent years, polymers have been considered a popular sensing candidate due to their low cost, outstanding processability, and excellent compatibility with other materials. Polyethyleneimine (PEI) is a polymer that can interact with CO2 molecules and generate measurable responses; thus, it’s been extensively explored in the development of CO2 sensors. Even though many researchers have studied the stability of pure PEI, there are few studies for their real applications (i.e., CO2 sensors) since it determines the sensor lifetime. Therefore, in this work, a systematic analysis of the screen-printed, PEI-based chemiresistive CO2 sensors was conducted with emphasis on the sensors’ aging behavior along with the mechanism. More importantly, we have demonstrated solutions to address the sensor aging by selecting the proper molecular weight PEI and doing the chemical modification on PEI. The produced sensors exhibit much better cycling stability compared to the control sample.

2:40 PM *MF01/MF02/MF03/MT03.08
Sustainable Production of High-Energy Density Flexible Supercapacitors through Direct Laser Writing on Environmentally Friendly Substrates
João Coelho1,2,3, Rodrigo Abreu4, Maykel d. Klem4,5, Sara Silvestre6, Tomás Pinheiro6, Neri Alves7, Elvira Fortunato7 and Rodrigo Martins7; 1Universidade de Sevilla, Spain; 2Instituto de Ciencia de Materiales de Sevilla (Universidad de Sevilla-CSIC); Spain; 3Universidade Nova de Lisboa and CEMOP/UNINOVA, Portugal; 4School of Technology and Sciences, São Paulo State University (UNESP), Brazil

Supercapacitors (SC) and graphene are two cutting-edge technologies at the forefront of energy storage and materials science. Supercapacitors, often referred to as ultracapacitors or electrochemical capacitors, are energy storage devices that bridge the gap between traditional capacitors and batteries. They are known for their exceptional energy storage and charge-discharge capabilities, making them essential components in a wide range of applications, from consumer electronics to electric vehicles and renewable energy systems[1]. Graphene, on the other hand, promises to revolutionize the field of supercapacitors, offering significant improvements in terms of energy storage, charge-discharge rates, and overall performance. This effect is mainly due to graphene’s high surface area, high electrical conductivity, exceptional capacitance and flexibility, and lightweight. Among a plethora of graphene synthesis and deposition methods, laser-induced graphene (LIG) is one of the most studied[2]. This innovative technique has attracted considerable attention for its potential to improve energy storage devices and scalability. However, in terms of energy storage, LIG has mostly been fabricated in polyimide, which compromises the sustainability of the fabricated devices. In addition, as an electrical double layer (EDL) material, LIG-based supercapacitors will always have a relatively low energy density[3].

In this work, we have developed a simple yet elegant sustainable strategy to fabricate LIG SC on paper and cork with improved electrochemical performance. Based on a fire-retardant treatment, the fabricated EDLC exhibited area-specific capacitances as high as 4.6 mF cm^-2 (0.015 mF cm^-2) for paper and 1.43 mF cm^-2 (0.1 mF cm^-2) for cork. In addition, the devices have excellent cycling stability (> 10,000 cycles at 0.5 mA cm^-2) and good mechanical properties[4,5]. In order to increase the energy density of the device, two different strategies were explored. In one approach, the substrate was impregnated with a precursor that is converted to graphene oxide, a pseudocapacitor material, upon laser irradiation. The other strategy involved electrodeposition the manganese oxide onto LIG electrodes. Both methods resulted in supercapacitors with relatively high energy densities. The advantages and disadvantages of both techniques will be discussed in detail in this talk.

Despite these promising advantages, it’s important to note that graphene-based supercapacitors are still undergoing extensive research and development to optimize their performance and cost-efficiency. Challenges related to scalability and production costs need to be addressed for widespread commercial adoption. Nevertheless, laser-induced graphene supercapacitors hold great promise for improving energy storage solutions and contributing to a more sustainable and energy-efficient future.

References

3:10 PM MF01/MF02/MF03/MT03.06
Omid Dadras-Toussi and Mohammad Reza Abidian; University of Houston, United States

3D printing is taking the stage in the forefront of technological and industrial advancements, particularly in the emerging field of organic micro/nano electronics. Amongst various 3D printing techniques, Direct Laser Writing based on Two-Photon Polymerization (DLW-TPP) reigns supreme, owing to its unique capability to construct arbitrary-shaped 3D architectures in sub-micron resolution. Herein, we have directly incorporated 2 organic semiconductor fillers, i.e. poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) and multi-walled carbon nanotubes (MWCNTs), in a photosensitive ink which can be fabricated into highly conductive microstructures via DLW-TPP. The photosensitive ink contains polymer crosslinker poly(ethylene glycol) diacrylate (PEGDA), two organic semiconductor precursors (PEDOT-PSS and MWCNTs), photo-initiator (ethyl(2,4,6-trimethylbenzoyloxy) phenylphosphinate), and two miscible agents (dimethyl sulfoxide and pentaerythritol tetrais (3-mercaptopropionate)). Formulation-wise, maximum content of PEDOT:PSS and MWCNTs in the conductive, homogeneous, and stable ink was found out to be 0.4 wt% and 0.15 wt%, respectively. Microstructures were constructed on flexible poly(dimethylsiloxane) substrates through 3D movement of XYZ stages and irradiation of 100 femtosecond pulses from two-photon laser, which solidified the resin at its focal point.

Current-voltage measurements revealed that conductivity of microstructures fabricated by the conductive ink was 140050 ± 29414 S m-1, almost ten orders of magnitude higher than their counterparts fabricated with inks without added conductive agent, i.e. 0.0002 ± 0.0003 S m-1 (n=5). Optical transparency of the conductive ink showed ink transmittance of 82% at 550 nm. Moreover, microstructures fabricated with the conductive ink presented average surface roughness of 258 ± 2 nm (n=4).

Fabrication and electrical/electrochemical characterization of various conductive microstructures was successfully demonstrated. In the space of flexible microelectronics and circuitry, printed circuit boards were fabricated via DLW-TPP based on the conductive ink. Functionality of sub-components such as resistors and capacitors were measured and confirmed. In another notable development, multi-site microelectronics were constructed via DLW-TPP. Electrochemical impedance spectroscopy and cyclic voltammetry revealed that recording sites exhibited low impedance (18.28 ± 5.58 kΩ at 1 kHz) and high charge storage capacity (48.13 ± 4.67 mC·cm^-2), which promises their application in potential neural recording/stimulation. Development of these 3D-printed microstructures via DLW-TPP forges the path forward for development of advanced printed circuitry and wearable implanted microelectronics.

3:15 PM MF01/MF02/MF03/MT03.07
3D-Printed Gy rid Architecture for Pressure Sensor Applications
Danielle Agron, Chao Bao and Woo Soo Kim; Simon Fraser University, Canada

The gyroid structure represents a design renowned for its high strength and exceptional energy-absorbing qualities, rendering it a suitable choice for deployment as an energy damping device. Within the family of related gyroid structures, we have opted for the Slab single gyroid (Slab SG) model. This model has been meticulously crafted using the 3D printing method, with the intention of utilizing it as the basis for a capacitance-based pressure sensor. In this work, we introduce a simulation model to homogenize the variations introduced by the FDM manufacturing...
The rapid and straightforward fabrication process of laser-induced graphene (LIG) has unlocked new possibilities in creating flexible sensors for emerging applications, such as wearable electronics and intelligent systems. While LIG exhibits remarkable conductivity as a strain sensor, its application as a printed conductor on flexible substrates faces limitations. In this talk, we present our recent work on a versatile technique to significantly enhance the electrical conductivity and resistive heating capabilities of LIG, making it an ideal choice for flexible conductors in printed electronics. We achieve highly conductive traces by directly writing LIG onto a polyimide film using a CO2 laser. Subsequently, we introduce functionalized liquid metal (LM), specifically eutectic gallium indium (EGaIn) particles, onto the LIG, leading to a remarkable ~400-fold increase in the electrical conductivity of LIG traces. This improvement is achieved while preserving mechanical flexibility and manufacturing scalability, all without the need for soldering. Electromechanical characterization of the LIG-LM traces reveals minimal resistance changes even under substantial bending deformations. Simultaneously, the enhanced electrical conductivity plays a pivotal role in improving the resistive heating performance, significantly reducing the input voltage requirement (by ~15 times) to achieve similar surface temperatures compared to pure LIG traces. By combining EGaIn with laser-synthesized graphene, we successfully fabricate flexible hybrid electronics, demonstrating the practicality of this technique through the creation of highly customizable patterns for flexible conductors and heating devices.

Inkjet Printing Multimaterial Electronics – A Multi-Laser-Based Additive Nanomanufacturing Approach

Masoud Mahiouri-Samani, Zabihollah Ahmadi, Aarsh Patel and Adib Taba; Auburn University, United States

Printed flexible hybrid electronics (FHEs) have emerged as a remarkable technology in recent years due to the simple, cost-effective fabrication, reduced e-waste, and development of multifunctional devices. The rising demand for consumer and industrial electronic products that are uniquely fabricated/designed and increasing usage is boosting the demand for this technology. Current techniques rely on ink-based printing technologies such as inkjet and aerosol jet printers, which suffer from contamination, expensive formulation procedures, and limited materials sources, making it challenging to print pure and multimaterial devices. In this contribution, I will demonstrate a multi-laser-based additive nanomanufacturing (ANM) technique that allows dry, pure, solvent-free printing of electronics and functional devices on various substrates. The Key technology advantages include 1) on-demand and in-situ laser generation of various pure nanoparticles without contaminations, 2) in-situ and real-time laser sintering of nanoparticles on various substrates with no further post-processing, 3) multimaterial printing of hybrid and tunable nanocomposite materials and structures. Several different mechanical and electrical performance tests like bending, cycling, and surface adhesion are performed on the printed devices, which demonstrate their exceptional performance and the considerable impact this technique has on the future of printed sensors and devices.
Utilizing the laser engraving to fabricate neuroprostheses could enable more efficient fabrication approach toward neural probe by eliminating the intricate and expensive microfabrication approach. We are utilizing polyelectrolyte to provide a pinhole-free, high flexibility, high mechanical strength, and biocompatible platform to construct implantable ACh-detecting sensors consisting of a working electrode (containing an acetylene organic sensing membrane) and a reference electrode (containing a reference membrane). The electrical potential (emf or electromotive force) between the ACh sensor and reference electrode correlates to the activity of ACh in the biofluid, according to the Nernst Equation (E = E° + (RT/2F) log[ACh]). Where, E° shows the standard potential, R the universal gas constant, T temperature, F the Faraday constant, n the charge of the ion, and[ACh] the activity of ACh. A theoretical slope of 59.2 mV/decade is expected at room temperature and is defined as the Nernstian slope. The fluorous-phase solid-contact LIG ion exchanger electrode showed a near Nernstian slope of 54.9 ± 0.8 and a 42 nM limit of detection.

2:15 PM MF02.02.02
3D Nanomanufacturing in Nano- and Microstructures and Applications
I. Huace1, Wei Xiong1,2, Chunsan Deng1, Tao Han1, and Hui Gao1; Huazhong University of Science and Technology, China; 2Optics Valley Laboratory, China
Microsystems can achieve high performance, smaller sizes, and lower power consumption through integrating three-dimensional (3D) functional structures of various metal oxides. However, the nanomanufacturing and heterogeneous integration of 3D functional metal oxides still face long-standing challenges. Currently, the mainsteam 3D manufacturing techniques of metal oxide structures can be classified into two methods including particle-loaded bonding and femtosecond laser direct writing (FLDW). Particle-loaded bonding technology utilizes material's jetting or extrusion to achieve the 3D printing and heterogeneous integration of various kinds of metal oxides. However, its manufacturing resolution (<10 µm) and quality (high roughness, low stiffness) are difficult to meet the application requirements of integrated microsystems. On the other hand, although the FLDW technology has nearly unrestricted 3D design freedom at the nanometer resolution, the 3D metal oxide structures manufactured by this technology commonly suffer from serious shape distortions, limited material applicability, and difficulties in heterogeneous integration.

To address the above issues, we propose a method for 3D nano-printing and heterogeneous integration of various kinds of metal oxides by FLDW the water-soluble resin of metal ion-coupled coordination. This method has the following three main advantages: 1) The mechanism of mutual promotion between acrylic acid and 1-vinylimidazole in coupled coordination with metal ions has been proposed, which breaks through the concentration limit of metal ions in the 3D structure manufactured by traditional methods, increasing the metal ion content to 30.5% in the 3D structure, thereby significantly reducing the degree of morphological distortion. 2) The resin for FLDW is designed to be water-soluble, which may potentially extend this method to the processing of oxide of all water-soluble metal elements. 3) Sequential 3D printing according to the priority of metal activity enables the 3D heterogeneous integration of various functional metal oxides. The successful design of this printing method enables us to manufacture 3D nanostuctures and heterogeneous integrated structures of various types of metal oxides, including MnO2, Cr2O3, ZnO, NiO, and Co3O4. Furthermore, we demonstrate a high-sensitivity 3D ZnO hybrid-integrated sensor with a sensitivity of up to 1.113 million in a 200 ppm NO2 environment, which is much larger than the sensitivity of the 2D device. Therefore, this printing method expands our capacity to manufacture 3D metal oxides at the nanoscale and demonstrate its significant application potential in the field of integrated sensing devices, integrated medical endoscopes, nanogenerators, and other 3D microsystem applications.

2:30 PM MF02.02.03
Selective Laser Sintering of Functional Polymer Powders for Precise Fabrication of 3D Hierarchical Composites
Weimin Xu; University of Akron, United States
Selective laser sintering (SLS) (also named powder bed fusion) has been regarded as the most promising polymer 3D printing technology for many industrial applications. Its unique advantages compared with extrusion- or photopolymerization-based technologies include the ability to fabricate complex geometries without support structures, highly isotropic properties of the printed parts, and batch production of multiple parts in one printing. However, the major disadvantage is that the SLS is limited polymer powder selection (95% is based on polyamide) and difficulty in multi-material printing. Here, I will present our recent progress in the development of new types of polymer/composite microparticles for SLS, and more importantly, the simultaneous laser-induced graphitization of polyimide microparticles into 3D hierarchical graphene structures with precisely controlled geometry and internal structure. 3D graphene-metal oxide structures can also be fabricated by this strategy, which have superior electrochemical properties for energy storage and catalysis applications.

2:45 PM BREAK

3:15 PM MF02.02.04
Direct Freeform Laser Fabrication of Multimaterials for 3D Electronics
Jian Lin; University of Missouri-Columbia, United States
In the past decade, direct laser fabrication (DLF) has been witnessed an exponential growth in various applications. Among them, one prominent field is sensor and electronics. Despite much progress, the mainstream application of DLF is restricted to planar fabrication capability. In this talk, we will discuss our recent progress in bringing such a capability in the conventional 2D plane to 3D free space. The first technological advance is to develop a 5-axis laser-processing platform. With the two additional two degrees of freedom, the laser beam can be focused on arbitrary surfaces for freeform laser induction (FLI) of representative laser induced graphene (LIG), metals, and metal oxides as high-performance sensing or/and electrode materials in 3D conformable electronics. To make a new stride based on this success, recently, we developed a freeform multimaterial assembly platform (FMAP) by integrating 3D printing (fused deposition modeling (FDM), direct ink writing (DIW)) with the FLI technique. 3D printing performs the 3D structural material assembly, while the FLI can fabricate and pattern the functional materials in predesigned positions of the 3D structures by synergistic, programmed system actuation. By this platform, crossbar LED circuit, touchpad for human-machine interaction, multiple sensors, sensor-enabled springs, electromagnets, force feedback manipulators, and microfluidic reactors with embedded heating elements were fabricated to demonstrate the versatility and effectiveness of the technique.

3:45 PM MF02.02.05
High Temperature Reactions in Laser-Assisted Ceramic Additive Manufacturing
Leonard Siebert, Philipp Schadte and Rainer Adelung; Kiel University, Germany
Ceramics are the most temperature- and oxidation-stable materials known. Usually only strong acids or bases are capable of inducing ceramics to react. When dealing with extreme temperatures over 3000 °C, however, oxides can be induced to lose an oxygen and become reactive. This can be used in laser-assisted additive manufacturing (AM) of ceramics. Lasers are used here to sinter or melt the ceramics layer-by-layer. Additionally, each layer and even each spot can be irradiated with almost arbitrary high power and thus extreme heating, which leads to extraordinary reaction kinetics.

As an example, irradiating SiO2 with a CO2-laser (λ=10.6 µm), it can be evaporated with ease, while more stable ceramics like ZrO2 can be reduced to ZrO, losing one oxygen in the process. This state can be stabilized in inert gas atmosphere and quenched to room temperature, while in oxygen-rich atmosphere the recapture of oxygen takes place upon cooling. When in its reduced state (i.e., ZrO), can react with other substances to form intermediaries that are usually hard to produce. For instance, by varying the gas atmosphere to forming gas (5% hydrogen, 95%
Additionally, the solid phase can trigger certain reactions as well. The addition of Ti powder and a forming gas lead to the formation of an interpenetrating phase composite made from TiN and E-Textile Enabled by Femtosecond-Laser-Induced Graphene Formation on Kevlar wearable systems is evaluated through various human trials toward precision nutrition, stress/mental health assessment, and chronic disease management (e.g., systemic inflammation hormones, proteins, and drugs. Laser engraving enables the manufacturing of high-performance nanomaterials-based biosensors at large scale and low cost. The clinical value of our LEG-based analysis. Such wearables can autonomously access body fluids (e.g., human sweat) across the activities and continuously measure a broad spectrum of analytes including metabolites, nutrients, personalized e-textiles, a simpler design and patterning strategy is essential.

**References**
high-performance e-textiles. Nonwoven textiles consist of randomly aligned yarns mechanically bonded or adhered together. They have high strength but low stretchability. Knit textiles, made from intersecting yarn loops, are inherently stretchable, resembling a mechanical spring. Woven textiles involve interlacing weft and warp yarns, creating special bending sensing networks when subjected to strain.

In this study, we introduce a straightforward method for creating multi-modal e-textiles. We achieve this by one-step, maskless patterning of LIG using near-infrared ultra-short femtosecond laser pulses on various Kevlar textiles, including nonwoven, knit, and woven varieties. Our approach directly transforms common textiles into e-textiles in a cost-effective and simple manner, without the need for fiber weaving, while preserving their flexibility, adaptability, and air-permeability with minimal ablation. This direct laser writing method is faster, more accessible, and allows for better carbon ratio control compared to conventional techniques like chemical vapor deposition (CVD) and thermal reduction. Nonwoven textiles, with their high mechanical strength and resistance to external strains, are suitable for applications unrelated to mechanical strain, such as energy storage devices and temperature sensors. The supercapacitor demonstrates a specific areal capacitance of 36.17 mF/cm², and the temperature sensor exhibits a thermal coefficient of resistance (TCR) of -0.097% per degree Celsius within the temperature range of 5 to 100 degrees Celsius. The knit structure, known for its wide stretchability, is ideal for creating strain sensors to detect human motion, with a gauge factor (GF) reaching 117.9 within a 0-3% strain range. The woven structure, characterized by a lattice-like network, is suitable for fabricating a bending sensor for voice recognition, with a GF of 230 within a 0-4.5% strain range. These designs demonstrate the capability of femtosecond laser pulses for one-step, maskless patterning of LIG sensors and energy storage devices, paving the way for future wearable multi-modal e-textiles.

10:00 AM BREAK

10:30 AM MF02.03.04

Laser-Induced Dewetting for The Formation of Monometallic and Bimetallic Nanoparticle Arrays on Patterned Dimpled Tantalum Substrates and Their Electrochemical Properties V拼音 Shu, Stephanie N. Bonvicini, Annie Huang and Vilola Birs, University of Calgary, Canada

Highly ordered metal nanoparticle (NP) arrays have attracted great research interest due to their unique electronic, optical and magnetic properties, leading to their diverse applications as model electrodes for electrocatalysis in fuel cells, sensors, in magnetic memory arrays and catalysts for the growth of semiconductor nanowires. Here in this work, we report the use of pulsed laser-induced dewetting (PLID) for the fabrication of metallic NP arrays, including monometallic (Au, Pt) and bimetallic Au-Pt, on a pre-patterned dimpled Ta substrate. In PLID, the metal is quickly heated to above its melting point within a short duration of the incident laser irradiation and the molten film breaks up to form metal NPs to reduce the free energy of the film-substrate-ambient system. The highly ordered dimpled Ta substrate, formed by anodization of polycrystalline Ta in a H2SO4 + HF solution, consists of a self-assembled array of inverted hemispherical caps, or nanodimples. It has been shown that highly ordered Au, Pt, and Au-Pt NP arrays can be produced on the dimpled Ta substrate with excellent monodispersity, long-range order and good dimple coverage. Combined with thermal dewetting, which is a solid-state dewetting method driven mainly by surface diffusion, PLID is more efficient and better suited for metals of high melting point. The size of monometallic Au and Pt NPs can be controlled by the initial film thickness as the dewetting process is shown to follow the spinodal dewetting mechanism. For the bimetallic Au-Pt NPs, the total bilayer metallic film thickness plays a determining role. We have also shown that the metallic NPs formed by PLID are more spherical in shape than those by thermal dewetting. The produced bimetallic Au-Pt NPs have a configuration of a Pt-rich core and Au-rich shell. Finally, characterization of the electrochemical properties of the Pt-rich core/Au-rich shell NPs reveals strong Pt-O bonding on the bimetallic NP surfaces. In addition, while Au is enriched on the bimetallic NP surfaces, a significant Pt content, ranging from 10% to close to 40%, is still present on the NP surfaces, which makes the produced Au-Pt NPs useful for bifunctional electrocatalytic reactions.

11:15 AM MF02.03.06

Laser-Induced Oxidation and Defect Formation of Thin-Film Materials for High-Throughput Materials Discovery Drake R. Austin1,2, Brian Everhart2, Michael Altvater1,2, Mario Hofmann3, Rahul Rao2 and Nicholas Glavin2; 1UES Inc., United States; 2Air Force Research Laboratory, United States; 3National Taiwan University, Taiwan

The discovery of nanomaterials is an exceptionally slow process requiring many years of development in order to translate fundamental research to real capabilities. Consequently, a rapid materials discovery approach is needed to understand and tailor the properties of materials for specific applications. In this work, we present a high-throughput laser-processing methodology for producing and characterizing hundreds of modified regions on a single precursor sample. In particular, laser-induced oxidation and defect formation in transition metal dichalcogenides is presented, where the thermodynamics of the process is controlled by scanning a continuous-wave laser across the sample surface at varying scan speeds and intensities. Coupled with in-situ Raman and photoluminescence spectroscopy, this allows for the generation of laser-processing diagrams indicating the conditions necessary to produce varying stoichiometries, crystal structures, and defect densities. With additional ex-situ optical and electrical characterization, this method can be used to identify novel materials with properties of interest for a variety of applications including sensing, photocatalysis, and neuromorphic computing.

11:30 AM *MF02.03.07

Laser-Matter Coupling Mechanisms Governing Nanoparticle Damage on Patterned Doped Tantalum Substrates and Their Optical Properties Manyaibho Matthews, Lawrence Livermore National Laboratory, United States

The recent fusion ignition breakthrough at Lawrence Livermore National Laboratory’s National Ignition Facility has generated a renewed interest in improving high harmage threshold optical materials. While decades of improvements in optical material processing for high power laser systems has led to unprecedented levels of laser damage tolerance, surface contamination on surfaces generated during laser operation, optic assembly or handling can still lead to damage initiation and local failure of the optic. Laser micromachining of optics for damage repair and laser-induced damage cross-contamination can also introduce nanoparticulate debris, compromising the issue further. In addition to local damage initiated at the site of the debris and leading to failure, non-local mechanisms associated with contamination have been recognized wherein nano- to microscale particles on the entrance surface of optics can lead to Fresnel diffraction of incident light and damage on the exit surface. The dynamics of the laser-particle interaction involve high gradients of pressure, temperature and corresponding changes to thermodynamic material properties, plasma formation and aerodynamic effects that drive nanoscale morphological changes to the optical surface. In addition, the formed plasma can interact with the laser pulse while the melted material layer on the particle is thus heated to a high temperature.

In this talk, I will present a study of the interaction of microscale, metallic and glass particles bound to optical surfaces with nanoscale and picosecond laser pulses at 1064- and 355-nm that results in nanoparticle ejection and nanoscale modification of the optical surfaces. Our in situ experimental platform allows direct measurements of the particle velocity, plasma formation, and the kinetics of the ejected nanoscale material. Large aperture damage tests were also performed to assess damage probabilities and probe the stochastic nature of particle-induced damage events. We use FDTD, Fourier beam propagation and ray tracing to understand the effect of particle shape and particle-induced nano-pitting on beam propagation. By varying the combination of particle and substrate materials, we are able to gain important insights to the governing mechanisms of laser-particle interactions which could lead to improvements in inertial confinement fusion laser system designs. This work was performed under contract DE-AC52-07NA27344.

SESSION MF02.04: Laser-Induced Graphene Processing Methods and Applications
Session Chairs: Antje Baeumner and Rahim Rahimi
Wednesday Afternoon, April 24, 2024
Described will be the initial discovery of laser-induced graphene in 2013 and early rapid developments over the next few years. This will be a historical outlook, noting the initial post docs, graduate, and undergraduate students, that laid the foundation for this remarkably simple method to patterned graphene surface and devices. The science of materials conversion to graphene will be discussed. The surfaces will be outlined, starting with polyimide, and then branching into nearly any carbon surface through simple adjustments to the laser. Early devices will be presented, including energy devices and sensors that set the groundwork for enormous advances in engineering designs around the world.

In this presentation, we will discuss finding from reactive molecular dynamics simulations (ReaxFF) to investigate LIG formation from five different polymers structures. Our research revealed that the initial molecular structure of the parent polymer significantly influences the resulting graphitic structure. During the early stages of LIG formation, the polymer transforms into an amorphous structure, resulting in various graphitic layers with varying degrees of disorder. The resulting LIG exhibits out-of-plane undulations and bends due to the presence of numerous 5- and 7-member carbon rings throughout the structure. Our simulated molecular structure aligns well with recent experimental observations in the literature. Moreover, we observed that LIG yield is higher in inert conditions compared to oxygen-rich environments. Specifically, LIG derived from polybenzimidazole demonstrated the highest surface area and yield among the five polymers studied. These findings enhance our understanding of LIG formation mechanisms, offering valuable insights for various bulk LIG applications such as sensors, electrocatalysts, microfluidics, and precise polymer welding through targeted heating.

Infrared (IR) lasers, such as the carbon dioxide laser popularly used by hobbyists and various industries for precision cutting and marking/engraving, are increasingly employed in the conversion of carbonaceous precursors into a mesoporous graphene-like carbon material, known as laser-induced graphene (LIG). In this presentation, I will delve into my research group's recent explorations into the potentials and limitations of utilizing this technique to create electrodes for batteries and supercapacitors. Our focus centers on the carbon precursor polyfurfuryl alcohol (PFA), a common component for crafting glassy carbon electrodes, derived from waste biomass. By amalgamating PFA with IR transparent salts, we aim to extend the laser's penetration depth, thus producing electrodes with an enhanced surface area or greater areal mass loading. Our findings reveal that typical salts, such as sodium chloride or sodium sulfate, not only achieve these objectives but also serve a dual role as a templating and doping agent, markedly improving the areal capacitance of symmetric supercapacitors. Furthermore, by incorporating this system with metal salts or catalyst precursors, we engineer unique compositions and nanostructures exhibiting significant electrochemical activity towards the oxygen reduction reaction. Our studies show that the process of direct laser writing on air-cathodes is a superior method to develop high-performance zinc-air batteries.

Our studies show that the process of direct laser writing on air-cathodes is a superior method to develop high-performance zinc-air batteries. Our investigations have proven that LCNFs are highly promising for the development of point-of-care testing where high analytical performance can be achieved together with high affordability.

Laser-Induced Graphene for Electrochemical Sensing: From Process Development to Real-World Applications

Michael A. Pope
University of Waterloo, Canada

Described will be the initial discovery of laser-induced graphene in 2013 and early rapid developments over the next few years. This will be a historical outlook, noting the initial post docs, graduate, and undergraduate students, that laid the foundation for this remarkably simple method to patterned graphene surface and devices. The science of materials conversion to graphene will be discussed. The surfaces will be outlined, starting with polyimide, and then branching into nearly any carbon surface through simple adjustments to the laser. Early devices will be presented, including energy devices and sensors that set the groundwork for enormous advances in engineering designs around the world.

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Laser Reactive Sintering of Complex Oxides

Jeldrik Schulte, Martin A. Schroer and Markus Winterer; Universität Duisburg-Essen, Germany

UV laser sintering allows densification and microstructural transformation of granular systems. The high photon energy of an UV laser leads to resonant heating if the energy is higher than the band gap of the irradiated material. Due to this effect, the heat load is strongly localized, and for nanostructured materials temperatures up to 2000°C and extremely high heating rates are reached at low laser powers [1]. Therefore, UV laser sintering is a versatile tool for materials engineering, as it enables reactive sintering of binary metal oxides to generate complex oxides with short process times. It is also feasible for processing (printed) electronic components with structures in the micrometer range.

The complex oxide CuAlO2 is a transparent conductive oxide (TCO) with p-type conductivity [2]. TCOs are widely used in photovoltaics and optoelectronic devices like flat panel displays or solid-state lighting. However, the production of p-type TCOs is still significantly lower compared to n-type TCOs. This impedes the production of high-performance p-n junctions, needed as key components for active electronic devices. Complex oxides with delafossite structure, like CuAlO2, have shown great potential to overcome this problem [3].

The production of the CuAlO2 delafossite is a challenge, because of the complexity of the binary phase diagram. In this contribution, we will present the generation of CuAlO2 by reactive UV laser sintering of copper and aluminum nanoparticles and their characterization, including μXRD diffraction.


Acknowledgements: Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation): SCHR 1753/1 & WI 981/19-1 (project nr: 531185908), INST 20876/395-1 FUGG


Beatrice De Chiara, Fulvia Del Duca, Mian Zahid Hussain and Bernhard Wolfraum; Technical University of Munich, Germany

Electrochemical sensors have gained widespread recognition and utilization across diverse domains, encompassing applications such as clinical diagnosis, biochemical detection, and environmental monitoring. In the pursuit of enhancing these sensors, metal-organic frameworks (MOFs) have emerged as highly promising material candidates. MOFs are known for their porous structures, which exhibit substantial surface areas, remarkable stability, and a unique capacity for functionalization. Here, we aim to integrate MOF structures into laser-induced graphitic (LIG) electrodes to improve the performance of electrochemical sensing devices. LIG electrodes present certain advantages over classical noble metal electrodes, such as reduced cost and ease of fabrication. We investigate the disparities between LIG sensors and LIG-MOF sensors, both of which are fabricated using direct laser scribing, a fabrication technique with the remarkable capability to convert non-conductive materials into active electrode materials, all while generating desired patterns directly onto polymer substrates. Central to this investigation is the conversion of MOFs into patterned derived carbon utilizing an ultraviolet (UV) laser system. The process entails several steps. Initially, a solution containing MOFs is drop-cast onto a polyimide (PI) foil substrate. Once the MOF composite is deposited onto the substrate, the electrode is directly patterned with the UV laser. Importantly, the MOF composites are confined to the electrode area, while the feedline and contact pad exclusively consist of LIG. For the passivation of the structures, Parylene C (poly(p-xylylene)), a flexible dielectric polymer, is chosen due to its good insulation properties and conformability. A thin film of Parylene C, approximately 5 micrometers thick, is fabricated using direct laser scribing, a fabrication technique with the remarkable capability to convert non-conductive materials into active electrode materials, all while generating desired patterns directly onto polymer substrates. Central to this investigation is the conversion of MOFs into patterned derived carbon utilizing an ultraviolet (UV) laser system. The process entails several steps. Initially, a solution containing MOFs is drop-cast onto a polyimide (PI) foil substrate. Once the MOF composite is deposited onto the substrate, the electrode is directly patterned with the UV laser. Importantly, the MOF composites are confined to the electrode area, while the feedline and contact pad exclusively consist of LIG. For the passivation of the structures, Parylene C (poly(p-xylylene)), a flexible dielectric polymer, is chosen due to its good insulation properties and conformability. A thin film of Parylene C, approximately 5 micrometers thick, is deposited via a chemical vapor deposition. Subsequently, the electrode area and contact pad are precisely opened using the laser.

The characterization of the resultant sensors was conducted using scanning electron microscopy, Raman spectroscopy, impedance spectroscopy, cyclic voltammetry, and differential pulse voltammetry. These characterizations revealed the emergence of a highly porous carbonaceous material, with low-impedance observed in the case of the LIG-MOF sensors. This approach not only expands our understanding of MOF integration into electrochemical sensing but also underscores the potential for applications where high charge injection capabilities and low impedance at an electrode/electrolyte interface are required.

Electrochemical CO2 Reduction to HCOOH Catalyzed by Ag6(NO3)4 Clusters prepared by Laser Ablation at The Air-Liquid Interface

Teppei Nishi, Shunsuke Sato and Takeshi Morikawa; Toyota Central R&D Labs., Inc., Japan

Nanostructures generated via laser ablation in liquid have been developed because of the capability to generate nanoparticles without chemical reagents. However, it is difficult to obtain monodispersed and small (~2 nm) nanoparticles. We have reported laser ablation at the air-liquid interface to obtain monodispersed and small (ca. 5 nm) nanoparticles [1]. Here, we report laser
ablation at the air-liquid interface using colloidal nanoparticles as a target to obtain smaller clusters [2]. Colloidal target was prepared by laser ablation of Ag powder precipitated on the bottom of the flask. Pulsed laser was irradiated through the bottom of the flask. After laser irradiation for 60 min, Ag nanoparticles stably dispersed in pure water was obtained. This colloidal exhibited a large absorption peak at 400 nm. This colloidal solution was agitated at a measuring flask during laser ablation at the air-liquid interface. After laser ablation at the air-liquid interface, we obtained colorless and transparent solution, indicating the drastic size reduction. UV-Vis absorption spectra exhibited peaks in UV region. It indicated small shatter cluster formation. The size was assessed by electrospray ionization-mass spectrometry. It revealed Ag(NO3)2 clusters. In our experiment, to investigate the electrocatalytic activity, Ag(NO3)2 clusters were deposited on carbon paper substrate. Electrochemical activity for CO2 reduction was assessed in CO2 saturated aqueous 0.1 M KHCO3 solution at an applied potential of -1.2 V vs RHE with Ag/AgCl reference electrode and Pt wire counter electrode. As well-known, micro and nano-sized Ag catalyst as comparisons generated CO via electrochemical CO2 reduction. In contrast, Ag(NO3)2 clusters generated HCOOH with a Faraday efficiency of 33%. The results indicated a drastic change in the selectivity induced by laser ablation at the air-liquid interface. Because the unique selectivity, carbon source of HCOOH was determined by isotope tracer analyses using 13CO2 and KH13CO3 together with ion chromatography-mass spectrometry. Because only 13C/12C peak was confirmed, it can be concluded that HCOOH was generated from CO2. Both the catalyst size and modification by NO3 potentially explain the results.

For highly active electron transfer and ion diffusion, electrically and thermally conductive 3D graphene foams (3D GFs) heavily rely on precise control of their surface wettability with respect to different polarities of fluids. For their practical applications, either hydrophilic or hydrophobic 3D GFs are prepared in advance; even though there have been many different ways of controlling their surface wettability, such as solvent treatment, heteroatom doping, ultraviolet or laser irradiation, and plasma treatment, they are time-consuming and even high-cost processes, limiting them to be only applicable for 2D graphene or powders. Here, we present a novel and rapid superwettability switching of 3D GFs in a reversible and reproducible manner, as mediated by solvent-exclusive microwave arcs. As the 3D GFs are pre-coated with vaporized solvents exclusively, short microwave radiation (≤10 s) leads to plasma hot-spotted production of polar or nonpolar radicals. Upon immediate radical chemisorption, the 3D surfaces become either superhydrophobic (water contact angle = -170°) or superhydrophilic (≤0°), and interestingly, the dramatic wettability transition can be repeated many times due to the facile exchange between previously chemisorbed and newly introduced radicals. Our microwave-mediated, quick and reversible wettability switching would be applicable for many different applications (e.g., energy storage, sensing, microfluidic transportation, and water-oil separation). Importantly, our superwettability switching is applicable for all kinds of carbon-based nanomaterials, including 2D graphene and carbon nanotubes.

First, we test the fabricated electrodes by measuring the sheet resistance of the generated graphitic carbon material over gold, where we select the optimal laser parameters for best performance. Firstly, their patterning or selective removal requires a series of additional lithographic steps. Secondly, a major hindering factor is the stability of the polymer-metal adhesion under mechanically-challenging conditions within electrolyte environments. Direct laser scribing of organic substrates has recently emerged as a rapid and straightforward method for patterning conductive tracks directly from insulating layers. Laser-induced graphene (LIG) electrodes are fabricated in a one-step process. A laser beam irradiation of suitable organic precursors thermally converts the insulating material into a multilayered graphene 3D structure with various degrees of porosity. Typically, CO2 infrared lasers are employed for LIG fabrication over organic substrates with thickness down to 25 µm, but more commonly in the range of hundreds of µm. While LIG structures offer advantages such as direct fabrication, large storage for supercapacitors applications, and high effective surface area for biosensing, their higher feedline resistance compared to metals hinders their usability and advancement. Vomero et al. [Sci. Rep. (2018) 8:14749] fabricated parylene-based LIG electrodes over a 25 µm-thick metal foil, showing the possibility of employing LIG sensors in combination with metal feedlines. Typically, the conductive layers used in microelectrode arrays (MEAs) and flexible electronics are hundreds of µm thin. Here, we present a material to fabricate carbonic electrodes by direct laser scribing of insulating polymers over such thin metal layers, effectively opening the electrode sites with graphitic carbon without damaging the underlying metal tracks. The MEAs are fabricated by depositing an insulating layer of 5 µm parylene-C over a detachable substrate, then etching and patterning a conductive layer of 100 nm gold, and insulating again with 5 µm parylene-C. Then, a UV (355 nm) nanosecond pulsed laser is used to carbonize the parylene-C locally over the gold to open the electrode sites and contact pads. The 10-µm-thin electrodes are then released from the substrate. Therefore, no dry etching and hard mask patterning are required to open the electrode insulation, and the conductive material is directly generated from the insulating layer. First, we test the fabricated electrodes by measuring the sheet resistance of the generated graphitic carbon material over gold, where we select the optimal laser parameters for best performance. Then, we test the electrodes in phosphate-buffered saline to measure the electrochemical impedance and the charge storage capacity, as well as the charge injection capabilities for neural stimulation applications. The mechanical stability of the adhesion between graphetic carbon and gold is also tested both in dry and aqueous environments, relevant to the contact pads and electrode sites, respectively. We also investigated the miniaturization limits of the fabricated electrode sites by laser scribing in different writing modes and with different line writing densities.
In summary, we propose a new and rapid method for electrode fabrication applicable to thin-film and polymer-based electronics.

5:00 PM MF02.05.10
In-Field Monitoring of Plant Stress with a Low-Cost Electrochemical Sensor Sina Khazaee Nejat and Maral Mousavi; University of Southern California, United States

Environmental challenges, like drought, severe temperatures, pests, and diseases, have adverse effects on the growth, development, and yield of plants. Salicylic Acid (SA) serves as a plant hormone responsible for signaling in response to stress, and it plays a crucial role in plants' defense mechanisms against certain types of pathogens. Elevated levels of salicylic acid in plants serve as an indicator of stress. It is essential to monitor and assess plant stress to ensure the well-being and productivity of crops, as well as a steady food supply. The on-site measurement of salicylic acid aids in the early detection and diagnosis of plant stress, enabling prompt actions to reduce harm and sustain crop productivity.

Point-of-care diagnostic technologies have emerged as an advancement in medical analysis and monitoring. These technologies offer a decentralized and cost-effective approach, making accessibility to crucial diagnostic services easier. As a rapid first line of diagnosis, they serve as a frontline defense.

In this work, we introduce an affordable electrochemical tool designed for the purpose of tracking plant stress by detecting Salicylic Acid (SA). The device is equipped with wireless connectivity, allowing it to transmit data to a smartphone via the Bluetooth Low Energy (BLE) protocol.

Methods
Electrochemical techniques have been used to monitor SA levels. We've utilized laser-induced graphene (LiG) electrodes, a low-cost and scalable 3D porous carbon material created through laser-based polymer-to-graphene conversion, which shows promise for electrochemical sensors.

We've developed an affordable, portable potentiostat to continuously monitor salicylic acid (SA) levels in plants, with the collected data being transmitted to a nearby smartphone via Bluetooth Low Energy technology.

Results
The ability to efficiently scale the production of LiG electrodes offers a cost-effective method for creating these systems. Examination of these electrodes reveals the formation of a graphene layer on the Pi film. Moreover, by optimizing laser machine parameters, we have achieved electrodes that not only consistently reproduce but also exhibit impressive electrochemical capabilities.

Square-wave voltammetry measurements were conducted using the LiG sensors, with varying concentrations of SA in buffer. The peak current value demonstrates a linear relationship with the SA concentration, with a sensitivity of 130.54 µA/mM, and linearity range between 5 µM and 150 µM. The limit of detection is 1.75 µM.

Conclusion
An affordable device based on laser-induced graphene (LiG) for monitoring plant stress is created, and it is seamlessly integrated with a portable potentiostat. This device enables the detection of salicylic acid, a phytohormone vital for plant stress signaling. The detection is achieved using a LiG electrode design, and our system has successfully demonstrated this capability.

5:00 PM MF02.05.11
A Nafion-Modified Laser-Induced Graphene Sensor for Spontaneous Monitoring of Caffeine and Vanillin Haozheng Ma, Stephanie Bartholomew, Jay Yoo, Caden Pak, Abdulrahman Al-Shami, Mona A. Mohamed and Maral Mousavi; University of Southern California, United States

Introduction: Coffee is a globally consumed beverage, widely known for its main active ingredient, caffeine. Although a daily caffeine limit of 400 mg is considered safe, exceeding this limit can lead to adverse effects such as depression, anxiety, irritability, and other health issues. Another frequently used compound in the food and beverage industry is vanillin, which provides a characteristic sweet and creamy aroma. Like caffeine, excessive consumption of vanillin can also lead to adverse effects like headaches and gastrointestinal disturbances. Despite the widespread consumption of caffeine and vanillin, accurately determining their content in different foods and beverages is challenging. This complicates the monitoring of daily intake, making it difficult to manage potential health risks effectively. Laser-Induced Graphene (LiG) is a specialized form of 3D porous carbon nanomaterial with unique properties. It is created through a process called direct laser writing, which is performed on certain polymer materials in ambient conditions. The technique is both simple and quick, making LiG an attractive material for a variety of applications. Due to its excellent physical and chemical attributes, including a large surface area and superior electrochemical performance, LiG has become particularly valuable in the development of medical sensing devices.

Methods: We fabricated Laser-Induced Graphene (LiG) with 30 W 9.3 µm CO2 laser engraver (VLS 2.30, Universal Laser System), and used it as working electrode by applying a Nafion monolayer to its surface. The electrode was then dried at room temperature for 30 minutes. A LiG reference electrode was prepared using screen printing to cover silver ink on LiG, leaving the counter electrode blank. The sensor's performance was tested using varying concentrations of caffeine and vanillin in PBS (pH=7.26). Testing methodologies included cyclic voltammetry and square wave voltammetry with an electrochemical working station (CHI760E, CH Instruments, Inc.).

Results: To facilitate the monitoring of daily caffeine and vanillin intake, we have utilized Nafion-modified LiG sensor to develop an electrochemical point-of-care sensor. Based on the extensive surface area and superior electrochemical performance of LiG and the protective Nafion layer that imparts high stability for long-term storage and multi reproducibility, this novel sensor can detect caffeine, that shows a peak around 1.4 V, and vanillin which has a peak around 0.6 V, both within a linear range of 10 µM to 200 µM.

Conclusions: The developed Nafion-modified LiG sensor offers a promising approach for effectively monitoring caffeine and vanillin consumption. This technological advance aids in better dietary management, thereby contributing to overall health.

Acknowledgment: Haozheng Ma would like to acknowledge the Viterbi Graduate School Fellowship.

5:00 PM MF02.05.12
Laser-Induced Pyrolytic Jetting of Porosity Variable Silica Thin Film for Fog Harvesting Kounqun Min1,2, Hyunko Lee1,2 and Ji Hwan Lim1,2; 1Hanyang University, Korea (the Republic of); 2BK21 Four Erica-Ace Center, Korea (the Republic of)

Laser direct writing (LDW) is a renowned maskless manufacturing technology that employs laser beams for the direct creation of micro and nanostructured devices. It overcomes the limitations of conventional multi-step manufacturing processes such as lithography and molding. LDW has a significant impact in a multitude of sectors, spanning from microelectronics and optics to medical devices and beyond, thanks to its merits, including rapid prototyping, customization flexibility, precise control, and adaptability to various materials.

For PDMS, its exceptional optical transparency across a broad spectrum of wavelengths fundamentally constrains the potential applications of laser patterning technology. However, recently, successive laser pyrolysis (SLP) has been proposed as an on-demand laser-based transparent polymer patterning process, relying on the controlled sequence of photothermal pyrolysis phenomena guided by a continuous-wave (CW) laser. After effectively removing the pyrolysis by-product, SLP offers the rapid digital patterning of high quality 2D and even 3D PDMS microstructures, wherein the laser beam is directly utilized without the need for supplementary post-processing steps. Moreover, the by-products generated in the SLP process, including SiC and the silica layer on the surface, present versatile opportunity for utilization as microstructure in various applications including surface treatment such as wettability modification. In our study, to harness the extensive utility of the surface silica layer, we employed the SLP process on a PDMS-glass hybrid substrate, facilitating the creation of a tunable silica film with controlled porosity through the pyrolytic jetting phenomenon.

The PDMS-glass hybrid substrate is prepared through the deposition of a thin PDMS layer onto a soda-time glass substrate via a spin-coating method. During the SLP process, the gas generated as a result of PDMS pyrolysis is effectively contained by the glass substrate, directing gas concentration towards the PDMS surface, thereby facilitating the requisite pressure for the ejection of the silica film. Furthermore, the glass substrate plays a dual role by not only acting as a gas barrier but also composing the PDMS layer, thereby optimizing the efficiency of the silica film pyrolytic jetting process by providing a stabilizing counterforce.

In a more detailed approach, we have developed a microporous silica film with dimensions of approximately 10 µm through the optimization of laser power, laser-scanning speed, and scanning interval, in the pyrolytic jetting process. Furthermore, by adjusting these variables, we achieved the capability to tune porosity under 50%. Through water contact angle measurements, it was determined that silica films with approximately 45% porosity exhibited hydrophobic characteristics, while those with around 10% porosity demonstrated hydrophilic properties. The microporous silica film was employed in a fog harvesting application, wherein it was affixed to a 2 cm x 2 cm surface area of a PTFE rod. Real-time measurements of the harvesting rate resulted in an average yield of approximately 55 mg/min. This level of performance aligns with that of several mesh-style fog harvesting applications sharing analogous structures, underscoring the potential viability of this approach in the field.

5:00 PM MF02.05.14
Laser Induced Formation of Functional Metal Oxides for Enhanced Electrochemical Sensing Devendra Samaiik, Sotodeh Sedaghat and Rahim Rahimi; Purdue University, United States

The use of electrochemical sensors in different sectors has highlighted the need for sensors with high sensitivity, low cost and high stability over time. However, the high cost, and low long-
term stability of biomolecule electrochemical sensors have yielded the need for other approaches. Alternatively, metal oxides have shown promise to be used for sensing applications without the need of receptors but have yet to be widely adopted due to the complicated and expensive multistep manufacturing process associated with producing them. To develop the functional metal oxide sensors, laser processing has been seen as an alternative, owing to the low costs, high degree of control and rapid processing time which can be adapted to more scalable manufacturing processes. The use of laser induced oxidation has shown great promise by creating highly localized modifications of the surface morphology without affecting the bulk properties of the metal, while providing a more stable and robust electrical connection between the oxide and bulk metal layer. Laser induced oxidation was used to develop of low cost, rapid detection electrochemical sensors, taking advantage of the create three-dimensional micro/nano oxide structures which exhibit enhanced electrocatalytic properties compared to that of bulk metal. Copper and nickel were laser processed to obtain the rapid, low-cost and scalable manufacturing of electrochemical sensors for the detection of nonenzymatic glucose. The obtained laser-induced oxidized copper (LIO-Cu) and laser-induced oxidized nickel (LIO-Ni) contained highly nano/micro porous oxide structures which greatly increased the electrocatalytic activity enabling the detection of glucose. A systematic study of the composition, crystallinity, microstructure and wettability was conducted through the use characterization techniques including scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, and water contact angle measurement. The electrochemical sensing performance of the devised sensors were tested against a range of glucose concentrations to test sensitivity and detection limit. The LIO-Ni sensor demonstrated a high linear sensitivity of 5222 ± 1 μA mM⁻¹ cm⁻² over a wide range of 0.1 μM to 5 mM glucose concentration. The obtained results demonstrate the capability for laser processing to be adapted for a scalable manufacturing environment to produce rapid, low-cost and highly sensitive electrochemical sensors, which have application in various fields including medicine and agriculture.

5:00 PM MF02.05.16
Fabrication Defect-Insensitive Minimal Surface-Based 3D Metamaterial at Nanoscale Dahy Shiri1,2, Kisun KIM2, Sanghyun Nam2, Seokwoo Jeon2 and Dongchan Jang2; 1Agency for Defense Development, Korea (the Republic of); 2Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Material scientists have been striving to break the conventional relationships between mutually exclusive materials’ properties such as density-strength and to fill the white area in the materials’ property space. One effective way to explore the empty space is harnessing nanoarchitectures to develop lightweight and strong artificial materials not only by the architectural designs but also by embedding the benefits of nanoscale effects of materials into hierarchical nanostructures. Generally, in fabrication aspects of those nanoarchitectures, multi-step procedures are required including fabrication of architecture frames and material conversions. During these complicated procedures, fabrication defects are almost inevitable, especially when we considering mass production too. Therefore, at some point, the design of architecture itself is demanded to be defect insensitive with high tolerance of fabrication defects. For that purpose, we make the best use of 3D minimal surface structure to the design of nanoarchitectures. Since the minimal surface is a local minima of surface area under given constraints by minimizing the surface area, it has been expected that a nanoarchitectural design will provide high strain capability without micro structural defects so that to bring additional opportunities for the inelastic deformation even in intrinsically brittle materials. This unexpected inelastic deformation of the ceramic body makes the TPMS structure defect-insensitive. Experimental data from monoatomic and cyclic micropipette compression tests reveals that our nanoarchitecture exhibits damping behavior, high strength and low scaling exponent of 1.07 in density-strength chart even with severe geometric defects. This new minimal surface nanoarchitecture will contribute to creating superior engineering ceramics with capability of mass production through its high defect tolerance.

5:00 PM MF02.05.17
Simultaneous Electrochemical and Fluorescence Sensing of Myocardial Infarction Biomarkers Using a Femtosecond Laser-Fabricated Fiber-Optic Platform Homyaooon Soleimani Dinani1, Bohang Zhang2, Rex Gerald2, Zheng Yan2 and Jie Huang2; 1Missouri University of Science and Technology, United States; 2University of Missouri-Columbia, United States

The need for rapid and precise detection of biomarkers indicative of myocardial infarction has been emphasized in medical diagnostics and patient care. Conventional sensing approaches primarily utilize electrochemical or optical detecting mechanisms, each characterized by unique advantages and limits. This study aimed to design an advanced fiber-optic platform that integrates simultaneous electrochemical and fluorescence sensing. The integration of these two techniques enables the reliability and comprehensiveness of biomarker identification. Microscopic Laser-Induced Graphene (LIG) electrodes were fabricated on the outer surface of polyimide-coated optical fibers using femtosecond laser technology. The proposed innovation is presented as a scalable, reproducible, and economically viable approach to sensor manufacturing. The electrochemical sensing module was tailored explicitly to target myoglobin, an imperative biomarker for myocardial infarction. Enhanced sensitivity and specificity were achieved through a suite of electrochemical analyses encompassing Cyclic Voltammetry (CV), Square Wave Voltammetry (SWV), Differential Pulse Voltammetry (DPV), and Electrochemical Impedance Spectroscopy (EIS). The electrochemical sensing process was controlled by redox reactions and principles of charge transfer, facilitating high-accuracy measurements. Concurrently, fluorescence sensing was integrated into the platform, adding an auxiliary layer of biomarker validation. The fluorescence signal was used to quantify the fluorescence quantum yield and absorption coefficients of specific fluorophores extant in the blood. This auxiliary mechanism offers supportive evidence and exhibits the potential for identifying other associated biomarkers or substances. The amalgamation of these bifaceted sensing modalities into a unified fiber-optic platform enriched the data acquisition process and accelerated the diagnostic timeline. The provision of multi-faced, real-time data by the platform paves the way for sophisticated, point-of-care health monitoring systems. The research represents significant progress in sensor technology, particularly integrating electrochemical and optical sensing methodologies. The robust and versatile nature of the platform characterizes it as an optimum choice for diverse applications in medical diagnostics and technology, further improving the efficiency of health monitoring applications.

5:00 PM MF02.05.18
Diagnosis and Monitoring of Milk Fever with a Laser-Engraved Calcium Sensor Ali Soleimani, Farhad Amirghasemi, Abdurahman Al-Shami, Sina Khazaee Nejad, Alici Tsung, Delaram Parvin and Maral Mousavi; University of Southern California, United States

Milk fever is a metabolic disorder that occurs in dairy animals and its occurrence is more prevalent a few months before and after calving and can lead to a range of clinical symptoms, including loss of appetite, muscle spasms, lateral recumbency, and eventually coma or death if left untreated. The primary cause of these symptoms is a decrease in blood calcium levels, which can lead to muscle spasms and convulsions. Therefore, it is essential to diagnose milk fever early to prevent severe consequences. The current methods for diagnosing milk fever are based on measuring blood calcium levels using laboratory tests, which can be time-consuming and require specialized equipment.

The research presented in this paper focuses on the development of a laser-etched calcium sensor that utilizes laser-induced oxidation of copper and nickel to create a porous oxide structure. The sensor was designed to be scalable, cost-effective, and capable of real-time monitoring of blood calcium levels. The fabrication process involves laser-induced oxidation of copper and nickel, followed by a heat treatment process to enhance the electrocatalytic properties of the oxide layer.

In this study, we have fabricated laser-etched calcium sensors using a femtosecond laser to create a porous oxide structure on the surface of the metal. The resulting oxide layer has enhanced electrocatalytic properties, allowing for the sensitive detection of calcium ions in blood samples. The sensors were tested against a commercial calcium sensor, and the results showed a linear sensitivity of 5222 ± 1 μA mM⁻¹ cm⁻² over a wide range of 0.1 μM to 5 mM glucose concentration. The obtained results demonstrate the capability for laser processing to be adapted for a scalable manufacturing environment to produce rapid, low-cost and highly sensitive electrochemical sensors, which have application in various fields including medicine and agriculture.

The next steps in this research include testing the sensors in real-world scenarios with dairy animals and comparing their performance with traditional methods. The goal is to develop a portable and affordable tool that can be used by farmers and veterinarians to monitor blood calcium levels in dairy animals, enabling early detection and timely treatment of milk fever.

Conclusion: We have fabricated a laser-etched calcium sensor that shows outstanding sensitivity and selectivity towards calcium ions. Furthermore, the sensor shows %4.54 error compared with a commercial electrode that is suitable and acceptable for in-field detection of subclinical milk fever. Moreover, using a laser as an inexpensive, fast, and mass-scalable method for fabricating the sensors makes them a suitable choice for in-field frequent use.
Metal 3D Printing was utilized to design novel Ti-alloys for load-bearing implant applications focusing on improving biocompatibility, minimizing bio-tissue corrosion and related metal ion release, and adding inherent infection resistance. Successful alloy design can minimize adverse local tissue response (ALTR) from total hip implants (THAs) taper corrosion and septic loosening due to polymicrobial infections, eventually reducing implant failure in vivo. In one case, we designed a Ti-Ta-Cu alloy where Cu offers intrinsic microbial resistance and Ta-enhanced biocompatibility to mitigate potential Cu toxicity. Instead of using Ti6Al4V alloy, vanadium and aluminum contents were reduced to design a Ti3Al2V alloy for metallic implant applications. The biological and mechanical properties of Ti3Al2V alloy were measured. A 10% Ta and 3% Cu were added to the Ti3Al2V alloy to enhance biocompatibility and impart inherent bacterial resistance. Additively manufactured implants were investigated for resistance against pseudomonas aeruginosa and staphylococcus aureus strains of bacteria up to 48 h. A 3% Cu addition to Ti3Al2V showed an improved antibacterial efficacy, between 76 and 81% higher than CpTi and Ti6Al4V. Mechanical properties for Ti3Al2V-10Ta-3Cu alloy were measured, demonstrating excellent fatigue resistance, good shear strengths, and better tribological characteristics than Ti6Al4V. In vivo studies using a rat distal femur model showed improved early-stage osseointegration for alloys with 10Ta addition than CpTi and Ti6Al4V. Ti6Al4V-ZTA-HA metal matrix composites were designed and investigated for load-bearing femoral heads in another alloy design. The composites were fabricated via 3D Printing. A rabbit distal femur 16-week in vivo study for implantation and histological characterization was conducted. An induced in vitro 16-week applied polarization study of the Ti6Al4V and Ti6Al4V-zirconia toughened alumina (ZTA)-hydroxyapatite (HA)-based composites was conducted to investigate the coupled taper-corrosion behavior. The Ti6Al4V-ZTA-HA composites displayed increased hardness, decreased wear volume, increased surface passivation during tribological testing, and faster passivation post-tribological testing, validated by increased contact resistance and more cathodic open circuit potential. Finally, a first-of-a-kind table-top joint simulator was designed and manufactured to simulate volumetric tribio-corrosion of femoral heads. The simulator mimics the gait-like motion of the hip joint. Ti6Al4V+ZTA+HA metal matrix composite femoral heads were produced via 3D Printing. The ability to move into volumetric articulating-based testing has shown promising results for improving these innovative materials to address the shortcomings of currently used metallic biomaterials in load-bearing orthopedic devices where corrosion and wear are of concern. The presentation will discuss 3D Printing-based alloy design and related characterization of next-generation Ti-alloys for load-bearing implants.

**MF02.06.02** Laser Assisted Selective Texturizing and Alloying of Titanium Implant surfaces for Enhanced Bactericidal and Osteointegration Properties Akshay Krishnakumar, Sotoudeh Sedaghat, Vidhya Selvamani, Sina Nejati and Rahim Rahimi, Purdue University, United States

Orthopedic device-related infections (ODRIs) in implants represent a critical and multifaceted healthcare challenge, necessitating a comprehensive understanding of their impact on patient well-being, management, and prevention. While titanium-based (Ti) implants are commonly used due to their favorable corrosion resistance, excellent biocompatibility, and mechanical properties similar to that of bone, the development of bacterial infections owing to ORDI remains a daunting concern. Functionalizing the implant surface with antimicrobial agents, without altering the bulk properties of the Ti alloy, presents an effective approach to improving the efficacy of orthopedic implants and elevating patient outcomes. In this context, we have developed a two-step process involving laser texturing and alloying of silver (Ag) nanocomposites into the widely used titanium alloy (Ti6Al4V) implant surfaces, thereby conferring antibacterial properties. The process involved spray coating silver nanoparticles onto the implant surface, followed by heat sintering and laser-induced alloying of Ag into the Ti alloy. The local heat generated by the laser process enables simultaneous intermetallic alloying and texturing of the implant surface, enhancing its surface roughness without affecting its bulk mechanical properties. A systematic study was conducted by varying the laser beam power to analyze the structural, morphological, and elemental composition of the surface, utilizing X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX) analysis. The results demonstrated that the developed laser-textured surface exhibited enhanced wettability, increased surface roughness, and effective alloying of silver on the implant surface without compromising bulk mechanical properties. The optimized laser-textured surface was subjected to a seven-day antibacterial test against a model population of gram-positive (Staphylococcus aureus) and gram-negative bacteria (Escherichia coli). Furthermore, the osteointegrative properties of the developed surface were assessed through in-vitro bone mineralization assays using Mesenchymal Stem Cells (MSC), and the calcified extracellular matrix levels were measured. The results indicated a two-fold increase in bone cell mineralization and long-term antibacterial properties for the optimized laser-textured surface compared to the control Ti alloy surfaces. By modifying the implant surface, the antibacterial properties can help prevent bacterial colonization, while the enhanced osteointegration properties can promote bone cell adhesion and colonization. Ultimately, this scalable laser-assisted alloying approach holds the potential to enhance the long-term success of orthopedic implants and improve patient outcomes.

**MF02.06.03** Laser-Induced Graphene Composites for Electrically-Mediated Antimicrobial and Environmental Applications Christopher J. Arnschü; Ben Gurion University of the Negev, Israel

Laser-induced graphene (LIG) is a three-dimensional, porous, electrically conductive graphene material generated predominantly by irradiation of polymer substrates with a 10.6 µm CO2 laser. Since 2014, this material has been shown to be useful in a myriad of applications. In this presentation, I will discuss the synthesis and exceptional properties of LIG composites in antibacterial or antiviral environmental applications including air and water treatment technology. Electrical effects and electro- and photo-thermal heating for bacterial killing will be shown and insights into the mechanism of action will be discussed. Notably, LIG surfaces can deactivate bacteria when low currents are passed through the surface, when the surfaces are used as electrodes, or as heaters. Also, LIG dense and porous substrates exhibited an electrically mediated antifouling effect. To understand any laser-induced effects on membranes, we studied by comparing porous polymeric PES membranes fabricated using the non-solvent induced phase separation (NIPS) method with membranes obtained using the vapor-induced phase separation (VIPS) method. Membrane fabrication conditions, such as the polymer concentration of the casting solution and the exposure time to the non-solvent, were varied, and the NIPS method resulted in membranes with a finger-like substructure morphology, while the VIPS method resulted in membranes with an asymmetric cellular morphology. LIG-membranes prepared on NIPS membranes resulted in large permeability changes, while LIG on VIPS membranes gave only very minor changes. The antimicrobial activity of these LIG-membranes as porous electrodes was dependent on applied voltage and solution contact time, and 4-6 log of bacteria at 10 V was achieved. Understanding LIG formation on porous polymeric membranes will minimize processing steps and might lead to electrically conductive membranes with controlled separation properties.

References
Laser-Assisted Synthesis and Texturing of Graphene Electrodes for Biosensing Devices

Euclydes Marega; University of Sao Paulo, Brazil

Perovskite films have been attracting tremendous attention as promising candidates for applications in photonics and optoelectronics, including light-emitting diodes, photo-detectors, energy-harvesting devices, etc. Such applications are sensitive to changes in crystallization, size, and distribution of grains in the perovskite films. Hence, studies have been carried out to improve the quality of thin films and investigate the effect of sintering on the crystalline phase of the sample. Even though several sintering methods have been developed, fs-laser sintering has appeared as a versatile and rapid option, offering precise and localized energy distribution to the sample. The fs-laser sintering can produce highly crystalline devices with complex structures, although it depends on the processing parameters.

This study demonstrates the crystallization of Er/Yb:BaTiO3 Perovskite Induced by fs-Laser Pulses. Cleber Mendonça, Jose Clabel, Kelly Tasso, Marcelo Pereira-da-Silva, Jose Vollet-Filho, Filipe Couto and Euclydes Marega; University of Sao Paulo, Brazil

The impact of fs-laser sintering on the crystalline phase of Er/Yb:BaTiO3 (BTEY) was investigated. The fs-laser sintering was found to be highly effective in inducing crystallization in the perovskite films, with good control over the crystallite size and distribution. The results demonstrate the potential of fs-laser sintering for applications in photonics and optoelectronics, including light-emitting diodes, photo-detectors, and energy-harvesting devices.

Laser-Induced Carbonization of Polyimide Films for Physically Unclonable Anticounterfeiting Applications

Srinivas Gandla; Changgyun Moon and Sunkook Kim; Sungkyunkwan University, Korea (the Republic of)

Laser-induced carbonization (LIC) is a powerful technique for fabricating physically unclonable tags (PUs) that have unique and unpredictable patterns. This method uses a laser to pyrolyze polymer films, resulting in the formation of carbon-based tags. LIC tags are highly secure and customizable, making them ideal for anticounterfeiting applications. In this study, we demonstrate the fabrication of a unique physically unclonable tag using the LIC method. The LIC method offers several advantages over traditional techniques, such as low cost, high scalability, and the ability to produce tags with unique patterns.

Laser-Assisted Manufacturing of Functional Materials for Sensors and Actuators

Amir Barai and Lia Stanciu; Purdue University, United States

The pressing global demand for rapid, point-of-care detection of enveloped RNA viruses necessitates innovative sensor manufacturing approaches. We present a biosensor manufacturing method, focusing on flexible electronics employing graphene inks printed on flexible polymeric substrates. These are subsequently cured and laser-textured under conditions specific to our experiments, incorporating optimized electrode geometries. A crucial component of our advancement is the novel 2D layer-structured electrode coating geometry. These advancements enable the development of biosensing devices with enhanced performance and scalability.

Potential Application of Laser Reduced Graphene Oxide Electrode for Pressure Sensing

Yiping Stabile; Union College, United States

Reduced graphene oxide (rGO) has attracted attention as an active electrode material for flexible electrochemical devices due to the high electric conductivity and large surface area. Compared to the other reduction strategy, laser reduction is a single-step, precise, low-cost, and chemical-free processing that can be directly applied on the graphene oxide (GO) membrane under ambient conditions. In general, the quality of the rGO is limited to that of pristine graphene due to incomplete reduction, and oxygenated defects involved in the reduction process. The partially removed functional groups not only influence the impedance of the electrode, but also make it sensitive to the humidity of the working environment. Most of the studies are focused on the laser irradiation parameter optimization to achieve the lowest O/C ratio. This study aims to explore the potential of applying the Laser reduced graphene oxide (LiGO) for pressure sensing. Beyond the laser irradiation parameters including intensity, frequency, and scan speed, the impact of partially reduced GO on the bottom and the interlayer distance increase during the

SESSION MF02.07: Laser Assisted Manufacturing of Functional Materials for Sensors and Actuators

Thursday Afternoon, April 25, 2024 Room 324, Level 3, Summit

1:30 PM *MF02.07.01 Laser-Assisted Synthesis and Texturing of Graphene Electrodes for Biosensing Devices

Amit Barai and Lia Stanciu; Purdue University, United States

The pressing global demand for rapid, point-of-care detection of enveloped RNA viruses necessitates innovative sensor manufacturing approaches. We present a biosensor manufacturing method, focusing on flexible electronics employing graphene inks printed on flexible polymeric substrates. These are subsequently cured and laser-textured under conditions specific to our experiments, incorporating optimized electrode geometries. A crucial component of our advancement is the novel 2D layer-structured electrode coating geometry. These advancements enable the development of biosensing devices with enhanced performance and scalability.

2:00 PM MF02.07.02 Potential Application of Laser Reduced Graphene Oxide Electrode for Pressure Sensing

Yiping Stabile; Union College, United States

Reduced graphene oxide (rGO) has attracted attention as an active electrode material for flexible electrochemical devices due to the high electric conductivity and large surface area. Compared to the other reduction strategy, laser reduction is a single-step, precise, low-cost, and chemical-free processing that can be directly applied on the graphene oxide (GO) membrane under ambient conditions. In general, the quality of the rGO is limited to that of pristine graphene due to incomplete reduction, and oxygenated defects involved in the reduction process. The partially removed oxygenated functional groups not only influence the impedance of the electrode, but also make it sensitive to the humidity of the working environment. Most of the studies are focused on the laser irradiation parameter optimization to achieve the lowest O/C ratio. This study aims to explore the potential of applying the Laser reduced graphene oxide (LiGO) for pressure sensing. Beyond the laser irradiation parameters including intensity, frequency, and scan speed, the impact of partially reduced GO on the bottom and the interlayer distance increase during the
reduction is studied to improve the sensing performance of LrGO. Our results demonstrate the potential of applying LrGO in the pressure sensing field through facile post treatment.

2:15 PM MF02.07.03
Laser-Induced Graphene (LIG) based Green Gas Sensor Cheolmin Kim, Hanku Nam, Mingu Kang, Kichul Lee, Youngjin Kim and Inkyu Park; Korea Advanced Institute of Science and Technology (KAIST), Korea (the Republic of)

In recent years, the global electronics industry has experienced rapid growth, driven by advances in technology and increasing demand for electronic devices. However, this growth has come at a significant cost to the environment, as electronic products consume vast amounts of energy and resources during their production, use, and disposal. As a result, there is a growing need for more sustainable and environmentally friendly electronics, also known as “green electronics”. Green electronics refers to the design, production, and use of electronic products and systems that minimize environmental impact, reduce energy consumption, and promote sustainability throughout their lifecycle. The global green technology and sustainability market was valued at $13.28 billion in 2021 and is expected to expand at a compound annual growth rate (CAGR) of 22.4% from 2022 to 2030. In the field of gas sensors, the development of green gas sensors that are easy to dispose of after use by using sustainable materials such as cellulose and gelatin has been actively developed in line with the changing times.

Recently, femtosecond lasers and their use to create laser-induced graphene (LIG) have received a lot of attention. The femtosecond laser used in this study to fabricate the gas sensor is a pulsed laser that can have a very high peak power of terawatts by focusing the photon energy of the laser beam in a very short time of femtoseconds. Femtosecond lasers are useful in many applications because they have a very high frequency, resulting in high energy and minimal heat transfer to surrounding materials. These characteristics make a process using femtosecond lasers suitable for fabricating the laser-induced graphene (LIG)-based gas sensors in this study. When certain materials containing carbon are irradiated with a laser beam, they carbonize and produce a three-dimensional porous material, which is known as LIG. LIGs have excellent electrical and mechanical properties, and their three-dimensional porous structure makes them ideal for use in gas sensors. In addition, LIGs created in wood do not require any special chemical treatments during fabrication, making them eco-friendly, easy and quick to manufacture, and inexpensive to make in any desired design.

In this work, we present a novel approach for the fabrication of a LIG-based eco-friendly gas sensor coated with a sensing material and patterned on wood substrates using a one-step process. The combination of LIG and the sensing material coating allows for the creation of a highly sensitive and selective gas sensor. This sensor is not only eco-friendly but also has the potential to be cost-effective due to the use of a renewable, sustainable wood substrate and a one-step fabrication process. The one-step patterning process allowed for precise and efficient production of the sensor, while the use of wood substrates made it environmentally sustainable and biodegradable. The gas sensors are reactive to CO, NH₃, and CH₄ gases, and are fabricated in an array by doping different materials to effectively detect different types of gases. The gas sensor also demonstrated its potential as a forest fire monitoring system by using deep learning algorithms to detect different types of gases in a fast time.

2:30 PM BREAK

3:00 PM MF02.07.04
Scalable Laser-Assisted Manufacturing of Chipless RFID Sensors on Metallized Films Muhammad Masud Rana, Sarath Gopalakrishnan, Akshay Krishnakumar, Sotoudeh Sedaghat, Sina Nejati, Ulisses Heredia and Rahim Rahimi; Purdue University, United States

The global food packaging industry, valued at 311.4 billion dollars in 2020 and projected to reach 456.6 billion dollars by 2027, is witnessing growing demands for improved food quality and safety. Monitoring the quality of packaged food plays a vital role in reducing spoilage and enhancing food safety. Key indicators like humidity levels, pH, and chemical changes in meat products necessitate sensors for effective monitoring. Current solutions, such as colorimetric sensors and active sensors, have limitations. While colorimetric sensors are cost-effective and suitable for transparent packaging, they cannot be used in non-seen-through packages, requiring labor-intensive manual inspection. Active sensors, though automated, are expensive and may not always be biocompatible due to batteries and electronic chips.

Battery-less chipless wireless sensors, due to their low cost and wireless capabilities, are becoming increasingly popular in food packaging. However, challenges in the commercialization of chipless sensors are associated with their manufacturing processes. Scalable manufacturing techniques like printing have been employed for chipless sensors in applications like moisture sensing, soil analysis, and identification. These techniques reduce the complexity and resources needed for sensor production but introduce challenges related to ink formulation, custom screens, and drying and sintering times.

Our Scalable Laser-Assisted Manufacturing (SLAM) process offers a solution for large-scale, roll-to-roll production. It enables one-step patterning of a conductive aluminum layer on paper or PET sheets while concurrently creating high-surface-area Al₂O₃ nanoparticles within the laser-ablated regions, enhancing the sensitivity of the wireless sensor.

This work presents a systematic investigation of different laser processing conditions on metalized paper films to optimize structures. These structures provide high-performance antennas while minimizing structural damage to the underlying paper substrate. Results demonstrate that optimized processing conditions yield concurrent patterning of the metalized film into desired antenna structures and high-surface-area metal oxide nanoparticles within the ablated region. This results in exceptional sensitivity (linear sensitivity of -87 kHz/RH in a relative humidity range of 0% to 85%), surpassing standard RFID sensors produced using conventional photolithography methods.

The second part of this work demonstrates the post-functionalization of laser-patterned resonators and antennas to achieve responsive sensitivity to pH and hypoxanthine (HX), biomarkers relevant to food spoilage and fresh meat and fish produce. This technology opens new possibilities for scalable and cost-effective sensor production, paving the way for their implementation in smart packaging to address the challenges associated with food waste.

3:15 PM MF02.07.05
Bandgap Engineering of Laser-Patterned Diamond-Like Carbon Structures Naveen Narasimhaear Joshi, Ben Sekely, Pranay Kalakonda, Sachin Kadian, John Muth, Roger Narayan and Jagdish Narayan; North Carolina State University, United States

We report the formation of Si-DLC thin films on Si (100) and sapphire (0001) substrates via plasma-enhanced chemical vapor deposition (PECVD) technique. Subsequently, these thin films were irradiated with nanosecond ArF excimer laser pulses (λ = 193 nm; pulse duration = 20 ns) of varied energy density (0.6 J cm⁻², 0.7 J cm⁻², and 0.8 J cm⁻²). The pulsed laser annealing (PLA) technique melts the Si-DLC films in a super-undercooled state that can be quenched rapidly. As such, the sp² content in the films can be modified by controlling the energy density of the laser pulse. We show that the optical bandgap of Si-DLC structures can be controlled by suitably tuning the sp² content in Si-DLC thin films through the PLA technique. Raman spectroscopy and XPS studies were employed to determine the sp²/sp³ ratio in the as-deposited and PLA-treated Si-DLC thin films. Absorption spectra were obtained by UV-Vis spectroscopy and used to determine the optical bandgap (Tauc’s method) and Urbach energy and correlated with the sp² content in the films. This study shows that PLA is a powerful technique for controlling the functional properties of DLC thin films for state-of-the-art optoelectronic applications.

SYMPOSIUM MF03

Sustainable Polymers—From Fundamentals to Advanced Manufacturing and Applications
April 23 - April 26, 2024

Symposium Organizers
Processing Fun with Nanocellulose Jeffrey P. Youngblood; Purdue University, United States

Cellulose Nanomaterials (CNMs) are an attractive material class for possible applications in nanocomposites reinforcement, nanomaterials and biomedicine as they have high strength and stiffness, yet are renewable, biodegradable, non-toxic, and cheap. They are also of particular interest for rheology control. However, as nanoscale objects they can prove challenging to process due to water binding ability and lack of dispersion. Here we detail our journey towards processing various materials with CNM. Of particular note will be our recent efforts at additive manufacturing with CNM and CNM as an additive in cement.

Highly Effective Nanocellulose-Based Flocculants for Use in Freshwater and Saltwater Conditions Wim Thielemans; KU Leuven, Belgium

The rigidity of cellulose nanocrystals and the ability to modify them at different surface planes makes them interesting candidates as flocculants for larger particles or organisms because they can flocculate using a patch mechanism and coiling under high salt conditions is avoided. Therefore, we investigate cationically modified CNFs for the flocculation of microalgal. Cellulose nanocrystals (CNs), extracted from cotton via a standard H₂SO₄ acid hydrolysis, were chemically modified with methyl-imidazolium (MIM) and pyridinium (PYR) grafts at various degrees of substitutions (DS). The extent of grafting was determined by elemental analysis and FTIR and EXPS spectroscopy, while retention of crystallinity and morphology were confirmed by WAXS and AFM respectively.

When testing Chlorella vulgaris (freshwater microalgae) flocculation, it was found that the flocculation efficiency did not vary significantly with surface graft or with DS. However, the required done varied virtually linearly with DS and remained independent of graft type (Fig 1(a)). Applying these flocculants to marine microalgae Nanochloropsis oculata, flocculation remained effective and flocs could readily be removed using a large pore filter (Fig 1 (b)). Adhesion force histograms and rupture distance measurements by securing (1) a microalgal cell on the AFM tip and probing a film of modified CNs or (2) modified CNs on the AFM tip and probing microalgal cells in solution, both showed that the interaction is governed by electrostatic interactions. This explains the linear relation between DS and required dose for flocculation. The interaction force for PYR-CNcs with Chlorella vulgaris was only a third of that for MIM-CNcs but that did not seem to affect its flocculation efficacy. Therefore, the strength of interaction does not seem to be a very important parameter so that our results show that increasing DS is more important than optimizing the type of cationic charge. This work was then extended to prepare fully biobased materials, using glycine betaine as the surface grafts on CNCs, giving similar results to pyridinium and methylimidazolium modified CNCs. We also investigate CO₂-sensitive grafts allowing us to add the CNCs to the microalgal growing medium, after which CO₂ could be bubbled through the medium redering the CNCs positively charged thereby flocculating the microalgae. Finally, we are currently investigating in more detail the interaction strength between cationically modified CNCs with microalgal cell walls to be able to devise models capable of predicting flocculation performance.

Our work thus shows that CNCs offer great potential as biobased flocculants, even in high-ionic strength conditions. Extending this work to the removal of particulate matter in waste water is currently in progress and shows similar excellent flocculation performance, showing the wide applicability of cationic CNCs as flocculants.

The Importance of Crystallite Bundles in the Chiral Self-Assembly of Cellulose Nanocrystals: Origin, Morphology and Function Thomas G. Parton1,2, Kevin Ballu², Bruno Frka-Petesc2, Richard M. Parker2 and Silvia Vignolini1,2; 1Max Planck Institute of Colloids and Interfaces, Germany; 2University of Cambridge, United Kingdom

Cellulose nanocrystals (CNCs) are elongated negatively-charged nanoparticles produced by acid hydrolysis of cellulose biomass (e.g. cotton, wood pulp). CNC suspensions spontaneously form a left-handed cholesteric mesophase, which has a periodicity (pitch) determined by the characteristics of the individual CNCs (e.g. morphology, surface chemistry) and the suspension formulation (e.g. solvent, additives). This helicoidal arrangement of CNCs can be preserved as the suspension is dried, resulting in films with vibrant structural color. The chiral self-assembly of CNCs is thus a promising route to create materials with a tunable optical response from a sustainable biopolymer feedstock, but understanding how the properties of the large-scale structure emerge from the behavior of individual nanoparticles has been a persistent challenge.

First, by gradually tuning the size and shape of CNCs using ultrasonication, and correlating the morphology of individual particles with their cholesteric mesophase behavior in suspension, we found that CNC “bundles” (i.e. clusters of laterally-bound elementary crystallites) are essential for the formation of a cholesteric phase. These bundles appear to act as chiral dopants, analogous to those used for molecular liquid crystals, whereby an increase in dopant concentration leads to a decrease in cholesteric pitch (and blueshifted film color). We then compared common ways to induce aggregation in CNC suspensions (e.g., post-hydrolysis centrifugation or excess ionic strength). This investigation revealed that the formation pathway significantly affects the morphology of the bundles and thus their effectiveness as chiral dopants. These findings demonstrate that the “making” and “breaking” of crystallite bundles offers a facile way to tailor the self-assembly behavior of CNC suspensions.

Making Active and Responsive Materials Using Rod Shaped Fillers: Structuring Nanocomposites Johan Foster; The University of British Columbia, Canada

Cellulose nanocrystals (CNCs) are high-aspect ratio, mechanically stiff fibers which can serve as both a bio-renewable reinforcing agent in nanocomposites, as well as a handle for adding stimuli responsiveness. CNCs can be extracted from a wide range of natural cellulose materials, with characteristics such as crystal structure, crystallinity and aspect ratio fluctuate widely between sources.

Here, we report functionalized cellulose prepared for reinforcing materials in a variety of environments, ranging from cement to implantable materials in the human body. Moieties attached to the surface of cellulose show that both reversible and reversible changes can be induced by application of an external stimuli. These specifically designed materials are mechanically tunable, matching use conditions, while creating surprising mechanical properties.
Nanocellulose networks have been extensively surveyed as so-called nanopapers for packaging applications on one hand and membranes for purification purposes on the other. Despite the two distinct ways of end use, the fundamentals of the network structure and its function remain the same. This presentation aims to introduce a fundamental discussion from both sides by consolidating both aspects. For example, hemicellulose is seen as a binder molecule when assessing the tensile properties of dry nanopapers but its water-acculumulating capability in wet state is rarely discussed in membrane technology or even with hydrogels. Similarly, porosity is among the central properties of membranes but it is not usually considered with nanopapers, notwithstanding its pivotal role in strength development of any cellular material. The aim here is to address similar parameters from different application perspectives.

Meeting the requirements for “green” materials, cellulose nanocrystals (CNCs) have been demonstrated as good additives and stabilizers in emulsions, however their exact role is not always clear. Our work on minimulsion, microsuspension, and seeded semi-batch emulsion polymerization has demonstrated that polymer latex properties (e.g., size, surface charge, surface roughness, polymer degree of polymerization) can be highly tuned through the incorporation of CNCs. Most notably, the addition of CNCs always improves all performance metrics in latex-based pressure sensitive adhesives (PSAs). This is uncommon given that additives that increase adhesive properties normally decrease cohesive properties and vice versa. We have investigated nano-scale adhesive properties and their link to macroscopic tack, peel and shear strength to elucidate how CNCs act as “anchor points” for polymer entanglement, improve wettability and latex film coalescence, and form percolated networks throughout PSA films. Most recently, we have studied the effect of CNC surface chemistry (sulfated vs. carboxylated) as well as polymer-modified CNCs on PSA properties – the trends are not straightforward as changing the CNC surface affects aggregation/disperabilility, colloidal stability, the location of CNCs in the latex, and the tendency for coagulation to occur during polymerization. This talk will explain the main conclusions across a series of papers on CNCs in latex-based PSAs and recommendations for when/if to modify CNC surface chemistry. While the focus is on latex-based PSAs we believe the work is translatable to a range of latex products including paints, coatings, inks, toners and rubbers.

3:20 PM MF03.02.03

Lateral-Based Pressure Sensitive Adhesives with Unmodified vs. Polymer-Grafted Cellulose Nanocrystals
Julia Antoni1, Michael Kiriakou2, Vida Gabriël1, Michael F. Cunningham4, Marc A. Dube3 and Emily D. Cranston1
1University of British Columbia, Canada; 2Anomera Inc., Canada; 3University of Ottawa, Canada; 4Queen’s University, Canada

Meeting the requirements for “green” materials, cellulose nanocrystals (CNCs) have been demonstrated as good additives and stabilizers in emulsions, however their exact role is not always clear. Our work on minimulsion, microsuspension, and seeded semi-batch emulsion polymerization has demonstrated that polymer latex properties (e.g., size, surface charge, surface roughness, polymer degree of polymerization) can be highly tuned through the incorporation of CNCs. Most notably, the addition of CNCs always improves all performance metrics in latex-based pressure sensitive adhesives (PSAs). This is uncommon given that additives that increase adhesive properties normally decrease cohesive properties and vice versa. We have investigated nano-scale adhesive properties and their link to macroscopic tack, peel and shear strength to elucidate how CNCs act as “anchor points” for polymer entanglement, improve wettability and latex film coalescence, and form percolated networks throughout PSA films. Most recently, we have studied the effect of CNC surface chemistry (sulfated vs. carboxylated) as well as polymer-modified CNCs on PSA properties – the trends are not straightforward as changing the CNC surface affects aggregation/disperabilility, colloidal stability, the location of CNCs in the latex, and the tendency for coagulation to occur during polymerization. This talk will explain the main conclusions across a series of papers on CNCs in latex-based PSAs and recommendations for when/if to modify CNC surface chemistry. While the focus is on latex-based PSAs we believe the work is translatable to a range of latex products including paints, coatings, inks, toners and rubbers.

3:15 PM MF03.03.01

From Synthesis of Functional Lignin Nanoparticles to Their Catalyst-Free Ozonolysis: Closing The Loop
Alexandros E. Alexakis and Mika H. Sipponen; Stockholm University, Sweden

Recent years have seen a growing interest in lignin nanoparticles (LNPs) based on technical lignins extracted from plant biomass. A common method to produce LNPs involves diluting a lignin solution in an aqueous organic solvent by adding water or evaporating the organic phase. Our group has contributed to overcoming obstacles of LNPs such as their instability in aqueous and organic solvents. These approaches aim to preserve the spherical shape and allow for chemical modification before or after particle preparation. Hydroxymethylation of lignin with subsequent production of colloidal particles and their hydrothermal processing gave rise to particles that remain stable at acidic media as well as alkaline pH 13 and anhydrable organic solvents.1 Another means to produce LNPs with tailored functionality involves first fractionating lignin into solvent-soluble and insoluble fractions, epoxidation of one of these fractions, and their combination in original mass ratio.2 When epoxidized high-molecular weight lignin fraction was combined with the low Mw fraction the particles could be internally cross-linked via simple heating at 100 °C in colloidal state.

Ferruti et al. (2023) established a method to stabilize LNPs using only natural components.3 By co-aggregating urushi, a black oriental lacquer, with softwood kraft lignin, hybrid particles were formed. Owing to its catechol-type structure with unsaturated hydrocarbon chains linked to the aromatic ring urushi served as a renewable stabilizer through hydration barrier effects and MS. Although the chemical composition of the materials was significantly affected even after 15 min of ozonolysis, the size and spherical morphology of the LNPs was retained for one hour after ozonolysis. The products of CML estrification are shown to alter thermoplastic properties of biopolymer (PLA). This research, along with the greener chloromethylation approach for lignin, holds the promise of shedding new light on lignin valorization, rendering it economically attractive and environmentally benign.

4:00 PM MF03.03.03

Semicrystalline Polymers from Lignin-Derivable Monomers
Ty Christoff-Tempesta, Garrett F. Bass and Thomas Epps; University of Delaware, United States

Lignin, a highly abundant biopolymer characterized by its elevated carbon content and substantial aromaticity, holds immense potential as a valuable resource for fuel production and the synthesis of platform chemicals. However, despite its promising attributes, lignin remains underutilized within the spectrum of lignocellulosic biopolymers. Lignin's innate versatility can be harnessed through various chemical modifications at both "upstream" and "downstream" stages following its extraction. The chemically modified lignin exhibits the potential to serve as a precursor for the development of nanomaterials tailored for drug delivery, coupling amongst its source, chemical alterations, and physicochemical properties.

Efforts to improve lignin's utility have predominantly involved "upstream" chemical modifications, which either target the hydroxyl groups for alteration or introduce new chemically active sites, thereby expanding its applications.3 Yet, the quest for a versatile and environmentally friendly method for these modifications persists. In this context, the concept of a greener chloromethylation process, currently experiencing renewed interest and offering extensive prospects for "greener" applications, remains unexplored within the realm of lignin. In this study, we present a novel method for the chloromethylation of lignin, which has paved the way for the creation of a diverse range of lignin-based products utilizing chloromethylated lignin (CLM) as the starting material.

The resulting lignin-based materials encompass catalytic agents, antibacterial formulations, and thermoplastic additives. Our lignin-based catalyst exhibits several advantages over other catalysts, including straightforward synthesis, heterogeneity, recoverability, and recyclability. Furthermore, we have demonstrated the efficacy of the lignin-based catalyst in a range of carbon-carbon bond forming reactions, such as Suzuki-Miyaura, Sonogashira, Heck reactions, and hydrogenation. The introduction of various quaternary amines with variable chain lengths to chloromethylated lignin has resulted in a series of innovative surface-active materials with enhanced antibacterial activity against Gram-negative and Gram-positive clinical isolate bacteria. The products of CML esterification are shown to alter thermoplastic properties of biopolymer (PLA). This research, along with the greener chloromethylation approach for lignin, holds the promise of shedding new light on lignin valorization, rendering it economically attractive and environmentally benign.
Semicrystalline chain-growth polymers from lignin-derivable compounds are desirable for their potential to combine material sourcing from renewable feedstocks with performance-advantaged material properties (e.g., higher tensile strengths and improved barrier properties in comparison to their amorphous polymer counterparts). Despite significant effort in the synthesis of vinyl monomers from lignin-derivable molecules, the resulting chain-growth polymers to date have been dominantly amorphous. Here, we describe the chemical transformation of lignin-derivable molecules into monomers that enable the generation of semicrystalline macromolecules. We harness living polymerization strategies to synthesize these polymers with stereoregularity under mild conditions, and we further probe the impacts of synthesis conditions on molecular weights, crystallinities, and thermal properties. This work introduces a strategy for utilizing lignin-derivable molecules to generate semicrystalline polymers with tunable properties, providing a pathway to valorize lignin for a new range of polymer applications.

4:15 PM MF03.03.04
Sonochemical Synthesis of Lignin Nanoparticles and Their Applications in Poly(vinyl) Alcohol Composites

Dylan D. Edmundson, Anthony Dechiara and Rick Gustafson; University of Washington, United States

Lignin is a common and abundant byproduct of the pulp and paper industry and is generally burned to produce steam. Opportunities exist to acquire greater value from lignin by leveraging the properties of this highly conjugated biomacromolecule for applications in UV absorption and polymer reinforcement. These applications can be commercialized by producing value-added lignin nanoparticles (LNP) using a scalable sonochemical process. In the present research, monodisperse LNP have been synthesized by subjecting aqueous dispersions of alkali lignin to acoustic irradiation. The resulting particle size distribution and colloidal stability, as determined by dynamic light scattering, transmission electron microscopy and zeta potential analysis, of LNP can be adjusted by varying the solution pH and ultrasonication energy. As-synthesized LNP with a mean diameter of 204 nm were incorporated into poly(vinyl) alcohol (PVA) to prepare thin and flexible nanocomposite films using a simple solvent casting method. The addition of 2.5 wt% LNP increased the material’s Sun Protection Factor up to 26 compared to 0 for neat PVA, while maintaining light transmission above 75% in the visible spectra. In addition, the tensile strength and elastic modulus of the PVA nanocomposites improved by 47% and 36%, respectively. The presence of LNP also enhanced the thermal stability of the materials. Significantly, the proposed sonochemical process may be generally applicable to the synthesis of a range of naturally-derived LNP for a variety of value-added applications.

SESSION MF03.04: Poster Session I
Session Chairs: Kunal Masania and Eleftheria Roumeli
Tuesday Afternoon, April 23, 2024
Flex Hall C, Level 2, Summit

5:00 PM MF03.04.01
Synthesis and Antibacterial Properties of Lignin-Based Quaternary Ammonium and Phosphonium Salts

Muthendri Kohothiti Mohan1, Harleen Kaur2, Angela Ivasi2, Jean-Manuel Raimundo3, Tit Lukk1 and Yevgen Karpichev1; 1Tallinn University of Technology, Estonia; 2Institute of Molecular and Cell Biology, University of Tartu, Estonia; 3SINaM - Aix-Marseille University, France

Lignin, a naturally occurring aromatic polymer, possesses diverse biological functions, particularly in the defense mechanisms of plants against pathogenic microbes. The prospect of utilizing isolated lignin as an eco-friendly antimicrobial agent presents a promising avenue for enhancing the value of lignin. Furthermore, as lignin derives from plant photosynthesis, its integration into the antimicrobial industry carries the potential to reduce carbon emissions. While numerous studies have explored lignin’s utilization for the development of antimicrobial agents across various applications, the highly heterogeneous nature of lignin, encompassing variations in monomer composition, linkages, molecular weight, and functional groups, has obscured the relationship between lignin’s structure and its antimicrobial properties.

To bridge these knowledge gaps, we conducted a comprehensive study in which we synthesized forty-two quaternary ammonium/phosphonium organosolv lignin samples from Aspen, Pine, and Barley straw, representing hardwood, softwood, and grass sources, respectively, employing a recently developed versatile intermediate known as chloromethylated lignin. These lignin samples were systematically evaluated for their antibacterial potential against E.coli and clinical isolates of Gram-positive (MRSA) and Gram-negative (K. pneumonia) bacteria strains. Our findings indicate that the antibacterial activity of these lignin samples exhibits a notable increase with the length of the hydrophobic chain, up to C14, beyond which it begins to decline. Ongoing research is also exploring the antimicrobial activity of ammonium and phosphonium surfactant materials, both individually and in combination. This research underscores the significant enhancement in lignin’s antimicrobial efficacy through chemical modification and highlights the potential for further improvements by incorporating additional chemical structures, such as cationic functional groups through chemical modification. This study opens new avenues for maximizing the antimicrobial potential of lignin, contributing to sustainable and eco-friendly solutions for pathogen control.

5:00 PM MF03.04.02
Tough 3D Printable Hydrogels Based on Force Responsive Protein Unfolding

Ana Paula Kitos Vasconcelos, Naroa Sadaba, Antonio Vazquez and Alshakim Nelson; University of Washington, United States

The field of mechanochemistry has primarily focused on small molecules as the mechanophores that undergo mechanically-induced chemical transformations. Nature, however, uses macromolecules, such as proteins, as mechanically-responsive elements in biological signaling and response. 3D printed thermosets based on the globular protein bovine serum albumin (BSA) as a biologically-derived mechanochemical system have demonstrated high strength, toughness, and hysteresis memory, demonstrating the mechanical-responsiveness protein unfolding and refolding. However, these properties were not observed for the associated hydrogel. Herein, we develop a photopolymerizable hydrogel with a highly defined network topology based on norbornene functionalized BSA and poly(ethylene glycol) diol and a loosely-crosslinked interpenetrating network to observe mechanically-induced BSA unfolding. Harnessing BSA as a force-responsive crosslinker imparts high strength, toughness, ductility and tear resistance in 3D printable hydrogels, due to the disruption of the protein native structure and subsequent release of stored length as an energy dissipation mechanism to resist material failure. The development of this network enables the incorporation of a vast array of proteins as stimuli-responsive crosslinkers in vat photopolymerizable hydrogels.

5:00 PM MF03.04.04
Scalable Advance Manufacturing of Complex Multilayer Structures Film with Simultaneous Slot Dies Deposition Method

Minwoo Jung; Georgia Institute of Technology, United States

The application of slot die coating manufacturing techniques has been widely studied due to their scalability, continuous process, and relatively cost-effectiveness. Slot die coating is applied to manufacturing organic thin film transistors (OTFT), organic capacitors, organic solar cells (OSC), and membranes. However, OTFT, organic capacitor, OSC have multilayer complex structures for their functionality, and advanced membrane often requires multilayer and patterned structure. Fabricating such products that have multiple-layer complex structures requires multiple manufacturing steps since the most widely used slot dies are limited to a single layer. With additional layers, a separate single-layer slot die and drying oven are needed, which often require significant energy consumption and requires space for extra manufacturing tools. Therefore, reducing manufacturing steps to a minimum can be beneficial in terms of cost and environment. To overcome limitations of single-layer slot die, current technology allows depositing two layers at single steps using a bilayer slot die but limited to two layers and patterning deposition using a co-deposition slot die but limited to a single layer. However, these techniques still require more than two steps to fabricate the abovementioned products. To further reduce the extra steps for a multilayer complex structure, the co-deposition slot die, and Bilayer slot die can be deposited simultaneously on top of each other. Simultaneous deposition of co-deposition slot die and Bilayer slot dies can reduce the drying step, which consumes a large portion of the energy in the slot die process. Furthermore, removing drying ovens can reduce the footprint of the manufacturing line as mentioned above.

Using advanced manufacturing methods by simultaneous co-deposition of co-deposition and bilayer slot die, unique structure of simple capacitor can be achieved. Poly(1,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was used as conductive polymer, Polyvinyl alcohol (PVA) as insulating polymer, and Sodium carboxymethyl cellulose (CMC) as viscosity modifier. The surface tension and viscosity of the PEDOT:PSS was modified to stabilize the co-deposition film while the bilayer was deposited on top. Co-deposition slot die deposit alternating strip pattern that consists of PEDOT:PSS for conducting layer and PVA for insulation between PEDOT:PSS strips. The bilayer deposits two layered films on top of the Co-deposition, without any drying step, that consist of PVA as the bottom layer and PEDOT:PSS as the top layer. The resulting film structure is a conductive polymer layer on the bottom of the film, an insulating layer for the middle layer, and another conducting layer on top resembling the capacitor’s structure. Even though the resulting capacitor performance is subpar due to low-grade PEDOT:PSS, the advanced manufacturing method using simultaneous co-deposition and bilayer slot die can be applicable to a variety of products that consist of complex structure in reduced steps.

5:00 PM MF03.04.05
Nanoceullulose Networks: Utilizing Colloidal Processing Principles to Tune The Mechanical Properties of Solid Foams

Aban Mandal, Hareesh Iyer and Eleftheria Roumeli; University of Washington, United States

Scalable Advance Manufacturing of Complex Multilayer Structures Film with Simultaneous Slot Dies Deposition Method
In recent years, nanocellulose has emerged as a sustainable and environmentally friendly alternative to traditional petroleum-derived structural polymers. However, the widespread implementation of nanocellulose is hindered by high energy-intensive extraction and processing methods, limited quality reliability, and cost-effectiveness [1]. In addition, the required fundamental understanding of process parameters that govern the morphology and structure-property relationships of nanocellulose systems, from colloidal suspensions to bulk materials, has not been developed and generalized for all forms of cellulose. This further hinders the more widespread adoption of this biopolymer in applications.

In this study, we focus on the tunability of mechanical properties of cellulose bulk structures, by investigating the intricate connections between thermodynamic, electrokinetic, and hydrodynamic interactions in nanocellulose networks, within the context of stability, phase transformations, and their profound impact on enhancing the properties of bulk materials. To delve into thermodynamic interactions, we examine different concentrations of various nanocellulose-solvent pairs with varying Flory-Huggins interaction parameters. Electrokinetic interactions are explored by manipulating surface charge densities, while hydrodynamic interactions are studied through concentration-based transitions. The interplay between thermodynamic and electrokinetic stabilization is elucidated through time-series polarized light and cross-polarized light imaging of the nanocellulose colloids. We employ Dynamic Light Scattering (DLS) to assess the Fluchs Stability Ratio and correlate the Diffusion Limited Cluster Aggregation (DLCA) and Reaction Limited Cluster Aggregation (RLCA) regimes [2] with the rheological properties of the colloids. This sheds light on the underlying mechanisms and the specific interactions responsible for the concentration-based Onsager's Isotropic to Nematic phase transition, and in addition, enables a co-relation of the properties at the colloidal state [3] and the final solid structures. Small-angle X-ray scattering (SAXS) is employed to comprehensively understand the influence of various processing parameters on the ordering of the final bulk structure and, subsequently, the structure-property relationships. Our study enriches the understanding of nanocellulose processing from a polymer physics and colloidal chemistry perspective. These findings hold the potential for extending to multicomponent biomass-based systems in the future, contributing to sustainable and high-performance biomaterials development.


5:00 PM MF03.04.06 Effect of Wet-Stretching and Confinement on Fiber Alignment in Bacterial Cellulose Films Kuotian Liao, Julia Blair, Kwon-Teen M. Chen, Esther Nicolaou and Eleftheria Roumeli; University of Washington, United States

Recent progress in sustainable materials has provided viable solutions to address the escalating challenges posed by non-renewable sourcing, environmentally harmful manufacturing processes, and the ultimate fate of synthetic plastics. Within this context, biopolymers have garnered increasing interest for their potential to be used as a replacement to petroleum-derived counterparts, offering the distinct advantage of reduced environmental impact across their entire lifecycle. Bacterial cellulose (BC) stands out as a particularly compelling candidate, combining a high molecular weight, high degree of crystallinity, and a scalable, adaptable biosynthetic manufacturing process. Unlike plant-derived cellulose, BC circumvents the need for extensive extraction procedures, rendering it more accessible and environmentally benign. Following drying, the naturally grown BC hydrogels, called pellets, can be transformed into self-supporting, lightweight yet mechanically robust films with promising applications in structural panels or protective garments. This study delves into the effect of mechanical stretching/confinement as means of aligning the fibers in BC pellets and their impact on the overall mechanics of the resulting dried films, aiming to offer fundamental insights into the structure-property interplay of this networked polymer. The results will not only enrich our fundamental understanding of polymer physics pertaining to BC-based networks, but also pave the way for future tailoring of the properties of the resulting films to cater to a diverse array of applications.

5:00 PM MF03.04.08 Understanding 3D Networks Structure during Biosynthesis of Cellulose from Bacteria Julia Didier Amorim1,2, Kuotian Liao2, Haresh Iyer2 and Eleftheria Roumeli2; 1Universidade Rural de Pernambuco, Brazil; 2University of Washington, United States

Materials sourced from renewable sources and synthesized under mild conditions offer coupled benefits in terms of sustainability, in contrast to petroleum-derived polymers, which are known contributors to pollution and adverse health consequences. Bacterial cellulose (BC) consists of high aspect ratio fibrils that bundle into fibers, forming 3D networks which can be influenced by growth conditions. BC pellets, which are produced in static conditions and are often used in research and applications, exhibit a layered structure at the mesoscale. These layers form as successive entangled fiber networks are deposited extracellularly during BC growth. The layered structure is a distinctive feature of BC pellets and contributes to their unique mechanical properties. The growth conditions during BC fiber synthesis significantly influence the alignment, crystallinity, and 3D morphology of the formed network. However, there is a lack of understanding of the fundamentals of cellulose fiber aggregation into network assemblies. Understanding how nanoscale fibrils bundle, entangle, and form larger structures at the mesoscale is crucial for tailoring BC's properties for various applications, from biotechnology to materials science. We investigate the intricate structural evolution of BC, spanning from the nanoscale to the mesoscale, with a specific focus on understanding entanglement phenomena. Furthermore, our investigation explores the significance of fibril entanglement in BC networks, providing insights into the intricate process by which individual nanofibrils interweave to construct the broader mesoscale framework. This research aims to provide a comprehensive understanding of BC's structural development.

5:00 PM MF03.04.10 Hydrogel-Ceramic Composite for Efficient Oil Water Separation in Emulsified System Harsh Rohu, Shobha Shukla and Sumit Saxena; Indian Institute of Technology Bombay, India

Water pollution due to oil remains a prominent environmental concern, primarily driven by escalating incidents of oil spills, intense petroleum operations, rapid expansion of the food industry, and the growth of textile, metal, and leather sectors. Oily wastewater discharged from these industries aggravates the problem, posing a significant threat to soil quality, water bodies, aquatic ecosystems, and human health. Ships discharge bilge oily water which is governed by MARPOL. Although numerous techniques and materials are available for oil-water separation, filtration material systems exhibit promise due to their expansible surface area, appropriate pore sizes, lightweight structure, and cost-effectiveness. Filtration systems being invested across the community are majorly made of polymers and ceramics. Polyacrylonitrile (PAN), Cellulose Acetate (CA), Sodium Alginote (NaAlg), Polyvinylidene fluoride (PVDF) are some of the polymers which, post morphological and chemical modification using functional groups are used for oil water separation. Across ceramic membranes, Titania (TiO2), Silicon Carbide (SiC), Alumina (Al2O3), Silicon Nitride (Si3N4) etc. have been explored. A novel composite of Hydrogel with ceramic membrane made of Alumina, Zirconia and SiC has been tailored for efficient oil-water separation. The composite shows very high separation efficiency (99%) with very good anti fouling properties. Furthermore, it is non-toxic and has very high pH and salinity resistance. The composite has potential to be used for pressure driven operations in industries (99%) for very good anti fouling properties. Furthermore, it is non-toxic and has very high pH and salinity resistance. The composite has potential to be used for pressure driven operations in industries for a high flux and better separation efficiency for continuous oil-water separation where water is in continuous phase.

5:00 PM MF03.04.11 Mycelium Bridge Behavior for Sustainable, Architectured Biocomposites Brandon Spitzer, Sabrina Shen and Markus Buehler; Massachusetts Institute of Technology, United States

There is growing interest in the design of sustainable materials based on mycelium, the root network of fungi, due to its robust, interconnected growth and its degradable end of life. In this study, we explore the fundamental interactions between mycelium, substrate materials, and void spaces, which can inform the design of complex and functional mycelium composites. In particular, here we investigate the ability of mycelium to bridge gaps of empty space within a waste-derived bio-composite material and observe the effects of varying nutritional content. The bio-composite substrate is suitable for 3D printing, which enables the creation of an array of complex structures. Our research aims to understand the formation and strength of mycelial bridges supports the future design of mycelium composite materials for self-healing, bio-welding, directed growth, and sustainable structure applications.

5:00 PM MF03.04.12 Sequence Control of Bioinspired Calcium-Responsive Protein-Based Polymers Marina P. Chang, Gatha M. Shambharkar, Winnie Huang, Kenny M. Hernandez and Danielle J. Mai; Stanford University, United States

Protein-based polymers offer improved sustainability over fossil-based synthetic polymers because of their biodegradability and their composition from abundant, renewable materials. Natural proteins exhibit a wide range of functions, providing biosensing for engineering responsive protein-based polymers. Responsiveness to biological signals, such as calcium ions, allows protein-based polymers to mimic biological functions like muscle contraction. The amino acid sequence of protein-based polymers is often modified to tune the function of the polymers without requiring additional steps of chemical synthesis and purification. Tunability is advantageous for applications such as scaffolds for tissue regeneration, where the mechanical properties of the scaffold can be matched to specific tissues. To create tunable, calcium-responsive, protein-based polymers, we take inspiration from a class of “Repeats-in-Toxin” (RTX) protein domains found in bacterial proteins. These RTX domains undergo a reversible conformation change from random coils to β-roll structures upon binding to calcium. RTX domains are characterized by the repetitive sequence GGXGDXUX, in which
glycine (G) and aspartic acid (D) are highly conserved in the calcium-binding region. For positions that are less conserved, U represents an aliphatic amino acid and X represents any amino acid. We explored the impact of amino acid substitutions at a non-conserved X site in the calcium-binding region. This amino acid substitutions probe the impact of monomer size, electrostatic interactions, and hydrophobicity of the calcium-responsive behavior of RTX domains. Additionally, we explored the impact of sequence variability by creating consensus RTX domains, which comprise tandem repeats of the simplified consensus sequence GGAGXDITYL. Circular dichroism reveals that some variants exhibit more ordered structures in the absence of calcium compared to wild-type RTX, particularly variants with smaller amino acid substitutions. By varying the amino acid sequence, we can tune the calcium sensitivity of RTX between 1 – 100 mM CaCl₂. Finally, RTX domains are incorporated into fusion protein polymers to create calcium-responsive materials with tunable stiffness for biomedical applications such as tissue scaffolds.

5:00 PM MF03.04.13

Rapid Photo-Triggered Release Kinetics of PPA Microcapsules

Youngsoo Shin1, Jared Schwartz2, Anthony Engler1, Brad H. Jones2 and Paul Kohl1; 1Georgia Institute of Technology, United States; 2Sandia National Laboratories, United States

Stimuli-responsive microcapsules have been investigated as a means to release special-purpose payloads such as catalysts inside solid polymer materials. These catalyst payloads have garnered recent interest in the recycling and upcycling of plastics. A microcapsule can be loaded into common commodity plastics and triggered to release a catalyst for depolymerization. Specific chemical conditions or structural changes have commonly been used to trigger microcapsules for controlled release, but these mechanisms tend to not be amplified or take substantially long times to induce release. Long times for release impact the cost of processing, especially for recycling that would otherwise require an outside-in mechanism. Unlike other stimuli, light has advantages in that it is readily available and convenient to use with low cost. This study utilized poly(phtalaldehyde) (PPA) microcapsules formulated with various UV-sensitive photo-acid generators (PAGs). Upon exposure to UV irradiation followed by heat treatment, PAGs generate and release strong acids that attack the PPA, which initiates rapid depolymerization back to the monomer. In the case of a microcapsule made with a PPA shell, the rapid depolymerization results in the immediate release of the capsule payload to its surroundings. PPA capsules were made using an oil-aqueous emulsification process in the presence of surfactants and their morphologies are a fraction of blueberry shapes (high loading of core) and a fraction of concave shapes (low loading of core). As UV dose increased, more capsules were depolymerized and more dodecane core was obtained, indicating core release. The percentage of dodecane release and depolymerized PPA were analyzed using ¹H NMR. The photo-triggered response was further tuned by varying PAG concentration, PAG type, and post-exposure heating time. The efficiencies of the PAGs were compared for their release kinetics and the energy required to fully decompose the shell. PPA microcapsules with UV-sensitive PAGs successfully released their core within a short time and with low UV doses.

5:00 PM MF03.04.14

Investigating The Pozzolanic Reactivity of Natural Zeolite as a Supplementary Cementitious Material: Correlations to Mechanical Performance

Brandon T. Lou, Dwayne Arola and Eleftheria Roumeli; University of Washington, United States

Cement, the binding material in concrete, produces a significant amount of atmospheric CO₂ in its production. Therefore, methods to reduce the amount of cement used in concrete production, while maintaining adequate strength and durability, has substantial environmental implications. Natural zeolites are being considered to replace a portion of cement content as a supplementary cementitious material (SCM) due to its high pozzolanic activity, which is attributed to their porous aluminate framework. However, the detailed reactions between the zeolite and cement, namely the effect of the hydration reactions, as well as zeolite’s contribution from physical characteristics, are not fully understood. Previous studies have characterized pozzolanic activity, assessed particle size and preprocessing contributions, mechanical properties, and performed chemical component analyses separately. However, there are inconsistencies among reported results and the materials science of the structure/processing/performance was not elucidated. Here, the pozzolanic activity of natural zeolite is characterized with respect to the degree of hydration of mortar mixes and correlated to the mechanical performance of concrete composites. The natural zeolite is first analyzed to understand its microstructure, elemental, and mineralogical composition using scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD). Bound water measurements are utilized to quantitatively assess the pozzolanic reactivity of the zeolite, and over a range of particle sizes (achieved via milling). We then varied the percentage of natural zeolite in mortar composites at different particle sizes and concentration with respect to cement content. The effects of particle size on the micromorphology, degree of hydration, and development of bonding environments of the composites is observed via SEM, thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR). The experimental results confirm that zeolite replacement of cement content in mortar composites enhances the mechanical performance at a discrete particle size and concentration. There are optimum parametric conditions to maximize strength that appear based on the increased degree of hydration stemming from increased pozzolanic activity of zeolite. Overall, this experiment demonstrates that natural zeolites are a viable SCM to reduce cement content in concrete composites and that further work could support the development of a truly superior sustainable concrete.

5:00 PM MF03.04.15

Energy-Efficient Manufacturing and Lightweight Applications of Expanded Ethylene-Propylene-Butene-1 Copolymer Bead

Peng Guo; SINOPEC Beijing Research Institute of Chemical Industry, China

Ethylene-propylene-butene-1 ternary copolymer (TPP) and ethylene-ethylene-propylene copolymer (EPC) were fabricated to produce expanded polypropylene (EPP) beads through batch-foaming followed by steam-chest molding. The microstructure and thermal behaviors of both TPP and EPC were investigated by nuclear magnetic resonance, gel permeation chromatography, wide-angle X-ray diffraction, analytical temperature rising elution fractionation, and differential scanning calorimetry. EPP beads made of TPP and EPC were prepared by an autoclave batch-foaming process using compressed CO₂ as the blowing agent. Polypropylene micropellets (average diameter is approximately 1 mm) were obtained using an underwater micro-pelletizer system, which shorten the CO₂ diffusion distance. The effects of CO₂ content on the melting temperature of two types of polypropylene were studied. Magnetic suspension balance was used to measure the solubility of CO₂ in semi-molten PP. The effects of introducing comonomers on the foaming processing and cell structure of EPP beads were preliminarily investigated. The addition of 1-butene played a significant role in enhancing the mechanical properties and decreasing the energy cost during both batch-foaming and steam-chest molding with reduced carbon dioxide emissions.

5:00 PM MF03.04.16

Engineered Wood Materials Utilizing Seaweed Biomass as an Adhesive

Mallory Parker1, Paul Grandgeorge1, Ian R. Campbell1, Hannah Nguyen1, Rebekah I. Brain1, Scott Edmundson2, Deborah Rose2, Chimmye Subban2 and Eleftheria Roumeli1; 1University of Washington, United States; 2Pacific Northwest National Laboratory, United States

The increasing concerns associated with petroleum-derived resources call for sustainable renewable sourced alternatives. Engineered wood materials are widely used in the form of panels and particleboards in structural applications, construction and packaging. Wood-products provide multiple advantages such as sustainable feedstocks and lightweight final products that can meet load-bearing requirements for a plethora of applications. However, engineered wood products, such as medium density fiberboards (MDF), most predominately rely on formaldehyde-based adhesives to achieve wood particle/fiber bonding. Such adhesives are not only petroleum-derived but also have detrimental health effects during use (formaldehyde emissions) and at their end-of-life. To further mitigate the environmental impact of construction materials, more sustainable bonding agents need to be investigated. In this work, we hypothesize that the biopolymers within seaweed biomass can form a strong hydrogen bonding network with wood particles, that can be sufficient to create a set of fully biobased engineered wood composites. The use of seaweed as an adhesive would offer the benefits of carbon sequestering and renewable sourcing, as well as non-detrimental end-of-life effects. We test our hypothesis using Ulva expansa (Ulva) as a proof-of-concept seaweed species and report the manufacturing of engineered wood composites with varying concentration of waste wood particles and Ulva, as well as a detailed study of their structure, bonding and mechanical properties. We demonstrate that upon hot-pressing, powdered Ulva flows in between the wood particles and provides a strong binding effect. We show that the flexural strength of engineered wood composites increases with increasing Ulva concentrations. We further report that the presence of Ulva attractively improves other properties such as water resistance and flammability. To highlight the bonding mechanisms at the biopolymeric level, we perform Fourier transform infrared spectroscopy (FTIR) studies. We also show that the resulting wood panels can be machined using traditional drilling or laser-cutting methods. Finally, we perform an analysis of the environmental impact of Ulva-bonded engineered wood composites.

5:00 PM MF03.04.17

Reusable Cellulose-Polymer Composites Using Silica Nanoparticle incorporated Nano- and Micron-Sized Cellulose Fibers

Jung-woo Park and Young-soo Seo; Sejong University, Korea (the Republic of)

Interest in sustainable and biodegradable plastic fillers has increased due to environmental concerns and legislative regulations. Therefore, cellulose fiber (CF) with excellent mechanical properties has attracted attention recently. However, there are issues when it is mixed with plastics, which are lack of dispersion and limited thermal stability of CF. CF that aggregates immediately when dried to capillary forces does not disperse well in plastic and oxidizes easily to render a brownish color during the melt mixing process reducing circularity. Here, to immediately when dried due to capillary forces does not disperse well in plastic and oxidizes easily to render a brownish color during the melt mixing process reducing circularity. Here, to
the textile industry is the second largest industry in manufacturing. The textile industry pays a huge contribution to the fashion and clothing industry by acting as its base, however with the high and on-going demand in clothing and garments “Fast Fashion”, and overconsumption are increasing as well more over leading to a substantial and sequential rise in environmental issues and concerns such as pollution. The textile and fashion industry are the highest polluting industries, playing a critical role in water consumption and pollution, solid waste pollution as well as resource depletion. Due to its greatly negative impacts on our environment in addition to our environment’s current deteriorating state, global organizations such as the European Union (EU) as well as individual designers and the fashion and textile industry as a whole’s implementing techniques for sustainable fashion in order to maintain a green environment and lifestyle as well as promote a circular economy. Clothing has a significant influence on Saudi Arabia’s tradition and culture. Saudi Arabia’s vision 2030 is following a green initiative and in order to succeed a sustainable approach Saudi designers and entrepreneurs are following sustainable fashion and clothing as an eco-friendly alternative. The essence of green chemistry as well as up-cycling redesigning are used in the sustainable clothing industry, in addition to implementing regulations and laws.

Non-isocyanate polyurethanes (NIPU) have received significant attention in sustainability research due to its potential to be synthesized without the inclusion of toxic isocyanate raw material and catalysis. In this study, CO$_2$ is further employed as an eco-friendly resource to afford poly(ether carbonate) polyols, which is then chemically transformed to introduce cyclic carbonate terminal groups (PECC). Separately, soy oil with cyclic carbonate functional groups (CSBO) is prepared as an example of sustainable raw material from bio-renewable resources. NIPU is then prepared through the ring-opening reaction of multi-aminies and the cyclic carbonate functional groups of PECC/CSBO mixtures. Characteristics of the resulting NIPUs including physical and thermal properties are investigated, demonstrating reasonable and tunable tensile properties. This study demonstrates the preparation of industrially important polyurethane materials from eco-friendly renewable resources, well exemplifying our current and increasing endeavors to realize sustainable polymers. This work was supported by Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government (MOTIE) (2020/4010/100080, Development of Demonstration for Synthesis of High Value Chemical using Captured CO$_2$).

Recycling of heterogeneous plastic waste poses a formidable challenge due to the strong incompatibility arising from the different chemical and molecular structures of the constituent polymers. This challenge inspires us to study industrially viable method to enhance the performance of polymer blends, leading to more homogeneous morphologies and improved mechanical performances. In this study, an azo-type radical initiator with azidoformate (AF) at both ends is firstly prepared, which is then employed for the radical polymerization of styrrene to afford AF end-functionalized poly(styrene-co-acrylonitrile) (AFAPS). The copolymerization and copolymerization capability of AF group of AFAPS allows the grafting reaction of AFAPS onto poly(propylene) (PP) to obtain grafted-PP containing azidoformate groups. This approach to imparting biodegradability to a polymer while achieving excellent mechanical characteristics consists of introducing fibrous structures into polymer matrices. This method not only endows the composite with good mechanical properties but also provides a vehicle for water and biodegrading enzymes to slowly penetrate the composite structure leading to complete biodegradation [7]. Recent research revealed that the incorporation of nanocellulose into polymer matrices can improve the composite performance both in terms of strength and biodegradability [1, 5, 7]. The present work reports the production of lignocellulosic nanomaterials from inexpensive wheat straw feedstock and alkali peroxide pulping followed by mild peracetic acid treatment at pilot scale [6, 7]. The resulting cellulose nanofibrils have been extensively characterized and applied to prepare thin, flexible, and translucent composite films with low poly(vinyl) alcohol contents (i.e. below 40 wt.%) using a simple solvent casting method. The mechanical, optical, and barrier properties of as-prepared composites have been thoroughly examined. This novel bioplastic has the potential to replace petroleum-derived plastics across a broad range of industries such as aquaculture, agriculture, food packaging, and more; promising applications include ground covers, drip lines, gooey duck tubes, aqua nets, and paperboard lining or film covering for food packaging [2, 3, 8]. Furthermore, this work provides an analysis of the techno-economic performance of the system accounting for optimization of operational efficiency, cost-effectiveness, and sustainability factors. The findings contribute valuable insights into resource allocation and investment strategies in sustainable bioprocess systems.

Experimental-Computational Design of Protein-Based Materials were applied in a series of experiments to predict the mass loss of approximately 10,000 structural and compositional variations of the 230 homo- and copolymers originally included in the manually curated experimental data that characterizes the weight loss behavior of fully biodegradable polyester copolymer samples in both water and soil natural environments. The models (such as weight loss over time) capturing degradation behavior of these materials as a function of chemical, geometric and environmental factors.

We devised a universal strategy to augment material strength and toughness by incorporating intrinsically disordered mussel foot protein fragments at the termini of these proteins. This approach leverages our recent advances in synthetic biology aimed at overcoming these hurdles. We have developed a range of synthetic biology tools that enable the stable expression of high molecular weight recombinant structural proteins. Furthermore, by carefully engineering their amino acid sequence, we can design entirely new structural proteins with properties inspired by natural structural proteins, but that do not exist in Nature, and use them to develop materials with e.g., adjustable mechanical properties, programmed functionalities, or the ability to adapt or respond to the environment.

Microbially-synthesized protein-based materials (PBMs) present an appealing alternative to petroleum-derived synthetic polymers. However, their widespread adoption has been hindered by challenges such as the repetitive sequences, high molecular weight of proteins, and skewed amino acid compositions, particularly for high-strength PBMs. In this presentation, I will introduce our recent advances in synthetic biology aimed at overcoming these hurdles. We have developed a range of synthetic biology tools that enable the stable expression of high molecular weight and highly repetitive proteins within engineered microbes. These tools are instrumental in the microbial production of recombinant spider silk of similar mechanical properties. We further engineered amyloid-like silk proteins which have a remarkable propensity to form nano β-crystals, resulting in fibers that possess exceptional mechanical properties. Additionally, we have devised a universal strategy to augment material strength and toughness by incorporating intrinsically disordered mussel foot protein fragments at the termini of these proteins. This approach promotes end-to-end protein-protein interactions, leading to the creation of protein fibers that surpass natural spider silk and petroleum-derived nylon fibers in both strength and toughness. Moreover, these fibers can be produced at a yield of 8 g/L.

9:15 AM MF03.05.02

Machine Learning-Aided Design of Biodegradable Polymers Jessica N. Lalonde1; Ghanshyam Pilaania; Babetta L. Marrone3; Chiho Kim1,5; Huan Tran5; Rishi Gurumani and Rampi Ramprasad2,3; Duke University, United States; 3GE Global Research, United States; 3Los Alamos National Laboratory, United States; 5Matterize, Inc, United States; 3Georgia Institute of Technology, United States

In the pursuit of sustainable materials, biodegradable polymers have emerged as promising alternatives to traditional plastics, finding applications across diverse industries. Particularly, the degradation products of traditional plastics are of specific concern, and fully biodegradable and non-toxic plastic alternatives offer promising solutions to this ongoing challenge. However, a rational design approach to engineer biopolymers for degradation after their intended use still remains elusive. This is largely due to our inability to understand and model performance metrics (such as weight loss over time) capturing degradation behavior of these materials as a function of chemical, geometric and environmental factors.

As an exciting development in this direction, we have established predictive machine learning models which utilize physics-informed deep neural networks (NN) on previously established, manually curated experimental data that characterizes the weight loss behavior of fully biodegradable polyester copolymer samples in both water and soil natural environments. The models were applied in a series of experiments to predict the mass loss of approximately 10,000 structural and compositional variations of the 230 homo- and copolymers originally included in the original training set. The predicted mass loss for these candidate biodegradable polymers over a period of 365 days allowed us to identify novel copolymers with the potential to replace existing chemistries while matching property values to the desired performance metrics. This talk will discuss our findings and future directions, including the integration of critical properties, such as, thermal and mechanical characteristics, into the screening and design workflow and thereby bringing us one step closer to realizing the grand vision of a sustainable circular economy.

9:30 AM MF03.05.03

Experimental-Computational Design of Protein-Based Materials Diego López Barreiro1; University College London, United Kingdom

Nature leverages the self-assembly propensity of structural proteins like elastin, resilin, collagen, or silk to generate sustainable functional materials with remarkable performance and that span a wide range of mechanical and structural properties: from soft to stiff, from porous to densely packed, from static to dynamic... This is inspiring scientists and engineers to use structural proteins as a sustainable and efficient material for fossil-based polymers in the manufacture of synthetic functional materials with applications in food, healthcare, adhesives, energy, textiles, or membrane technology, to name a few.

Structural proteins are normally harvested from animal sources (e.g., silkworm cocoons, animal tissue), but these suffer from batch-to-batch variability, presence of contaminants, and cultural or religious concerns that limit their commercial use. Fortunately, developments in engineering biology allow us to overcome these issues and biofabricate non-animal-derived recombinant structural proteins. Furthermore, by carefully engineering their amino acid sequence, we can design entirely new structural proteins with properties inspired by natural structural proteins, but that do not exist in Nature, and use them to develop materials with e.g., adjustable mechanical properties, programmed functionalities, or the ability to adapt or respond to the environment.

However, a complete framework that connects amino acid sequence to material properties is unavailable. Thus, de novo recombinant structural proteins are normally developed through low-throughput trial-and-error experimentation, which impedes rapid prototyping. In this talk, we will showcase our work on the combination of computational and experimental tools to accelerate the exploration of the design space of structural proteins. Specifically, we will present examples of how this approach has aided us in the design of new protein-based materials including flexible conductive films, bio-mineralizing films, or injectable stimuli-responsive hydrogels.

10:00 AM BREAK

SESSION MF03.06: Biomatter Processing, Properties

10:30 AM MF03.06.01

Pathways to Biorenewable Circularity in Plastics Brett A. Helms; Lawrence Berkeley National Lab, United States

Here, I will discuss how synthetic biology provides an inexhaustible toolbox for the creation of monomers useful for the creation of next-generation circular plastics collectively known as polydiketoenamines. I will highlight how materials properties are dictated not only by the diverse functionalization afforded such strategies, but also the importance of chirality, which is inherent to biology, but lacking or otherwise challenging to scale using conventional chemical approaches. From a materials perspective, not only is it interesting to understand factors governing materials properties stemming from biofunctionalization, but these choices also deeply impact how the materials undergo deconstruction to monomers. I will discuss a variety of phenomena unique to polymers compared to small molecules that guide our understanding of polymer reactivity, particularly as they manifest at different length scales and time scales. I will showcase operando X-ray and NMR capabilities that permit mechanistic studies unpinning deconstruction, which feedback into the materials design and biomolecular target selection.

10:45 AM MF03.06.02

Engineering Microbes to Produce High-Strength Protein-Based Materials Fuzhong Zhang; Washington University in St. Louis, United States

Microbially-synthesized protein-based materials (PBMs) present an appealing alternative to petroleum-derived synthetic polymers. However, their widespread adoption has been hindered by challenges such as repetitive sequences, high molecular weight of proteins, and skewed amino acid compositions, particularly for high-strength PBMs. In this presentation, I will introduce our recent advances in synthetic biology aimed at overcoming these hurdles. We have developed a range of synthetic biology tools that enable the stable expression of high molecular weight and highly repetitive proteins within engineered microbes. These tools are instrumental in the microbial production of recombinant spider silk of similar mechanical properties. We further engineered amyloid-like silk proteins which have a remarkable propensity to form nano β-crystals, resulting in fibers that possess exceptional mechanical properties. Additionally, we have devised a universal strategy to augment material strength and toughness by incorporating intrinsically disordered mussel foot protein fragments at the termini of these proteins. This approach promotes end-to-end protein-protein interactions, leading to the creation of protein fibers that surpass natural spider silk and petroleum-derived nylon fibers in both strength and toughness. Moreover, these fibers can be produced at a yield of 8 g/L.
Structuring Nanocellulose into Heat-Insulating Mesoporous Structures with Light Permeability

Understanding how to mitigate polymer disentanglement and bond scission is a significant challenge, especially in the development of active and shape-morphing materials. We report the application of light permeability to nanocellulose, which is used to create a structural aerogel-like material. This material is expected to reduce CO2 emissions in buildings and vehicles when used as the interspace material in double-glazed windows compared to normal heat energy-losing windows.

Decreasing the heat loss in buildings and vehicles is important for the realization of the low-carbon society. A transparent insulator applicable to windows is effective in reducing such a heat loss. Conventional candidates for transparent insulators are silica aerogels, with optical transparency and high thermal insulation. However, silica aerogels prepared through an unscalable supercritical-drying process are mechanically brittle. Herein, we report a structurally aerogel-like “cryogel” comprising sustainable wood-derived, mechanically strong cellulose nanofibers (CNFs) through a scalable freeze-drying process. Cryogels refer to freeze-dried porous structures. The optical transparency of the cryogels was achieved by suppressing the agglomeration of CNFs during freeze drying. The CNF cryogels exhibited good insulating properties and circularity. Such a heat-insulating yet light-permeable cryogel of wood resource with scalability and circularity is expected to reduce CO2 emissions in buildings and vehicles when used as the interspace material in double-glazed windows compared to normal heat energy-losing windows.

Synthetic biology – creating new capabilities with life – promises to create a greener future for planet Earth, from fields as diverse as pharmaceuticals to manufacturing, agriculture and nanotechnology. Progress can be stymied by such considerations as economics, politics, legal and philosophical issues surrounding GMOs. Often solutions to these problems already exist, so it is a difficult, new superior method to displace the old. As we move humans beyond Earth, to long duration stays in the International Space Station, and then onward to the Moon and Mars, the challenges of supporting human life will need radical new solutions. For example, while life on Earth uses an enzymatic machinery which evolved over 3.5 billion years ago, synthetic biology promises to be able to engineer the systems to adapt to current natural or industrial environments. A focus on solutions off planet require a focus on a circular economy. While there are new constraints, such as worrying about the mass of a solution, constraints offer opportunities for game-changing solutions that will then allow revolutions back on our home planet. Example projects include biomining and fungal-based habitats off planet.

Microbes are extensively used in industry to convert carbon sources into valuable end-product chemicals and have found applications in the food industry, waste treatment, water quality assessment and bioremediation. Among them, species of two microbial groups, diatoms and dinoflagellates, that exhibit appealing features for sensing devices were selected and encapsulated in hydrogels with different degrees of complexity to create 3D printed biocompatible materials with sensing behavior. We explore the encapsulation of such microorganisms within multifunctional hydrogels that supports the growth and proliferation of those non-mammalian cells by designing a set of ink and methods (direct ink writing-DIW or digital light processing-DLP) that allow to shape them in complex functional 3D structures. To accomplish our goals, we have first investigated the effect of the ink composition on the rheological behavior, printability, mechanical properties and cell growth in the hydrogels. The hydrogel inks were mainly composed of a suspension of microalgae (diatoms or dinoflagellates), polymers, water and nutrients. Next, we explored different printing methods to develop sensors to access water quality- and mechano-sensing hydrogels. The cell survival and activity upon encapsulation was confirmed and correlated to the mechanical properties of the hydrogels. We concluded that the proposed methods are promising for the design and fabrication of living materials with sensing properties such as water quality and force impact sensors.


The properties of myco-materials result from both the material's growth conditions and their subsequent treatment. The use of dynamic and static environmental control during the growth stage can significantly influence the mechanical and chemical properties of myco-materials. Dynamic environmental control, where the conditions are varied during growth, can lead to enhanced material properties compared to static conditions. The use of such dynamic control can improve the mechanical strength, porosity, and chemical composition of myco-materials, making them more suitable for various applications. Additionally, the selection of the appropriate growth conditions can help in the development of specific properties that are necessary for particular applications.
Fungi are remarkably adaptive organisms, modifying their behaviors and characteristics in response to their environment, including nutrient availability. Over the past 15 years, fungi have emerged as a promising source of sustainable materials, finding applications in areas such as packaging and building materials. However, there are still knowledge gaps in the field, compromising our ability to consistently produce reliable materials. In this presentation, we delve into the potential of manipulating growth environment to tune material properties, drawing from both the wider literature and our own research. Our aim is to contextualize the current state of the art and to ask the question: How can materials science leverage biological adaptation to develop functional mycelium-based materials?

4:30 PM MF03.08.03
Advanced Manufacturing with Engineered Living Materials for Sustainable Polymer Composites
Weinan Xu; University of Akron, United States

Engineered living materials (ELMs) are an emerging class of materials that combine living biological entities especially bacteria with functional soft materials. The incorporation of living bacteria provides the materials with biosensing, self-regenerative, and molecular computing capabilities. Recently, ELMs have also been used for direct ink writing-based 3D printing, which enables the fabrication of dynamic and active 3D structures for various applications. In this talk, I will discuss our recent progress on 3D printing with functional bacteria embedded in a supporting matrix or 3D printed bioink so that an actual biofabrication. The bacteria can be genetically engineered to have specific functions, such as generating bacterial cellulose or reacting to external stimuli. We have demonstrated that 3D cellulose structures can be generated by in situ biosynthesis in the 3D printed templates followed by controlled shape transformation, which provides an efficient and versatile approach for fabricating 3D customizable bio-scaffolds for tissue engineering. More importantly, programmable microbial biosynthesis with two or multiple types of bacteria can be integrated with 3D printing, so that programmable biosynthesis of organic-inorganic biocomposites can be achieved in 3D printed bioink. We have shown that 3D hierarchical biocomposites with bioanion buildup matrix and mineral nanofibers with defined shape and internal structure can be produced, which provides a new platform for bone mimetic materials and tissue engineering.


4:45 PM MF03.08.04
Enhancing Food Security with 3D Printing Technology
Woo Soo Kim and Hyung Ju Ryu; Simon Fraser University, Canada

The global challenge of food security is intensifying due to various factors such as population growth, insufficient agricultural investment, and inefficient distribution systems. As a result, food security is often a complex interplay of elements including diseases, processing methods, and distribution challenges. These issues are particularly acute in vulnerable regions where traditional food safety testing methods are often impractical for detecting foodborne diseases. In response to these challenges, 3D printing technologies and 3D printed sensors emerge as a transformative solution. They provide a means to develop portable, precise, and cost-effective sensors that bridge the existing gaps in food security. This presentation explores the pivotal role of 3D printed sensors, especially for disposable 3D printed sensors in addressing food security concerns, encompassing detection, processing, and quality monitoring in the food supply chain, ultimately ensuring reliable access to nutritious and affordable food. Furthermore, we discuss the applications of 3D printing technology in the agriculture sector, with a focus on the promising future of plant wearables and plant health detection. This innovative approach not only advances food security but also holds the potential to revolutionize agricultural practices, contributing to a more sustainable and secure global food supply.

SESSION MF03.09: Biomass Processing, 3DP
Session Chairs: Yuanyuan Li and Eleftheria Roumeli
Thursday Morning, April 25, 2024
Room 323, Level 3, Summit

8:30 AM *MF03.09.01
Developing a Technology Platform based on The Spinning of Bio-Based Nanostructured Fiber-Based Materials
Daniel Soderberg1,2, KTH Royal Institute of Technology, Sweden; 2Wallenberg Wood Science Center, Sweden

Translating from promising scientific findings to practical engineering technologies often presents significant challenges. One such advancement lies in spinning high-performance reinforcement fibers from nanocellulose. We have been working broadly, spanning several projects, around a spinning technology built on the concept of flow-focusing spinning, which has shown some potential.1-3 These previously published scientific results represent a substantial leap beyond current state-of-the-art techniques, particularly in achieving continuous and controllable conditions for nano assembly. This includes several routes for functionalization beyond the stress-strain curve. The challenge has been pursued by addressing some key challenges related to conventional filament (fiber) spinning, such as e.g., winding, online drying, and multi-filament spinning. In addition, the need for consistent processing and material properties has been addressed, a specific challenge when working with nanocomposites.

An overview of recent results will be presented, considering the performance of continuously spun fibers and attempts to fabricate composite materials based on fabrics constructed from these fibers. One example is the results show how the parameter space for processing and, specifically, drying strongly impacts the final material's properties. Another indicates that fibers spun with hydrodynamic flow-focusing show a surprisingly high thermal conductivity.2 Following this, the piezoelectric properties have been studied, as well as functionalization using other nanoparticles and polymers.

Finally, the possibility to fabricate significant amounts has also made it possible to evaluate the compatibility with various polymer resins and the performance as a composite, while the apparent result is that the composites become more or less transparent. Apart from the investigated property space, the vision is to develop further a technology platform that can provide society with innovative material solutions that are bio-based, lightweight, functional, sustainable, and resilient.


9:00 AM MF03.09.02
Unravelling The Governing Factors for Polysaccharide and Biopolyester Processing
Cecile Chazot1, Simonna G. Fine,2 Eleanor C. Grosvenor,1 Sara Bransovský1 and Gabrielle Wood1,2
1Northwestern University, United States; 2Howard University, United States

The production, consumption, and disposal of polymers for textile and packaging applications pose several problems for the environment, including carbon emissions and the persistence of microscale and nanoscale debris in the ocean. In recent years, biopolymers (e.g. Polybutylene adipate terephthalate or polybutylene succinate) have emerged as environmentally friendly alternatives to petroleum-derived polymers, due to their biodegradability, easy thermal processing and tailorability. Other biopolymer alternatives, such as polysaccharides (e.g. chitosan and cellulose ethers), are naturally abundant and have the potential to self-assemble in cholesteric liquid crystals with a tailored photonic bandgap, opening new opportunities for the development of functional optical materials. However, the widespread adoption of all these biopolymeric alternatives remains limited due to challenges in their large-scale synthesis and manufacturing. In this talk, we will discuss scalable processing of these polymers through fast and open-air reaction schemes, and their integration in the development of functional coatings and textiles with advanced functionality. We will discuss how chemical factors such as molecular weight and repeat-unit chemistry affect chain mobility and solution-based and thermal processing of biopolymers and polysaccharides. We will also discuss how interchain interaction can be leveraged to result in long-range order such as liquid crystal self-assembly, therefore enabling new advanced functionality such as colorimetric sensing and circular dichroism. These relationships are expected to assist in the large-scale deployment of biopolymer-based functional materials with tailored structure and properties.

9:15 AM MF03.02.02
Agarose Facilitating Functional Hydrogels
Olli Ikala and Hang Zhang; Aalto University, Finland

Agarose is polysaccharide that is extracted from seaweed and has amply been applied, e.g., in biological characterizations. It forms hydrogels by physical crosslinks, showing thermoreversible solid-gel transitions, wherein nanoscopic bundles of semiflexible fibrils are formed in the gel state in comparison to polymer coils in the sol state. In hydrogels it allows strain stiffening (1). Here we show that agarose facilitates new hydrogelation functionalizations. We combine agarose physical gel networks with poly(N-isopropylacrylamide), PNIPAm, chemical gel networks.
Cellulose and Nanocomposite 3D Printing in Optimized Dispersions for High-Performance Properties

...supplements the fluctuating flocculation caused by interfacial evaporation. Differing from the Rayleigh–Bénard convection, by the effect of capillary force, this spatial quasi-two-dimensional higher concentrations of the dispersions, Brownian motion gradually loses its dominance, and evaporation-induced Marangoni flow under the influence of viscous forces triggers spatial evaporation process using the Particle Image Velocimetry method. As the concentration of the dispersion increased, we observed that periodic convection gradually emerged within the cell. At... cm$^2$ allow to power autonomous sensing devices including a Bluetooth module and humidity and proximity sensors, all integrated onto mycelium flexible circuit boards.

Soft devices provide unique opportunities in our quest for a more sustainable future. Among the key issues to overcome are the search for high performance green materials, end-of-lifetime considerations in complex (soft) systems, and their energy efficiency. This talk aims at suggesting solutions for some of these grand challenges. We introduce bioderived materials and fabrication methods for soft systems that biodegrade, yet are of high resilience. Based on highly stretchable biogels and degradable elastomers, our forms of soft electronics and robots are designed for prolonged operation in ambient conditions without fatigue, but fully degrade after use through biological triggers. Electronic skins provide sensory feedback, while stretchable and biodegradable batteries enable autonomous operation. 3D printing of biodegradable hydrogels enables omnidirectional soft robots with multifaceted optical sensing abilities. Going beyond, we introduce a systematically-determined compatible materials systems for the creation of fully biodegradable, high-performance electrohydrodynamic soft actuators. These embodiments reliably up to high electric fields, show performance comparable to non-biodegradable counterparts, and survive over 100,000 actuation cycles. Pushing the boundaries of sustainable electronics, we demonstrate a concept for growth and processing of fungal mycelium skins as biodegradable substrate material. Mycelium-based batteries with capacities as high as ~3.8 mAh cm$^{-2}$ allow for flexible fully biodegradable, high-performance electrohydraulic soft actuators. These embodiments reliably up to high electric fields, show performance comparable to non-biodegradable counterparts, and survive over 100,000 actuation cycles. Pushing the boundaries of sustainable electronics, we demonstrate a concept for growth and processing of fungal mycelium skins as biodegradable substrate material. Mycelium-based batteries with capacities as high as ~3.8 mAh cm$^{-2}$ allow to power autonomous sensing devices including a Bluetooth module and humidity and proximity sensors, all integrated onto mycelium flexible circuit boards.

Cellulose, the main component in cotton, features a naturally occurred hierarchical structure down to the ångström scale, providing a scaffold with multiscale interspace and abundant functional groups. In this talk, I will talk about our work using cellulose as the material platform for flexible ionic and electronic devices. We will focus on the design principles as well as the application scenarios in energy generation, conversion and sensing.


SESSION MF03.10: Upcycling, Recycling, Depolymerization I

Cellulose and Nanocomposite 3D Printing in Optimized Dispersions for High-Performance Properties

Leiwei Wu and Kosuke Okeyoshi; Japan Advanced Institute of Science and Technology, Japan

Spontaneous pattern formation in polymer dissipative systems such as Turing patterns is highly valued in material design. However, the process of fixing patterns to the substrate through evaporation strategy involves a complex pathway from equilibrium to disequilibrium and back to equilibrium as the dispersed particles undergo deposition from saturation to supersaturation. Understanding the non-equilibrium process is essential for the advancement of materials innovation and applications. However, because of high viscosity, polymer dispersions have often received limited attention, presenting processing challenges. Inspired by the viscous fingering phenomenon, we use aqueous polysaccharide dispersions to induce stable spatial patterns within Hele-Shaw cells through controlled water evaporation. These spatial patterns effectively formed deposition patterns in the fluids, dividing the space from one into multiple with anisotropic polysaccharides membrane, splitting the monolayer. In this study, we meticulously tracked the evolving behavior of internal fluids of aqueous polysaccharide dispersion during the evaporation process using the Particle Image Velocimetry method. As the concentration of the dispersion increased, we observed that periodic convection gradually emerged within the cell. At higher concentrations of the dispersions, Brownian motion gradually loses its dominance, and evaporation-induced Marangoni flow under the influence of viscous forces triggers spatial periodic Marangoni convection, taking over as the dominant behavior. This quasi-two-dimensional convection encourages particles to aggregate at specific areas in the dispersion, which supplements the fluctuating flocculation caused by interfacial evaporation. Differing from the Rayleigh–Bénard convection, this spatial quasi-two-dimensional convection can be immobilized into polymer membranes with self-assembled polysaccharide structure through evaporating. This aggregation effect of evaporation is not limited to this kind of biopolymer but also can be extended to various functional polymer particles, complementing what has been achieved in assembling particles from fluids using convection fields.


Cellulose and Nanocomposite 3D Printing in Optimized Dispersions for High-Performance Properties

Rigoberto G. Advincula; The University of Tennessee/Oak Ridge National Laboratory, United States

The interest in renewable, natural, and bio-based polymers has a high potential, especially for commodity plastic replacement. From miscanthus grass, abaca fibers, chitin, and coconut coir, the key is determining their ability to form synergistic blends and composites. This means investigating their miscibility and dispersion properties, including a fundamental understanding of their secondary and tertiary structures(alpha-crystallinity and beta-sheets). The nanostructuring involves utilizing their sometimes high-aspect ratio or non-covalent interactions to determine the need for compatibilizations. Then, they must determine their minimum percolation threshold for the desired property at a minimum cost. These "optimization" protocols often unlock their true technoeconomic value rather than simply using them to "replace the plastic". In this talk, we will describe strategies and projects where we have focused on preparing nanocomposites for high value in applications with coatings and 3D printing. Utilizing nanocellulose or cellulose nanocrystals, it is possible to unlock those advantages by emphasizing nanostructuring and derivatization. This is evident in their use with various dispersions in photopolymerizable resins, hydrogel metal precursors, and polyelectrolyte complexes. AFM/ML strategies are emphasized as a method of improving optimization for additive manufacturing.

Characterizing The Softness of Wool via Structure-Property Relationships

Serafina R. France Tribe and Cecile Chazot; Northwestern University, United States

State-of-the-art evaluation of textile touch sensation (e.g., scratchiness) follows broadly-adopted qualitative and time-intensive procedures that rely on consumer-based studies. This is due to the lack of understanding of how material properties and fiber morphology affect the surface interaction of the fabric with human skin. Wool, in particular, is an animal-derived fiber that can range from extremely soft to uncomfortably scratchy, due to the broad range of fiber properties depending on the source. Here, the morphological, compositional, and mechanical properties of a variety of natural wool fibers of reported consumer-based haptic feel are investigated. Using scanning electron microscopy (SEM) and a custom image analysis framework, we assessed the evolution of fiber morphology (e.g., diameter and roughness) across a large variety of animal sources. We also analyzed how fiber composition varies between sheep breeds through Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and x-ray diffraction (XRD). Last, we characterized the mechanical properties of the fibers such as tensile strength and viscoelastic moduli through dynamic mechanical analysis (DMA) and uniaxial tensile testing. This comprehensive study of wool fibers is essential in establishing structure-property relationships and quantifying how composition, microstructure, and mechanical properties impact fiber interaction with human skin and haptic feel. This will in turn enable the development of standardized human-subject-free test methods for fiber scratchiness and will guide the design of new fibers and textiles for the apparel and medical industries.
Nature has evolved the ability to create large and complex molecules in which the precise control over both the sequence and spatial arrangement of the atoms is critical to their performance. The 3-dimensional control over the arrangement of bonds is as important to the function and behavior of molecules as any other factor and is critical to the structure-function relationships that occur within biological systems. Specifically, the advantageous mechanical properties of most commodity plastics are intimately connected to their low glass transition temperature and crystallinity, the latter of which can be modulated by stereochimistry of the polymer. For polypropylene (PP), stereochimistry control of the pendant methyl group on the polymer backbone (isotactic, or alternating bond orientation) contributes to its useful properties. While this concept has similarly been leveraged to improve the thermomechanical properties (i.e. increase the melting temperature or tensile modulus) of biopolymers, (e.g. poly(lactic acid) (PLA)) these materials are incessantly plagued by brittleness, lacking the flexibility and toughness of petro plastics. By controlling the stereochimistry of polymer backbones, much more significant changes to polymer mechanics can be achieved. The most well known example is stereochimic differences between natural rubber (poly(cis-isoprene)) and gutta percha (poly(trans-isoprene)), which lead to a complete change in physical properties from an elastomeric to plastic material. Despite this being well known, the state of the are in synthesis has not made it possible to readily exploit this effect more widely. To this end, our work has focused on developing polymerization methods that can result in materials in which the stereochimistry can be used to leverage a wide range of materials properties from thermomechanical to degradation, in both linear polymers and networks, with a high level of tuneability.

Leveraging Stereochimistry to Advance The Design and Degradation of Sustainable Polymeric Materials Andrew P. Dove; University of Birmingham, United Kingdom

Current strategies to reduce CO2 emissions are insufficient—both point-source and direct-air-capture (DAC) must be considered to mitigate excessive atmospheric CO2 concentrations. Given the urgency of climate change issues and the immense challenges of developing viable methodologies for CO2 conversion, we posit that understanding structure-property relationships of organic/inorganic molecular reactivity across multiple length scales will lead to the evolution of remarkably efficient transformations of CO2 and revolutionize chemistries to control the fate of this greenhouse gas. Thus, we sought to investigate families of superbases (SBs) that serve as CO2 mitigating agents. This talk will focus on describing the wide-scope reactivity of a family of modular SBs that can be exploited in a variety of chemical transformations of CO2 from dilute and pure gaseous sources as well as polymerizations. We found that the SBs can form high-value products. A series of partially bio-based spiro polycyclocacetas were synthesized using bio-renewable feedstocks, such as vanillin and its derivative syringaldehyde, along with pentaerythitol and commercially available co-monomers including 4,4'-difluorobenzophenone and bis(4-fluorophenyl) sulfone. These spiro polycyclocacetas displayed high thermal stabilities (degradation temperatures in the range of 343 – 370 °C, as quantified by 5% mass loss) and glass transition temperatures (in the range of 179 – 243 °C). Importantly, these polymers were effectively degraded to small molecules under acid-catalyzed hydrolytic conditions in less than 7 h. The kinetics of hydrolytic degradation was quantified through in situ NMR analyses.

Covalent adaptable networks (CANs), sometimes called vitrimers, offer promise for overcoming long-standing recycling and polymer circularity issues associated with conventional, permanently crosslinked thermosets that cannot be recycled for high-value use. It is also vital to demonstrate that properties of reproducible networks can be optimized to meet the demands for high-performance materials. For example, it is important that the dynamic covalent bonds in CANS are robust at use conditions, including elevated temperatures where creep needs to be minimal, while ensuring reprocessability at yet higher temperatures that are well below conditions where degradation occurs. We have designed several classes of CANs that show that such performance demands can be met while contributing to polymer circularity and sustainability. Additionally, in many cases, such CANs can be derived from biobased or waste starting materials. We will provide examples ranging from non-isocyanate polyurethane networks, including both polyhydroxurethane networks and non-isocyanate polythiolurethane networks, that exhibit non-catalyzed dynamic chemistry of a dual associative and dissociative nature and can be made from a variety of biobased sources. We will also provide examples in which some polyolefins, including thermoplastic polyethylene, can be upcycled into CANs via simple one-step reactive processing with a radical initiator and an appropriate covalent crosslinker with dynamic chemistry that is strictly dissociative in nature, e.g. a dialkylamino disulfide or other disulfide-based crosslinker. For example, waste thermoplastic polyethylene can be can be transformed into crosslinked polyethylene exhibiting robust properties and reprocessability. Additionally, because of the dissociative nature of the dynamic chemistry, these CANs offer the possibility of being processed by conventional, continuous melt-processing methods such as melt extrusion.

3:00 PM BREAK

Depolymerizable and Recyclable Luminescent Polymers Wei Liu1,2, Yukun Wu1,3, Jianguo Mei1,2, Sihong Wang1,2,1 and Jie Xu1,2; 1Argonne National Laboratory, United States; 2The University of Chicago, United States; 3Purdue University, United States

3:30 PM MF03.10.05

Dissolupolymerisable and Recyclable Luminescent Polymers Jason Y. Lim and Derrick Fam; Institute of Materials Research and Engineering (IMRE), Singapore

4:00 PM MF03.10.07

A General Strategy for Upcycling Plastic Commodity Waste to Self-Healable and Fully-Recyclable Materials Hauix Xu; University of Southern California, United States

The rapid expansion of the plastic industry has led to significant environmental and ecological harm due to plastic waste. Considering the drawbacks of traditional recycling methods, as most of the plastic wastes are down-cycled into low-value products such as garden furniture or pots, upcycling has garnered increased attention for transforming plastic waste into high-value products. This study presents a general strategy to upcycle commodity plastic waste to a class of fully recyclable and self-healable polymers. Coumarin and its derivatives are light-sensitive and can self-react when triggered by ultraviolet (UV) light at varying wavelengths. Upon exposure to 365 nm UV light, coumarin undergoes dimerization and forms a cyclobutene ring. Conversely, exposure to 254 nm UV light results in the cleavage of the ring and a reversion to its original state. We demonstrate that after embedding the coumarin groups into our polymer matrix, thanks to...
The photodegradation and photoelectronoc occurring on the coumarin group C=C bonds under 254 nm and 365 nm UV light, our materials exhibit four distinct properties: light-tunable mechanics, reprocessing ability, light-activated self-healing, and recyclability. We show our strategy is universal to various commodity plastic wastes, such as PS, PP, PET, and PE. This transition from plastic waste to multifunctional materials offers a new strategy for upcycling various plastic wastes into a category of high-value products.

4:15 PM MF03.10.08
Effects of Nickel on The Acceleration of Radiation-Induced Decomposition of Polytetrafluoroethylene (PTFE) Hao Yu Akira Iseki, Kimio Yoshimura, Akihiko Hiroki and Yasunari Maekawa; National Institutes for Quantum Science and Technology (QST), Japan

Introduction
High-performance plastics, such as PTFE (Polytetrafluoroethylene) and PEEK (Polyether ether ketone), have extensive applications in various industries. However, recycling and reusing these plastics pose challenges due to their exceptional heat resistance. This study presents our findings on a new method to reduce the decomposition temperature of PTFE. The method involves utilizing the catalytic effects of Nickel (Ni) for the radiation-induced decomposition of PTFE.

Materials and Methods
PTFE (Mw=5,000–20,000) and Ni/AlO2/SiO2 powders were purchased and used. The PTFE or the mixture of PTFE with Ni was irradiated with an electron beam under air or argon gas. The maximum dose of the electron beam was 15 MGy, and the dose rate was measured using a cellulose triacetate (CTA) film dosimeter. Mixtures containing different mixing ratios of PTFE and Ni catalyst were prepared to investigate the impact of proportion of catalyst. The mixing time was varied before and after irradiation to observe the sequential effects of irradiation and catalyst. To perform quantitative analysis, the weight change of samples resulting from radiation was measured, and the solid residue remaining after irradiation was collected. The thermal decomposition of the samples with and without irradiation was measured using thermogravimetric differential thermal analysis (TG-DTA) from room temperature to 1000°C under argon gas. The gaseous products via thermal treatment were collected and introduced into a gas chromatograph-mass spectrometer (GC-MS) for their identification. Furthermore, the chemical groups were measured using Fourier transform infrared spectroscopy (FT-IR), the crystal structure changes were measured using X-ray Powder Diffraction (XRD), and the binding energy changes were measured using X-ray Photoelectron Spectroscopy (XPS), as a function of irradiation and temperature.

Results and Discussion
Both the use of Ni catalyst and irradiation accelerated the reduction of the decomposition temperature of PTFE. Increasing the proportion of Ni catalyst and irradiation dose had a positive effect on decomposition. In addition, the synergistic effect of Ni catalyst and irradiation had the greatest impact on the decomposition. In the presence of oxygen, when mixing was followed by irradiation, the 5% weight loss temperature of the solid residue is 103°C, which is 49°C lower than the pyrolysis temperature of pure PTFE (522°C). Under 15 MGy irradiation, approximately 40% of the PTFE equivalent experienced weight loss below 200°C. During the irradiation, several changes were observed in the PTFE. In PTFE alone, the presence of carbonyl groups (–CO–) was confirmed, and GC-MS analysis indicated the occurrence of oxidation (C2F4 to C2F6O). In the oxidative substances responsible for the decomposition of irradiated PTFE at lower temperatures. There were no changes in crystal structure or binding energy (C 1s, F 1s). In the presence of Ni, the presence of –CO– was also confirmed, but the gaseous products detected in GC-MS decomposed into smaller fragments (CF2O to CO2/COF).

Additionally, new crystalline structures were confirmed in the irradiation process involving oxygen. The binding energy of C 1s, Ni 2p3/2 remained unchanged, but a new peak of F 1s (F-, 685 eV) was confirmed, indicating the production of F- from the original PTFE (p(CF2-CF2), 689 eV) during irradiation. In summary, the presence of oxygen played a crucial role in the degradation of PTFE, and we propose that Ni acts as a catalyst to accelerate the decomposition of PTFE.

Acknowledgment: This work was supported by JST, CREST Grant Number JPMJCR21L1, Japan. The authors would also like to thank the operators of the Takasaki electron beam irradiation system for their cooperation.

4:30 PM MF03.10.09
Selective Deconstruction and Upcycling of Step-Growth Polymers Nick Galan1, Jackie Zheng1, Md Arifuzzaman2, Md Anisur Rahman1, Jeff Foster1, Bobby G. Sumpter1 and Tomonori Sato1,2, Oak Ridge National Laboratory, United States; 2The University of Tennessee, Knoxville, United States

Engineering plastics based on step-growth polymerization such as poly(ethylene terephthalate) (PET), polynamides (PA), polyurethanes (PU), and polycarbonate (PC) comprise ~30% of the global plastic production. The catalytic deconstruction is one of the major paths for chemical recycling of step-growth polymers. Although there has been progress on their chemical recycling especially PET, most step-growth polymers are not recycled because of the difficulty of depolymerization to pure building blocks especially from mixed state in an energy efficient manner. Here, we have developed a targeted organocatalyst to enable low energy depolymerization pathways for step-growth polymers. Our catalyst allows glycolysis of PET, PA, PU, PC and their multiple mixture at moderate temperature with high yield. A wide range of post-consumer plastics waste, such as bottles, packaging, foam, carpet, etc. is readily deconstructed into monomers with high efficiency. The Life Cycle Assessment indicates that the reproduction of various engineering plastics from the deconstructed monomers will result in a significant reduction in greenhouse gas emissions (82-95% reduction) and energy input (68-94% reduction). Furthermore, we have developed a path to deconstruct those step-growth polymers to selective length oligomers. We have utilized those deconstructed building blocks to synthesize upcycled polymers, and the upcycled polymers can be further deconstructed to reusable building blocks. Such circular design contributes to establishing new closed-loop circularity of polymers by energy efficient selective deconstruction and upcycling of various engineering plastics.

4:45 PM MF03.10.10
Itonacic-Copolyesters as Potential Replacement of Epoxy-Based Coatings in Metallic Food Contact Materials Jose Hector Ramirez Suarez and Julie Goddard; Cornell University, United States

Replacement of Bisphenol A (BPA) based food coatings has been of industrial interest for decades due to health concerns and consumer perception. Although polyester and acrylic-based resins have been introduced into the market as potential replacements, matching the chemical, mechanical, and thermal properties of BPA-based resins remain a challenge. Specifically, their remarkable performance in delaying the onset of corrosion in metal packaging, which protects the safety and quality of foods and beverages during their shelf-life. Unsataturated polyesters (UPs) are versatile, low molecular-weight thermoplastics that can undergo cross-linking reactions to yield thermosets or be functionalized to tailor their properties for potential use as additives in coating formulations. In an effort to improve the sustainability of petroleum-based UP thermosets, the incorporation of biomass-derived molecules in UPs, such as itaconic acid derivatives or short-chain diols, has been explored. However, the thermal and mechanical properties of the resulting UPs is often negatively affected, limiting their potential use as coatings.

In this research, we present the synthesis of novel itaconic-based unsaturated copolyesters with improved mechanical and thermal properties by copolymerization with monomers of high structural rigidity (i.e. cyclic, substituted, or aromatic). We found that the nature of the catalyst played a role in favoring side reactions during the polycondensation affecting the structure and size of synthesized UPs. Zinc acetate as the melt-polymerization catalyst, yielded UPs with molar mass in the range of 3,000 to 4,000 g/mol and controlled and narrower molar-mass distributions (PDI < 2) in comparison to dibutyltin oxide (PDI > 10). Additionally, the backbone-integrated unsaturated moieties and the hydroxy chain-end groups were better preserved for post-functionalization. Cross-linking of UPs was performed with branched thiol-functionalized or biomass-derived cyclic vinyl monomers by UV-initiated radical polymerization. Thiol-functionalized monomers yielded thermosets with a glass transition temperature of up to 60°C, due to the high degree of cross-linking promoted by the introduction of branching to the linear UPs and high efficiency of thiol-ene reactions. Further, only UPs containing branched or cyclic diols were able to form flexible, thin, free-standing films (15 – 20 μm) while formulations containing aliphatic diols yielded brittle films.

Ongoing work involves the characterization of tensile properties and protective performance against corrosion over time in saline and alcoholic standard solutions by electrochemical characterization to assess their potential use as coatings. Upon completion of this work, an industrially attractive and scalable UP-based thermostet capable of enhanced corrosion protection is developed as an alternative to epoxy based resins. This research addresses the need for high-performance and environmentally sustainable materials for the food packaging industry in their quest to maintain the quality and safety of foods and beverages.
Scalable Interfacial Polymerization of Thermally Processable Biodegradable Polymers

Sara Branzovský and Cecile Chazot; Northwestern University, United States

Aliphatic-aromatic polymers (AAPEs) have gained traction as sustainable alternatives to polyethylene-based packaging due to their superior biodegradability and comparable mechanical properties. Unfortunately, the large-scale deployment of these polymers remains limited due to manufacturing challenges such as time- and energy-consuming syntheses and difficulty with thermal processing due to depolymerization. In this work we describe the implementation of a stirred interfacial polymerization (IP) framework to enable the rapid, open-air, high-yield synthesis of AAPE with tailored chemical structures and properties. We explore the effect of reaction conditions – such as aromatic vs aliphatic character and additive concentrations – on polymer yield and thermal properties. We characterize the mechanical properties of AAPE films made via hot pressing and compare the results with state-of-the-art synthetic packaging. This IP synthesis has potential as a scalable manufacturing pathway for biodegradable polymer-based packaging with enhanced thermal processability and mechanical properties.

Water-Based Sustainable Ink Composed of Regenerated Silk Fibroin and Upconversion Nanoparticles for Printing/Painting on Arbitrary Surfaces

Hyeeun Cho, Jun Yong Ahn, Taehoon Kim, Fiorenzo Omenetto and Junyong Park; Kanoh Institute of Technology, Korea (the Republic of); Tufts University, United States

Regenerated silk fibroin derived from silkworm cocoons is considered as one of the promising sustainable materials for various fields such as biomedicine, photonics, and electronics. To date, a variety of unconventional material platforms have been demonstrated by engineering regenerated silk fibroin in various ways. In this study, we fabricate a nanocomposite composed of regenerated silk fibroin and upconversion nanoparticles (UCNPs) and demonstrate its printing/painting capabilities as an eco-friendly and biocompatible functional ink. The research is largely divided into three parts: 1) securing robust RGB emission spectra under 980 nm NIR excitation through systematic dopant control of citrate-capped hydrophilic UCNPs, which can be easily dispersed in aqueous silk fibroin solution; 2) selecting an appropriate auxiliary solvent that prevents the aggregation of silk fibroin and UCNPs to improve the room temperature storage and printability of ink; 3) expanding the color palette through mixing RGB inks and demonstrating printing/painting capabilities of the inks on arbitrary surfaces, including 3D curved substrates.

Facile Preparation of Anti-Mold Wood Fibers for Integration into Biocomposites

Yuqi Feng and Pervin Lau; City University of Hong Kong, Hong Kong

Public awareness of energy and climate change drives the development of energy-efficient buildings, leading to increased indoor air tightness and bio-based building materials. Wood-based materials, known for their ecological benefits, have gained attention in green building practices. Despite the energy-saving benefits of wood fibers, their susceptibility to mold contamination due to high moisture absorption is often overlooked. This challenges indoor air quality and human health, particularly in warm and humid climates and poorly ventilated buildings. While various coating strategies have been developed to protect wood surfaces hydrophobic and mold-resistant, coating durability issues remain. Therefore, this study aims to modify wood fibers for creating wood fiber composites with inherent anti-mold properties. Wood fibers with mold-resistant behavior are prepared by in-situ growth of Zn-containing layered double hydroxides combined with a hydrophobic modification process by stearic acid. The mechanisms of antifungal action of the treatments on fibers and mold cells are understood through molecular dynamics simulations. Mold growth on the composites of untreated and treated wood fibers is then investigated by laboratory tests. The effects of anti-mold coating on the water resistance, dimensional stability, and mechanical properties of the composites are also evaluated. The mold-resistant biocomposites developed here provide a viable candidate for indoor and outdoor construction materials, with great potential for application in green building designs that advocate the healthy and harmonious coexistence of humans and the environment.

Understanding the Influence of Morphology and Chemical Compositions of Algae on the Hydration Reactions of Portland Cement

Meng-Yen Lin, Brandon T. Lou, Paul Grandgeorge, Li-Yuan Lin and Eleftheria Roumeli; University of Washington, United States

Cement accounts for up to 10% of global carbon dioxide emissions and has become one of the targets of recent decarbonization efforts. Algae is an abundant and easy-to-cultivate biomass, which can sequester carbon during growth and can be used to replace cement. Recently, we showed that certain microalgae hinder the primary hydration reaction of ordinary Portland cement at high concentrations, significantly hampering mechanical performance. To optimize the structural performance of algae-cement composites, here we focus on the effects of morphology and chemical compositions of algal biomatters on cement hydration. Applying a bottom-up approach, we first study the effects of algae-related biopolymer building blocks, including proteins, carbohydrates, and lipids, on the resulting hydration products through thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM), and their relationships with the composites' compressive strength. To further characterize the influence of particle size, bonding structure, and chemical compositions of the algae on the composites, we then treat the microalgae and macromolecules through grinding, hot-pressing, and bioparticle extraction. SEM is used to investigate the effects of particle morphology on the bonding interfaces and distribution in the cement matrix. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) are used to characterize the bonding environment and chemical compositions of the biomass, which are correlated with the hydration products in the algae-cement composites and their contribution to mechanical properties. We show that using specific pretreatment for both algal biomatters, the strength of composites can be improved by up to twofold compared to the unprocessed algal biomatter. The proposed processing methods allow for higher algae replacement content, effectively reducing the environmental impact of the cement binder.
unlabeled fibers was developed based on tomograph histograms. To optimize the segmentation process, we embedded the handsheets in oil to eliminate the signals associated with air (background signal). After image processing, we successfully visualized the spatially and randomly oriented fibers within the handsheet plane at diverse loadings of iron-labeled fibers. Furthermore, we investigated the impact on mechanical properties of randomly oriented iron-labeled fibers in handsheets in comparison to unlabeled fibers to delineate the limitations of labeling fibers with iron nanoparticles as contrast agent for X-ray tomography.

This study not only provides valuable insights into the role of the large fraction of pulp fibers in reinforcing papers but also sheds light on how different kinds of pulp fibers are distributed in paper products and how the formation of a network impacts mechanical properties. A better understanding of the 3D distribution and network formation of fibers can be leveraged to support the development of high-value products based on high-quality mechanical pulp, aligning with opportunities toward sustainable and bio-based materials for the papermaking industry.

5:00 PM MF03.11.10
A Concept of Haze Matching for Cloaking of Bulk Anticounterfeiting Patterns Made of Silk Fibroin-Based Upconversion Nanocomposites
Seokhan Yun1, Taehoon Kim2, Fiorenzo Omenetto2 and Junyong Park1. 1Kumoh National Institute of Technology, Korea (the Republic of); 2Tufts University, United States

Since 2010, anticounterfeiting technology utilizing NaYF4-based upconversion nanoparticles (UCNPs), which can emit visible light under invisible near-infrared (NIR) excitation, has been extensively studied. Typically, upconversion patterns and codes are realized by printing viscous nanocomposites composed of a polymer matrix and UCNPs. There are two technical issues: the first is to select a sustainable and environmentally friendly polymer matrix, and the second is to increase the concentration of UCNPs doped in the polymer matrix, considering the extremely low quantum yield of UCNPs. However, when a large amount of UCNPs are concentrated in a unit volume, scattering by nanoparticles increases, creating an opaque pattern. Because bulk patterns are intuitively identifiable, codes can be generated based solely on differences in the colors emitted by NIR excitation. One could consider making the pattern transparent to a level similar to the background by extremely reducing the concentration of UCNPs, but this would exponentially increase the output of the 980 nm light required for decoding. As alternatives, invisible UCNP-doped microbarcodes or microprisms have been proposed, but their processing involves expensive lithography and still requires inconvenient microscopy systems for decoding. Therefore, the practicality of UCNP-based anticounterfeiting platforms in actual fields outside the laboratory is very limited.

In this study, we propose for the first time the concept of haze matching, a convenient way to conceal bulk anticounterfeiting patterns by making the background opaque to a similar level as the pattern. This approach has the advantage of being able to easily control the optical characteristics of the background regardless of the haze level of the pattern, allowing the use of high-concentration UCNPs with bright upconversion emission. Regenerated silk fibroin extracted from silkworm cocoons was used as a sustainable and eco-friendly medium to disperse UCNPs. Dopant-free NaYF4 nanoparticles synthesized under the same hydrothermal conditions were prepared as a medium for haze matching. Based on optical analysis of the transmittance and haze at various nanoparticle concentrations, we established the optimal conditions for the background to completely conceal the bulk pattern with extremely high concentrations of UCNPs. A variety of bulk codes and tags that appear selectively only under NIR excitation have been successfully demonstrated through printing/photographing techniques. In particular, opaque anticounterfeiting films containing haze-matched codes and tags were more difficult to identify on white surfaces such as paper or ceramics.

The strategy for upgrading the sustainable nanocomposite-based anticounterfeiting platform proposed in this study will provide new options for the practical use of UCNPs.

5:00 PM MF03.11.11
Vat Photopolymerization-Based Multi-Material 3D Printing of Overhangs with Highly Removable and Recyclable Thiol-ene Photopolymer Supports
Tengteng Tang, Prem Nawab, Parimal Prabhudesai, Saleh Alfarhan, Ivan Pesquesa, Kailong Jin and Xiaojia Li; Arizona State University, United States

Vat photopolymerization (VPP) based 3D Printing technology boasts the capability to print 3D structure with remarkable precision and rapidity. In the fabrication of complex structures beyond traditional capabilities, extensible additional support structures are often essential for creating overhanging and free-hanging features. Yet, these internal supports pose challenges as they are not directly removable, necessitating time-consuming manual removal and potentially causing unintended damage and surface imperfections. While specific materials like NaOH-soluble substances and wax have been employed for creating removable supports, these solutions are limited to specific printable materials and often result in considerable waste during the removal process. The current predicament lies in the fact that traditional vat photopolymerization 3D printing of overhangs employs a photosensitive liquid resin, which forms a permanently crosslinked polymer. This invariably leads to disposal of body and especially support structure after its usage due to the material’s non-recyclable nature.

To counter these drawbacks, this study leverages the properties of crosslinked thiol-ene photopolymer, such as polybutadiene and polyisoprene, which are renowned for their robust structures and excellent in-plane mechanical characteristic. The innovation lies in the utilization of liquid polydiene elastomer as a building block in VPP-based 3D printing, a technique yet to be thoroughly explored. The research focuses on creating a chemically recyclable crosslinked polydiene elastomeric liquid resin, capable of undergoing photoinitiated thiol-ene click reactions with commercially available materials, apt for VPP-based 3D printing. The approach involves using liquid polysulfides with photoactive thiol end groups and dynamic disulfide bonds, which react with polydiene’s carbon-carbon double bonds (ene groups) through photo-crosslinking. The internal disulfide bonds in the resulting crosslinked polydiene elastomers allow for base-catalyzed thiol-disulfide exchange reactions, leading to the decrosslinking or degradation into photoactive thiol oligomers. Combining conventional permanently crosslinked resin with developed recyclable resin allows for the printing of complex multi-material structures. Subsequent processing to recycle thiol-ene photopolymers can yield intricate overhangs, such as microfluidic channels, spinning tops, and interlocked Da Vinci drones. In addition, the impact of surface to volume ratio and crosslinking rate under grayscale projection on the recycling rate is extensively investigated. The optimized porous support structures exhibit properties that are highly removable and recyclable. By demonstrating this scalable method, the study opens up new avenues for fabricating overhangs with easily removable and highly recyclable elastomeric resins via VPP, maintaining material properties across multiple recycling. This development not only offers a superior alternative to current casting/molding manufacturing methods for elastomeric materials but also paves the way for more sustainable and environmentally friendly practices in 3D printing technologies.

5:00 PM MF03.11.12
Bio-Based Epoxy Resin via Algae Curing Agent
Keshan Lighty; North Carolina A&T State University, United States

A growing number of manufacturers are looking for environmentally friendly substitutes for conventional methods in order to cut down on carbon emissions. This research presents a viable path toward environmentally friendly manufacturing methods by investigating the creative use of bio-curing chemicals produced from algae as a novel technique to curing epoxy resin.

Given its abundance and quick development, algae provides a sustainable and renewable supply for bio-curing agents. The purpose of the study is to determine whether chemicals produced from algae may successfully replace traditional curing agents in epoxy resin formulations. Algae-based curing agents have the potential to perform on par with or even better than synthetic counterparts when their mechanical attributes, thermal stability, and curing kinetics are examined.

The use of curing agents generated from algae in epoxy resin formulations not only adds biodegradability and reduces toxicity, but also lessens the environmental impact of traditional curing agents. This move to bio-curing agents is consistent with the global movement toward a circular economy and more environmentally friendly industrial practices.

This research has important economic ramifications in addition to environmental benefits. The cultivation and processing of algae has the potential to generate additional revenue streams for bio-based material enterprises, hence promoting job development and portfolio diversification. Furthermore, the manufacturing industry benefits from increased resource security and resilience because of the decreased reliance on curing agents sourced from fossil fuels.

By highlighting the crucial role that algae play in changing material science and advancing a more robust and sustainable future, this research provides the foundation for a paradigm change in the manufacturing sector.

5:00 PM MF03.11.13
Automotive Plastics Recycling through Molecular Recycling Technologies: Technology Status, Material Advances and Challenges
Mahshid Mokhtarian1,2, Gary Hawkins3 and Hendrik Mainka2; 1The University of Tennessee, United States; 2Volkswagen Group of America, United States; 3Eastman Chemical Company, United States

The urgent need to address the global plastic waste crisis and its impact on climate change has created a demand for materials revolution. Volkswagen Group of America Inc. (VWGoA) in collaboration with Eastman Chemical Company, is taking the lead in driving circular economy solutions for plastics through groundbreaking molecular recycling technologies. This innovative approach enables the conversion of difficult-to-recycle plastics from the automotive industry into raw materials for producing new specialty plastics and fibers, while maintaining their quality and performance. Our primary focus lies in dealing with a wide range of plastic waste streams, including mixed plastics, colored plastic materials, post-consumer car carpets, and textiles. The collaboration between VWGoA and Eastman Chemical Company not only brings innovation but also addresses recycling challenges associated with these difficult materials, while providing environmental and sustainability metrics for the recycling process. The knowledge gained from this project contributes to global waste management efforts and fosters a cleaner and more sustainable future. With the molecular recycling process enabling the synthesis of various polymer types, it presents a direct alternative to virgin fossil-based plastics. This is particularly
Dye Emission Solvatochromism to Monitor Local Environment in Polyhydroxybutyrate Nanoparticles

Gareth Redmond
University College Dublin, Ireland

In this work, the use of Nile red as a solvatochromatic probe of biopolymer nano-environments was investigated. Firstly, relationships between measured dye fluorescence spectral maxima and solvatochromatic shifts were identified. Photoluminescence decay data for aqueous dispersions of PHB/NR NPs were also acquired and fitted by a double exponential function, suggesting that the NR dye molecules were located in regions close to the PVA surfactant stabiliser and the surrounding aqueous medium. The data also indicated that for NPs prepared with 5 and 8 min sonication, the dye molecules were more exposed to H-bonding effects. Statistical analysis of emission maxima obtained for particles prepared with different sonication conditions showed a clear trend of shifting NR nano-environment character, from higher to lower polarity/non-HBD type, with increasing sonication time from 2 min to 5 or 8 min. The mean extracted value for the local dielectric constant ε of the 5/8 min PHB/NR NPs is estimated as 8.5 ± 1.5, slightly larger than reported bulk values, suggesting that the dielectric response of these nanoparticles reflects contributions from the local environment.

Curdlan Hydrogels as Sustainable Scaffolds for Cell-Based Meat Production

Elizabeth Dobrzanski

Curdlan, a microbial polysaccharide, was used as the gelling agent, combined with three different types of proteins, including hemp, alfalfa, and black soldier fly. To characterize the scaffold and assess the mechanical and chemical properties of the scaffold, FTIR, differential scanning calorimetry (DSC), and rheology tests were selected to be performed before and after seeding cells on biomaterials. Additionally, patterned biomimics were developed to investigate the possibility of enhancing cell adhesion and differentiation.

Thermoplastic Starch Reinforced with Bamboo Fibers: A Biodegradable Composite Alternative

Nicolas A. Maricato, Vagner R. de Mendonça and Tamires d. Nossa
Federal Institute of Education, Science and Technology of Sao Paulo - IFSP, Brazil

Due to the large consumption of plastics and their frequent use in disposable applications, it is essential to direct studies toward the development of alternative materials that are biodegradable or come from renewable sources in order to reduce the impact generated by the disposal of these materials on the environment. This study focused on the production of a sustainable biocomposite, produced from a renewable and biodegradable source, using corn starch as a thermoplastic matrix, in which glycerol, a residue from the biodiesel industry, was used as a plasticizing agent. Different production parameters were studied through reactive extrusion in order to produce homogeneous filaments with a thermoplastic starch matrix (TPS), in the proportion 70:30 (% starch: % glycerol), reinforced with bamboo fibers with different filler addition proportions between 5%, 10%, 15%, 20% and 30% by mass. To incorporate the fibers, an alkaline treatment was carried out with sodium hydroxide (5% NaOH) in order to make the composite interface compatible. It was possible to verify an improvement in the mechanical properties of the formulation with the addition of 20% by mass of coconut oil, with an increase of approximately 37.5% in the tensile strength limit and 32.1% in the elongation at break and a reduction in moisture absorption.

Versatile Method to Produce Wood Particle Foams for Building Insulation

Elizabeth Dobrzanski1,1, Elisa Ferreira2,1, Praphulla Triwary3, Prashant Agrawal1, Richard Chen1 and Emily D. Cranston1,1; 1The University of British Columbia, Canada; 2Brazilian Nanotechnology National Laboratory, Brazil; 3Plantae Bioplastics Inc., Canada

Lightweight foams are excellent thermal insulators due to their structure, which traps layers of air pockets and results in low thermal conductivity. Modern buildings overwhelmingly use insulating foams derived from petrochemical sources, which not only contribute greenhouse gases during manufacturing but also end up in a landfill at the end of their life. Alternatives to petrochemical-based foams, such as mineral wool, have been linked to health concerns. As a result of these environmental and health concerns, the appetite for bio-based and environmentally-
Materials that are truly sustainable must be considered holistically, from their feedstock source to their manufacturing process to their end-of-life stage. Some examples of bio-based insulative foams are cellulose- and pulp-based foams, which are moving towards being fully sustainable but still require relatively high amounts of processing energy to transform them from their raw feedstock form. One feedstock source that is often overlooked is forest residues, materials generated by the forestry industry that have little to no economic value and includes bark, dead trees, off-cuts, and small-diameter trees. Due to their mechanical properties, they are often used for low-value products [2].

We previously showed that we can circumvent the poor macro-scale mechanical properties of forest residue wood by milling the feedstock to < 1 mm and recombining the wood particles as a lightweight, high bio-based content foam [3]. This previous work focused on pine beetle-killed wood, which refers to trees that have been killed by mountain pine beetles and may contribute to high-intensity fires if left in the forest [4]. To produce these foams, waste wood particles are foamed in water with surfactant and a water-soluble polymer binder and then oven dried [5], a relatively facile and low-energy method of solid foam production. The resulting foams have mechanical (density ca. 0.12 g cm\(^{-3}\)) and thermal (thermal conductivity ca. 0.042 W m\(^{-1}\) K\(^{-1}\)) properties that are competitive with conventional petrochemical-based foams. The promising performance of our foams is attributed to their low density and hierarchical pore structure consisting of polyhedral cells templated by air bubbles and natural honeycomb pores from the wood cell walls [3]. The end-of-life stage is also considered, as the foams are able to be re-wetted, re-foamed, and re-dried while maintaining their original properties.

Our current research pushes this method further by exploring different waste wood feedstocks, different particle sizes, and the replacement of our surfactant and polymer binder with bio-based materials alternatives. Verifying the potential of alternative waste wood feedstock and particle sizes is important for scalability and adaptability, while alternative surfactants and binders is important to create a fully bio-based product with no negative environmental impact. In most cases the thermal and mechanical properties of these alternative foams are competitive and have the potential to replace petrochemical-based foams. In alternative foams that do not meet ASTM or building standards may still be able to pass if the milling procedure is tweaked to allow for higher aspect ratio particles, which may result in more conginging of the wood particles and binder and produce a more cohesive solid foam structure.

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### 8:45 AM *MF03.12.01*

**Bio-Inspired Biomimeralized Bacterial Cellulose Composite Material**

Marie-Eve Aubin-Tam, TU Delft, Netherlands

There is an important need for sustainable structural materials that combine high mechanical strength, possibility of control over 3D shape, and ease in upsampling material production. I will present how we use microorganisms to fabricate inorganic-biopolymer composite materials that show a layered structure reminiscent of tough biomaterials in nature (nacre, bone, dentin). The inorganic component consists of calcium carbonate (CaCO\(_3\)) crystals formed by *Sporosarcina pasteurii* bacteria, and the organic components include bacterial cellulose and polyglutamic acid, produced by the bacteria *Glucosacetobacter hansenii* and *Bacillus paralicheniformis*, respectively. This ‘bacterial nacre’ reaches and exceeds the toughness of natural nacre, while being fabricated in an ecological, economical, and simple manner using bacteria. The 3D shape can be controlled via molding or direct ink writing. The resulting composite materials show promising applications as light weight structural materials.

### 9:15 AM *MF03.12.02*

**MICP Biomimeralization and Biotic Additive Manufacturing Toward The Design of Strong Bioocomposites**

Subrina Shen\(^1,2\), Ethan Viles\(^2\), Chelsea Heveran\(^2\) and Markus Buehler\(^1,3\), Massachusetts Institute of Technology, United States; \(^2\)Montana State University, United States

Microbially-induced calcium carbonate precipitation (MICP) has been explored as a more sustainable alternative for producing concrete-like load-bearing materials. Concurrently, additive manufacturing of bioceramic composites enables the production of complex hierarchical materials with minimally refined organic feedstocks. Such materials can be designed to be functional and highly biodegradable, however organic materials without a mineral phase are limited in mechanical strength, and material longevity is necessary for some applications. Here we explore MICP biomimeralization of additively manufactured bioceramic composites, and investigate the interaction between mineral formation and bio-composite structure at multiple scales. We characterize the resulting materials and consider how MICP biomimeralization and additive manufacturing can be used to design for strong and durable bio-composite materials.

### 9:30 AM *MF03.12.04*

**Decoating the Effects of Chemical Composition and Structural Confinement of Algal Biomatter on the Hydration Reactions of Portland Cement**

Meng-Yen Lin, Brandon T. Lou, Paul Grandgeorge, Li-Yuan Lin and Eleftheria Roumeli, University of Washington, United States

Decarboxylation of cementitious materials, which contributes to 10% global carbon emissions, is one of the primary targets to achieve carbon net zero by 2050. Utilizing the abundance, easy cultivation and carbon-sequestering ability of algal biomatters to reduce cement usage has received rising attention. We recently reported that certain algal strains in the unprocessed form hinder the hydration reactions of ordinary Portland cement, preventing the application of replacement at high algal content. Here, to understand the interactions between the algal biomatters and cement further, we aim to deconvolute the effects of chemical composition and structural confinement of algal biomatters on the performance of algal-cement composites. We first study the influence of algae-related biopolymers, including carbohydrates, lipids, and proteins, on the resulting hydration products using thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM), and their contribution to composites’ compressive strength. We then apply pretreatments, involving grinding, self-bonding induced by heat and pressure, and biopolymer extraction, to the macro- and microalgal respectively to investigate the impact of particle size, bonding structure, and chemical composition on the algal-cement interactions. The effects of varying particle size and morphology on the bonding interfaces and distribution in cement matrix are evaluated by SEM. The modified bonding environment and chemical composition of biomass are measured with Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), and then correlated with the hydration products and mechanical properties of the algae-cement composites. Compared to the unprocessed algal biomass, we significantly improve the strength of composites by twofold using specific pretreatment for both algal biomatters. The proposed processing method and mechanisms enable higher algal replacement in cement with low energy trade-off, showing great potential for reducing cement usage and carbon footprint.
Selective Mechanical Deconstruction of Multilayer Film Interfaces  
Naomi Deneke, Natalie Stinglein and Blair K. Brettmann; Georgia Institute of Technology, United States

Studies have investigated the use of mechanically heterogeneous interfaces having compliant and rigid components for control of adhesion strength. From Kirigami-inspired tapes to composite micropillars, a similar fashion, mechanically heterogeneous interfaces can be used to trigger delamination events due to localization of stress at the rigid-soft interface. This is especially useful for improving the circularity of multilayer films, which are difficult to recycle due to their multi-material chemistry and use of tie layer adhesives that prevent facile separation of the layers. I will present a material design that utilizes mechanically heterogeneous interfaces that when coupled with a mechanical trigger, selectively deconstructs a multilayer film. Rigid silica microparticles are placed at the tie layer (polyethylene acrylic acid (PEAA)) and aluminum foil interface of a tri-layer film comprised of polycarbonate, PEAA, and aluminum foil. A high intensity ultrasound pulse is sent through the sample, taking care to select a wavelength and voltage that will generate a pressure wave capable of generating significant mechanical stresses at the interfaces. Delamination of the foil layer was observed when 5 μm size particles were positioned at the interface and subjected to an ultrasound pulse, while no delamination was observed if no particles were used, suggesting that interfacial patterning with mechanically heterogeneous particles assists in delamination of the layers. Additionally, particle size, density, and location of within the bulk of the material play a significant role in the delamination mechanism. In this work, we design our multilayer materials with end-of-life in mind in order to improve recovery and reuse of layers used in multilayer films.

Biowaste Enabled Porous Carbon towards Ultrahigh Capacitance for Energy Storage  
Yingchao Yang; University of Missouri, United States

Lignin is the second most abundant biopolymer and the most abundant aromatic-containing polymer in nature. Typically, lignin accounts for 15–30% of plants and serves as an adhesive by forming a lignin-carbohydrate complex to bind cellulose and hemicellulose together. Lignin is a waste product in the production of paper or chemicals (e.g. ethanol) from biomass. If not removed, the lignin could cause the paper-derived wood pulp to weaken and discolor rapidly. Valorization of useless lignin to high value-added materials for advanced applications would help address the environmentally detrimental biowaste and satisfy the societal need. To date, lignin has been used as a functional component in polymer synthesis. For example, polyhydroxylkanoate (PHA)/lignin shows better microbial resistance than PHA alone due to the formation of strong hydrogen bonds. Lignin blended polyactic acid (PLA) exhibits a great non-flammable capability. Furthermore, monomers in lignin have been used to synthesize polymers, such as polyester and polyurethanes. However, owing to the chemically recalcitrant nature, it is very challenging and costly to convert lignin into value added biopolymers. Recently, the focus on using lignin and its derivatives has been shifted to fabricating energy storage devices, including lithium-ion batteries and supercapacitors. Regarding batteries, lignin has been used by either combining it with additives and binders as electrodes for lead-acid batteries or by fabricating it into three-dimensional (3D) hierarchical porous carbon as electrodes for lithium-ion batteries. Without a doubt, the lignin-based electrode is cheaper and greener, which is a great alternative to existing electrodes for energy storage. In this presentation, a thick freestanding electrode coupled by lignin carbon and sodium without any binder and additives was fabricated demonstrating a specific area capacitance of 19.7 F cm⁻² at a current density of 1 mA cm⁻², which is the highest among to date reported freestanding lignin carbon electrodes with similar thickness. This excellent electrochemical performance originates from high electro-positivity and oxygen content promoted by the sodium. Our brings a new strategy towards lignin utilization and energy storage through coupling lignin carbon and alkali metals.

Accessibility of Ring-Closing Depolymerization for Polycarbonates with Multiple Theory Validation  
Brandy Ransom, Dmitry Zubarev, Nathan Park, James Hedrick and Kristin Schmidt;  IBM Research, United States

We present an accelerated protocol to quantitatively screen polycarbonate monomers for viability of depolymerization in solvents of varying polarities. The largest barrier in the exploration of reaction kinetics is the necessary conformational analysis to identify lowest energy paths in depolymerization, which can depend on the solvent. Tight-binding DFT allows for an accurate quantification of depolymerization barriers as compared to DFT, with an increase in speed by up to 3 orders of magnitude. By a detailed featureization of over 30 compounds we verified that depolymerization barriers are not linearly correlated to the dielectric constant of the solvent. Volume of the molecules is explicitly not correlated with the depolymerization barrier; the solvent-molecule interactions and chemistry of the molecules is extremely influential due to the over coordinated oxygens in the transition state. Though computation of the solvent-solute interaction parameter is necessary for future predictive work in kinetic barriers, even alongside the 1800 Mordred features, conformational analysis is still necessary to determine the lowest kinetic barrier across solvents. We present multiple examples of the of-lowest-barrier polycarbonates in acetonitrile, tetrahydrofuran, and toluene to highlight the large opportunity in this field for development in this multi-dimensional optimization problem. For the current available simulation and predictive models, our high-throughput protocol can evaluate the ideal solvent for 6-member polycarbonate depolymerization. From this work, further investigation into solvent-molecule interactions for quick computing features will lead towards the goal of data-driven methods for polycarbonate discovery and optimization.

Using Piezoelectricity to Make Force-Responsive Polymeric Materials  
Sarah M. Zeitler and Matthew Golder; University of Washington, United States

Stimuli-induced polymerizations continue to gain interest as synthetic polymers become more desirable for materials, industrial, and medical applications. While traditional stimuli such as heat, light, and electrochemistry have been extensively studied, they still have shortcomings such as unwanted side reactions, lack of consistent penetrability, and irregular and irreproducible equipment setups. Additionally, high energy inputs and large amount of solvent are regularly used with such stimuli. Many of these shortcomings can be overcome by using force as a stimulus for polymerization. As has been shown in organic small molecule synthesis, the use of piezoelectric nanoparticles enables force to initiate redox reactions, thus making force an even more useful, accessible, and sustainable stimulus for polymerization chemistry. Herein, we show iodonium salts can initiate free and controlled radical polymerizations of acrylates upon the introduction of various types of force in the presence of piezoelectric nanoparticles, consuming less energy and solvent than traditional polymerization methods. These salts have demonstrated to be reactive with piezoelectric nanoparticles and useful in synthesizing high molecular weight polyelectrolytes with relatively low dispersities. Furthermore, these polymerizations have been effectively carried out in both solid and solution states with multiple force sources, including ultrasound, ball milling, and vortexing. Preliminary data also indicates that force might be a new useful tool for crosslinking materials and for force-curing in additive manufacturing taking advantage of the mentioned multiple force sources. This iodonium initiated mechanoredox chemistry unlocks the possibility to better utilize force in synthesizing polymers and creating useful adaptable materials.

Acknowledgements: This work was supported by a seed grant from UW MEM-C, an NSF MRSEC funded under DMR-1719797


Recycled Polymers for a Circular Economy Model: Case Study of 3D Printed Wind Energy Generator  
Vitaliano Duttito, Kunal Bachim, Nikhil Alagandala, Louis Sponton, Sarvenaz Ghaflari, Andrew Makeev and Michael Bozlig; The University of Texas at Arlington, United States

Polymers are essential components of society as they are versatile, lightweight, and low-cost materials. On the other hand, the growing amount of plastic waste creates a global environmental concern. It is therefore necessary to investigate innovative methods and technologies to achieve a circular economy based on the recycling of plastic waste followed by a reprocessing. In this work, we focus on retaining the original mechanical properties of polymers after recycling. We produce polymer composite fibers using recycled polyethylene terephthalate water bottles or polypropylene bottle caps, reinforced with various fillers, including graphene. We conduct tensile testing and analytical studies on these composites, and eventually demonstrate their 3D
Functional inorganic electronic materials design has undergone a shift from chemical-intuition-based strategies to data-driven synthesis and simulation. Numerous machine learning models have been developed to successfully predict materials properties and generate new crystal structures. Many existing approaches, however, rely upon physical insights to construct handcrafted features (descriptors), which are not always readily available. For novel materials with sparse prior data and insufficient physical understanding, conventional machine learning models may display limited predictability and are often applied to known structure types. In this talk, I will address this challenge by introducing a new paradigm of materials taxonomy, dubbed “structure complements,” by generalizing anti-structures (or inverse structures). Materials properties depend strongly on crystal geometry but also on the distribution of charge. Thus, our algorithm for classifying materials by geometry and cation/anion decoration proves not only useful as a novel categorization scheme but also as a framework for targeted materials discovery. As a use case, I will showcase our workflow which combines structure complement analysis, a transparent machine learning model, and high throughput density functional theory (DFT) calculations to discover novel ferroelectric materials. We then examine the microscopic origins of ferroelectricity in these new quasi-2D materials and compare them to state-of-the-art compounds. Finally, I propose how this workflow is designed to be integrated into an autonomous, closed-loop materials discovery platform which integrates a unified materials database, machine learning, simulation, and high-throughput synthesis and characterization.

8:45 AM *MT01.01.02
Combining Dataset Curation and Many-Body Calculations for describing Structurally Complex 2D and Quantum Materials Felipe H. da Jornada1,2; 1Stanford University, United States; 2SLAC National Accelerator Laboratory, United States

There is considerable excitement about the family of van-de-Waals-bonded materials, such as transition metal dichalcogenides (TMDs). They not only display unique electronic and optical properties when thinned down to a monolayer, but also allow for a radical new approach to making materials by judiciously stacking individual layers. However, there is a large phase space of possible layered materials when one considers the various possible interfacial stacking angles and layer chemical compositions. Polyethylene terephthalate (PET) dominates more than 50% of the textiles market and even if there are routes to recycle it, its presence in blended fabrics mostly in combination with cotton burdens its recyclability. Most of the recycling studies investigate either the depolymerization of PET or the dissolution of cotton in order to efficiently separate them. However, in most of the cases those processes are very energy and materials intensive.

Here we present an upcycling route in one-pot valorization of blended cotton-PET fabrics without separating the two constituents. We performed a mild chemical treatment of cotton-PET (1:1) fragmented post-consumer fabrics during which PET was inert but the cotton was functionalized with carboxyl groups and partially fibrillated. The reaction resulted in high yields (>90%) and the treated textiles were further mechanically disintegrated using a facile and short process in order to enhance their fibrillation and reduce their size. The treated textile mixture was then used for film casting which were oven-dried and cut into 1x1 cm pellets suitable for extrusion taking into account the thermoplastic nature of PET. The obtained filament was used as a feedstock for the Fused Deposition Modelling (FDM) 3D printer and several composite materials for water purification and commodity applications were printed. The presence of carboxyl groups enhanced the adsorption capacity of the polycotton fibers making it possible to manufacture advanced materials from discarded garments for water purification applications. Furthermore, several fashion products with various designs were also successfully printed extending the use of the same waste feedstock in the preparation of every day polymer-based accessories.

The facile fabrication of customised waste-based pellets followed by extrusion and the successful 3D printing of the developed filaments into water purification filters and commodity accessories highlight the potential for upscaling and widespread commercialization. Compared to traditional 3D printing feedstocks, the waste-based filaments offer a cost-effective on-demand solution which can be widely accessible.
yield structural information for chemically and symmetrically dissimilar materials. In parallel, we will comment on how similar techniques can be utilized to study the structural and dynamical
properties of such water harvesting technology to capture atmospheric water is the selection of optimal adsorbent materials. To date, tens of thousands of MOFs have been reported experimentally, while
amorphous materials exhibit various characteristics that are not featured by crystals and can sometimes be tuned by their degree of disorder (DOD). Here, we report results on the structures,
mechanical and thermal properties of monolayer amorphous carbon (MAC) and monolayer amorphous boron nitride (maBN). The pertinent structures are obtained by kinetic-Monte-Carlo (kMC)
simulations separately using empirical potential [1,2] and machine learning potentials (MLP) [3]. We find that despite conducting extensive validation on the reliability of empirical
potentials for kMC simulations, and obtaining results consistent with DFT, kMC simulations using empirical potentials and more accurate MLP still yield significantly different results. Z-CRN
containing crystallite instead of compositionally disordered “pseudocrystallite” is the favored structure of both elemental MAC and binary maBN. An intuitive order parameter, namely the areal
fraction Fx occupied by crystallites within the Z-CRN, is proposed to describe the DOD. The mechanical and thermal properties of MAC and maBN were found to be solely determined by Fx and are insensitive to the sizes and arrangements of crystallite. On the other hand, about two orders of magnitudes reduction in thermal conductivity was found in monolayer carbon after amorphization. The present results demonstrate the superiority of MLP over empirical
potentials in the study of amorphous materials and reveal the relation between structures and properties in monolayer amorphous materials. References:

9:45 AM AM *MT01.01.05
Sampling Complex Energy Landscapes in Material Science Using Data-Driven Force Fields Mihai-Cosmin Marinica; Université Paris-Saclay, France
Statistical methods, such as Machine Learning (ML) trained on physical data, can be invaluable when traditional approaches are limited or when their direct application is
hampered by challenges like high computational costs. In materials science the interaction and transformation of crystallographic defects give rise to an extraordinarily diverse
range of defect morphologies [1], Additionally, accounting for chemical disorder presents another layer of complexity that is often overlooked in the emerging field of machine
learning approaches. By utilizing the recently open-sourced MiLaDy (Machine Learning Dynamics) package [2] combined with accelerated Molecular Dynamics based on the
Bayesian adaptive biasing force method [2], we aim to sample the intricate energy landscapes of defects by: (i) using methods that can identify complex networks of minima and
saddle points at zero K; (ii) offering reliable force fields that handle intricate defects such as interstitials and dislocation loops; (iii) probing the atomistic free energy landscape of metals with ab initio accuracy up to the melting temperature [3]; (iv) examining chemical disorder in high entropy alloys (HEA); and, finally, (v) proposing surrogate models that sidestep traditional approaches to access challenging properties, like vibrational entropies [4].

10:45 AM AM *MT01.01.06
Physics-Based Molecular Modeling and Machine Learning for Accelerated Discovery of Metal-Organic Frameworks Diego A. Gomez Guadron; Colorado School of Mines, United States
Metal-organic frameworks (MOFs) are a class of crystals, whose chemically and structurally tunable pores have made them exciting prospects for a myriad of applications across chemistry,
engineering, and materials science. MOF tunability stems from a modular structure that can drastically (or subtly) vary by “mix and matching” potential constituent building blocks. This
 tunability, however, gives rise to an overwhelmingly large material design space that cannot be efficiently explored by experiments, or even by relying solely on traditional computational
methods such as molecular simulation. In this presentation, I discuss some of the ways molecular simulation and machine learning have been combined to accelerate the navigation of databases of
MOF computational “prototypes” for applications seeking to exploit selective sorption of molecules into MOF pores.
First, I discuss how the switch to a physics-based approach allowed us to address the issue of (sorption) data scarcity by allowing us to create “synthetic data” that led to the training of an effective
multitasking machine learning model to predict sorption of a diversity of molecules in MOFs at a variety of thermodynamic conditions. The use of this model to find promising MOFs from
a 50,000+ MOF database for removal of Xe and Kr in nuclear fuel reprocessing is demonstrated.
Second, I discuss the combination of physics-based MOF representations, traditional descriptor-based hierarchical screening, and iterative machine learning model training to efficiently
exploit an existing 10,000+ MOF database to find promising MOFs for product extraction in plasma reactors used for synthesis of NH3. The efficacy of the above combination of domain-knowledge and “off the shelf” machine learning tools is compared against more data-science involved approaches such as diversity-driven Bayesian optimization.
11:15 AM MT01.01.07
Large-Scale and Machine-Learning-Aided Investigations of Metal-Organic Frameworks for Water Harvesting Li-Chang Lin1,2; Yi-Ming Wang1, Zhi-Xun Xu1, Shiue-Min Shih1, J. Ting Sung1 and Archit Datar2,3; 1National Taiwan University, Taiwan; 2The Ohio State University, United States; 3Celanese Corporation, United States
Water adsorption in metal-organic frameworks (MOFs) has recently drawn considerable attention for its tremendous potential in mitigating water scarcity. An important key to the development of
such water harvesting technology to capture atmospheric water is the selection of optimal adsorbent materials. To date, tens of thousands of MOFs have been reported experimentally, while
only a modest number of candidate materials have been theoretically predicted. Given the large materials space of available MOF adsorbent, computational studies, by employing state-of-the-art
molecular simulations, play an important role in the selection of potential materials. In this study, a large-scale in silico screening, employing state-of-the-art Monte Carlo techniques, is
conducted to explore more than 10,000 MOF candidates that are included in the CoRE (Computational-Ready Experimental) MOF database for their potential in water harvesting. While the widely
used grand canonical Monte Carlo (GCMC) simulations to compute water adsorption can converge very slowly may therefore yield unreliable results, the large-scale computations
performed herein employ a method, denoted as the flat histogram-based C-map method reported by some of us [1,2], to determine the water adsorption capability and capacity of MOFs. Through
extensively studying a diverse set of MOFs, our results identify promising candidates as well as shed light on the structure-property relationships. Moreover, to facilitate the future
development of optimal water adsorbents, machine learning models are also developed. Specifically, tree-based methods such as random forest as well as convolution neural networks (CNNs)
are employed. For the former, aside from including commonly used structural features such as largest cavity diameter and surface area, a newly developed metric – the so-called continuously
adsorption channel (CAC) recently developed by some of us [3], is also used to help develop more accurate models. For the latter, computer vision techniques are exploited to “see” the

9:15 AM MT01.01.03
Ultrafast Nonadiabatic Dynamics in 2D Perovskites assisted by Machine Learning David Graupner and Dmitri Kilin; North Dakota State University, United States
An exploration of the on-the-fly non-adiabatic couplings (NAC) for nonradiative relaxation and recombination of excited states in 2D DionJacobson Lead-halide perovskites is accelerated by a
machine learning approach to ab initio molecular dynamics. Molecular dynamics of nanostructures composed of heavy elements is performed with use of machine learned force-fields
(MLFF), as implemented in Vienna Ab initio Simulation Package (VASP). The force field parameterization is established using on-the-fly learning, which continuously builds a force field using
ab initio MD data. At each step of MD it is determined whether to perform an ab initio calculation or to use the force field and skip learning for that step using a Bayesian-learning algorithm.
The total energy and forces are predicted based on the machine-learned force field at each time step of the MD simulation and if the Bayesian error estimate exceeds a threshold an ab initio
calculation is performed. Model training and evaluation were performed for a range of for a 2D Dion-Jacson lead halide perovskite models of different thickness and composition. The
MLFF-MD trajectories were evaluated against AIMD trajectories to assess quality of force field and skip learning. To examine the practical effectiveness of this approach we have used the
MLFF-based MD trajectories to compute NAC and excited-state dynamics. At each stage, results based on machine learning are compared to traditional ab initio-based electronic dissipative
dynamics. We find that MLFF-MD provides comparable results to ab initio MDs when the MLFF is trained in a NaT ensemble.

9:30 AM MT01.01.04
Structure, Mechanical and Thermal Properties of Monolayer Amorphous Carbon and Boron Nitride Yuyang Zhang1, Xi Zhang1, Yupeng Wang2, Shixuan Du1 and Sokrates Pantelides3; 1Chinese Academy of Sciences, China; 2Central South University, China; 3Vanderbilt University, United States
structures directly for model training, followed by making quantitative predictions. These machine learning models are also investigated to better understand the structure-property relationship in a quantitative manner. Overall, this work represents a synergistic effort between large-scale molecular simulations and machine learning studies, and we anticipate the outcomes achieved herein can facilitate future computational and experimental efforts on the development of optimal water adsorbents.

References:

11:30 AM MT01.01.08
Accelerating The Selection of High Uptake Covalent Organic Frameworks with Supervised Machine Learning for Methane Storage
Niraj Bhatt, Sandip Thakur and Ashutosh Giri; University of Rhode Island, United States
Covalent organic frameworks (COFs) have been identified as ideal candidates for natural gas storage and catalysis applications primarily because of their tunable microstructure as well as the vast design space for their chemical makeup. COFs with high gas uptake values at workable pressures are highly desired for applications such as gas storage, carbon capture and catalysis. Methane (CH4) storage is highly sought after because of the low carbon hydrogen ratio, high calorific value and natural abundance. However, the vast design space for COFs makes the screening of high CH4 uptake COFs very difficult as it requires time-intensive grand-canonical Monte Carlo (GCMC) simulations to calculate the uptake values. To overcome this challenge, we employ machine learning development of a model that captures the structure-property relationship in COFs using a large in-silico database of hypothetical COFs. A machine learned regression model based on powerful random forest algorithm is developed that maps the structural and chemical features of the 5000 COFs used in training to their uptake values. The validated model is then used to find the uptakes of COFs in the experimental database eliminating the need of resource intensive GCMC. Thousands of diverse COFs are selected from the database and featurized using MATMINER, a powerful inbuilt python library used in material’s informatics. The features are used to uniquely represent each COF which is mapped to their respective CH4 uptake values during training of the ML model. The feature space includes the chemical features such as elemental property features and structural features like radial distribution functions and density-based structural features. Various dimensionality reduction techniques like feature selection using co-relation analysis and feature extraction using principal component analysis are employed to make an accurate and efficient ML model. We employed this model to predict the CH4 uptake values for an experimental database of ~ 600 COFs and screened top performers with CH4 uptake values as high as 1260 molecules/unitcell.

11:45 AM MT01.01.09
Investigating The Binding Interactions between Newly Synthesized Metal-Organic Frameworks (MOF) and Organic Pollutants Using Computational Chemistry
Melissa Mapula, Shiri Lin and Manal Omary; Texas Woman's University, United States
Benzene and toluene are hazardous organic pollutants due to their potential health effects. Benzene is a known carcinogen and exposure to high levels of toluene can cause central nervous system depression. Applying porous materials for the removal of benzene and toluene can be an effective approach for mitigating the environmental and health impacts of these organic pollutants. Metal-organic frameworks (MOFs) are a type of porous material consisting of metal nodes connected by organic linkers. MOFs have unique properties such as high surface area, tunable pore size, and the ability to selectively adsorb small molecules, making MOFs promising candidates for various applications including removing pollutants. In our study, we apply computational chemistry methods to investigate interactions of organic pollutants and synthesized MOF structures, such as MOF-TW1, which was formed from the crystals of the reaction of Cu(I) and Ag(I) precursors with pyrazine (Pyz) and piperazine (Ppz) and boasting a significant surface area of (1278 m2/g) and porosity of 23.7% void volume. We investigate the adsorption ability of MOF structures toward organic pollutants, which can guide the design and modification of MOFs for more organic pollutant absorptions and removals. Furthermore, we apply machine learning algorithms to predict organic pollutant adsorption performances on synthesized MOF structures.

SESSION MT01.02: Machine Learning and Simulations II
Session Chairs: Raymundo Arroyave and Felipe H. da Jornada
Monday Afternoon, April 22, 2024
Room 320, Level 3, Summit

1:30 PM MT01.02.01
Invariant Graph Neural Network Models for Accelerated Prediction of Equilibrium Structure, Defect Energies and Electronic Properties of Semiconductor Materials
Brian L. DeCost, Kamal Choudhury and Francesca Tavazza; National Institute of Standards and Technology, United States
Accelerated material property predictions are an important component of large scale search and optimization of new semiconductor device materials. We present ongoing work developing and applying invariant graph neural network models for modeling the properties of multicomponent semiconductor materials. We use such models to predict defect energetics in semiconductor materials. Initial results on prediction of equilibrium interface structures and electronic properties in semiconductor heterointerface systems will be discussed as well. Robust and fast uncertainty quantification methods are of particular concern for predictable design of semiconductor heterointerface systems, for which currently-available reference data is limited. We will discuss how we use graph neural network uncertainty quantification for active learning of forest fields, out-of-distribution detection for predictive models, and for targeted allocation of theory-based modeling.

2:00 PM MT01.02.02
Uncertainty-Quantification-Driven Autonomous Workflows for Upscaling of Complex Materials Properties
Danny Perez; Los Alamos National Laboratory, United States
Many engineering models for require parametric or functional inputs that can in principle be obtained from lower scale simulations. For example, transport coefficients for radiation-induced defects computed from molecular dynamics can be used to inform kinetic Monte Carlo models, that can themselves inform cluster-dynamics simulation of microstructural evolution. However, in many cases, the number of lower-scale calculations required to obtain these higher-scale properties can be very large, which can lead to extremely long times-to-solution, especially when human intervention is needed at any step of the process. We demonstrate how tailored uncertainty-quantification approaches can be used to autonomously drive the execution of upscaling workflows at large computational scales. I will show how information can be systematically upcaled into different representations in order to develop reliable reduced-order models from simulation data.

2:30 PM MT01.02.03
A Physics-Informed Bayesian Optimization Approach for Material Design
Raymundo Arroyave; Texas A&M University, United States
The design of materials and identification of optimal processing parameters constitute a complex and challenging task, necessitating efficient utilization of available data. Bayesian Optimization (BO) has gained popularity in materials design due to its ability to work with minimal data. However, many BO-based frameworks predominantly rely on statistical information, in the form of input-output data, and assume black-box objective functions. In practice, designers often possess knowledge of the underlying physical laws governing a material system, rendering the objective function not entirely black-box, as some information is partially observable. In this study, we propose a physics-informed BO approach that integrates physics-infused kernels to effectively leverage both statistical and physical information in the decision-making process. We demonstrate that this method significantly improves decision-making efficiency and enables more data-efficient BO. The applicability of this approach is showcased through the design of NiTi shape memory alloys, where the optimal processing parameters are identified to maximize the transformation temperature.

2:45 PM MT01.02.04
Materials Discovery for High-Temperature Clean-Energy Applications (and Beyond) via Defect Graph Neural Networks
Matthew Witman1, Anuj Goyal2, Tadashi Ogitsu3, Anthony McDaniel4 and Stephan Lany2; 1Sandia National Laboratories, United States; 2National Renewable Energy Laboratory, United States; 3Lawrence Livermore National Laboratory, United States
We present a graph neural network (GNN) approach that fully automates the prediction of defect formation enthalpies for any crystallographic site from the ideal crystal structure, without the
need to create defective atomic structure models as input [1]. Using density functional theory (DFT) reference data for vacancy defects in oxides, we trained a defect GNN (dGNN) model that replaces the DFT supercell relaxations otherwise required for each symmetrically unique crystal site. Interfaced with thermodynamic calculations of reduction entropies and associated free energies, the dGNN model is applied to the screening of oxides in the Materials Project database, connecting the zero-Kelvin defect enthalpies to high-temperature process conditions relevant for solartochemical hydrogen production and other energy applications. The dGNN approach is applicable to arbitrary structures with an accuracy limited principally by the amount and diversity of the training data, and it is generalizable to other defect types and advanced graph convolution architectures. It will aid tackling future materials discovery problems in clean energy and beyond.


3:00 PM BREAK

3:30 PM *MT01.02.05

Machine Learning Based Electronic Structure Prediction: From Nanostructures to Complex Alloys Amartya S. Banerjee1,2, Shashank Pathrudpikar1,2, Shivang Agarwal1,3, Susanta Ghosh2,3, Stephanie Taylor1,2, Hsuan Ming Yu1 and Ponkrishna Thiragaranj2,3; 1University of California, Los Angeles, United States; 2Michigan Technological University, United States

I will describe our work on using specialized first principles calculations with machine learning tools to enable prediction of the electronic structure of various nanomaterials and bulk systems. I will focus on two related but independent directions. First, I will show how helical and cyclic symmetry adapted density functional theory calculations may be used to train interpretable machine learning models of the electronic fields of quasi-one-dimensional materials. The descriptors in this framework are global geometry and strain parameters. Through examples involving distorted carbon nanotubes, I will show how the framework can be particularly accurate in its prediction, even with limited training data. I will discuss the use of this framework for calculation of the electronic structure of bulk solids with defects, and compositionally complex alloys, from which, other material properties of engineering interest may be inferred. I will end with a discussion of future research directions.

4:00 PM MT01.02.06

Learning Polarization Using Equivariant Neural Networks Stefano Falletta1,2, Andrea Cepellotti1,2, Albert Musaelian1, Anders Johansson1, Chun Wei Tan1 and Boris Kozinsky1,2,3; 1Harvard University, United States; 2Robert Bosch Research and Technology Center, United States

Polarization is an essential physical quantity for understanding the properties of dielectrics and ferroelectrics [1]. The modern theory of polarization [1] and further developments on electric enthalpy functions [2] have enabled the study of polarization in periodic electronic structure calculations. Interestingly, predicting the polarization over a molecular dynamics allows for the determination of experimentally-relevant quantities such as infrared and Raman spectra from first principles. However, this remains a challenging problem in electronic structure calculations, because of their high computational cost.

Here, we introduce an equivariant neural network approach to efficiently learn and predict polarization for each atomic configuration, building on and extending state-of-the-art machine learning force field architectures. This allows one to determine the autocorrelation function of polarization over long-lasting molecular dynamics, thereby giving access to infrared spectrum, frequency-dependent dielectric constant, and Raman cross section from first principles. We implemented our scheme in the EL3-equivariant NeqGPff/Allegra framework [3,4], and interfaced it with the LAMMPS code for performing molecular dynamics calculations.


4:15 PM MT01.02.07

Ab Initio Investigations of a Two Dimensional form of Silicon featuring Dispersionless Electronic States Chenhauve Wang and Amartya Banerjee; UCLA, United States

Materials with dispersionless electronic states (or flat bands) have been intensely investigated in recent years, owing to their association with strongly correlated electrons. Due to the negligible kinetic energies of electrons in such states, the electron-electron interaction dominates, thus resulting in superconductivity, ferromagnetism, and other exotic phases of matter. While a number of bulk materials and heterostructures have been investigated for their connection with flat-band physics, the discovery of new, simple low-dimensional materials with such electronic features, continues to be an alluring possibility. Following this line of thought, and motivated by the consideration that silicon is a versatile material with many known low-dimensional allotropes that have already been experimentally synthesized, we investigate here a two-dimensional form of silicon in the decorated honeycomb (or star) lattice. The proposed material has a buckled structure similar to silicene, consists of dodecagonal rings, and features electronic flat bands near the Fermi-level. We describe extensive first principles investigations into the static and dynamic structural stability of the material and observe that in-plane strains stabilize it. Furthermore, the bandwidth of the flat band is found to be highly tunable with strains. Finally, we investigate the possibility of using substrates to apply such stabilizing strains, suggesting the fabricability of this novel two dimensional material under experimental conditions.

4:30 PM MT01.02.08

Atomistic Modeling of Advanced Transistor Gate Stack Using Graph Neural Networks Pratik Brahma1, Krishnakumar Bhattacharya1, Jack Bood2, Sinead M. Griffin2,3 and Sayeef Salahuddin2,3; 1, University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States

Modern microelectronic devices such as silicon transistors are composed of multiple material interfaces whose electronic interactions significantly affect electron transport and, ultimately, device performance. These complex interfacial interactions between various materials of crystalline, polycrystalline, and amorphous phases, as well as boundary effects such as quantum confinement, present a significant challenge to the atomistic modeling of electronic devices. Traditional modeling approaches often use ab-initio methods such as density functional theory for molecular dynamics and electronic structure calculations. However, these methods scale poorly with increasing system size as they rely on diagonalization of the quantum Hamiltonian, posing a challenge for fast and accurate simulations of electronic devices that contain thousands of atoms and various structural phases.

In this work, we demonstrate the viability of graph neural networks (GNNs) [1, 2] to overcome this scaling challenge. Our architecture is designed to accelerate ab-initio molecular dynamics and electronic structure calculations by characterizing the relationships between local chemical environments and global electronic transport properties such as carrier injection velocity and gate capacitance. For given macroscopic transistor dimensions, we use our neural network predicted atomic forces to generate the heterogeneous crystalline silicon channel–dielectric gate stack (amorphous SiO2:amorphous HfO2), with bond lengths within 3% of experimental values. Furthermore, we predict global electronic (density of states) and transport properties (injection velocity) of crystalline nanoscale silicon channels, showing good agreement—within 0.18% for density of states and 5.4% for injection velocity—with the baseline material simulation model for channel thicknesses outside the training domain, while also accelerating the simulation speed by four orders of magnitude. The obtained accuracies demonstrate that our neural network captures the structural confinement effects of thin silicon channels in advanced transistors. Overall, the scalability and accuracy of our predictions over a wide range of material and transport properties demonstrate the efficacy of GNNs to accelerate advanced electronic device simulations, paving the way for rapid design and modeling of next-generation transistors.


4:45 PM MT01.02.09

Stopping Electric Stopping Power Predictions from Machine Learning Andre Schleife1, Logan Ward2, Cheng-Wei Lee3, Ben Blaiszik2 and Ian T. Foster2; 1University of Illinois at Urbana-Champaign, United States; 2Argonne National Laboratory, United States; 3University of Chicago, United States


[1]. https://doi.org/10.1038/s41467-021-27504-0

We aim to develop an affordable computational approach that provides the electronic stopping power for arbitrary trajectories of ions impacting a target material with an accuracy comparable to that of modern quantum mechanical first-principles simulations. Currently, real-time time-dependent density functional theory can accomplish this in reasonable agreement with experiment. However, the computational cost of this method is high which limits the number of trajectories and host material atomic geometries that can be studied. This prevents a routine integration of electronic-stopping power, e.g. in the molecular dynamics simulation of radiation damage cascades. We use cutting-edge descriptrons of atomic geometries to train modern machine-learning models on data from real-time time-dependent density functional theory. We find very low error bars and very high accuracy at million-fold reduced computational cost of the trained model for proton irradiated aluminum. We also are able to predict velocity dependent electronic stopping and entire Bragg peak simulations with our models. In this presentation we discuss our framework in detail as well as its broad applicability in the particle-radiation community, including target materials with complex atomic geometry or low-dimensional materials.

SESSION MT01.03: Machine Learning and Simulations III
Session Chairs: Joshua Agar and Elfie Ertelkin
Tuesday Morning, April 23, 2024
Room 320, Level 3, Summit

10:30 AM MT01.03.01
Ultra-Compact and Parsimonious Machine Learning Frameworks for High-Velocity Scientific Discovery in Materials Microscopy
Joshua Agar; Drexel University, United States

Machine learning (ML) offers unparalleled opportunities for accelerating advancements in materials microscopy. Yet, practical implementation often stumbles due to the lack of models that are both machine-interpretable and conforming to underlying physical laws, as well as the absence of specialized computational infrastructure for automated data analytics. We address these bottlenecks by focusing on the codelign of microscopy technique, ultra-compact physics-aware ML models, connection to physics-inspired models, and bespoke hardware solutions. Our contribution is three-fold. First, we present a robust infrastructure for the automated aggregation and management of high-velocity synthesis data, including real-time in-situ diagnostics. We broaden a federated, searchable scientific data management system optimized for high-throughput analysis. This infrastructure allows robust linkages between experiment and theory. Second, we go beyond traditional ML approaches by introducing highly parsimonious, physics-conforming neural networks specifically tailored for real-time analysis of band-excitation resonance force microscopy data. These models are meticulously codeligned to be executable on field-programmable gate arrays (FPGAs) for edge-real-time analytics. Lastly, we unleash a neural network architecture aimed at automating 4D–scanning transmission electron microscopy strain mapping. Leveraging a cycle-consistent spatial transforming autoencoder, we incorporate an affine transformation layer to parsimoniously capture the governing equations of geometric transformations. This is further optimized through advanced compression, regularization, and optimization strategies to facilitate the otherwise computationally intensive training process. Remarkably, our method outperform traditional template-matching techniques, achieving a sub-pixel precision of 0.3, as benchmarked against pyODSTEM. In sum, this work offers a comprehensive blueprint for seamlessly incorporating ultra-compact and parsimonious AI systems into the analysis of large-scale, high-velocity, and noise-prone experimental datasets. This facilitates closer connections between experiments and theory thereby revolutionizing the practical utility of AI in scientific discovery.

11:00 AM MT01.03.02
Learning Latent-Variable Representations of Microstructure Accounting for Materials Stochasticity
Saijad Hasherni1; Michael Guerzhoy1,2 and Noah H. Paulson3; 1University of Toronto, Canada; 2Li Ka Shing Knowledge Institute, St. Michael's Hospital, Canada; 3Argonne National Laboratory, United States

Over the past decade, generative machine learning has found applications in the design of materials with tailored properties. Generative latent-variable models represent high-dimensional data in low-dimensional spaces. The original data is n-dimensional, for example, 2-D/3-D image-based representations of materials microstructure with k pixels/voxels. New plausible examples of image-based representations can be generated from points in the low-dimensional space. The variational autoencoder (VAE) is a popular latent-variable model. The VAE is learned by optimizing the L2 distance in data space (2-D/3-D) between real and generated examples (in addition to regularization). This is suboptimal, since materials microstructure is stochastic. Therefore, image-based representations should be considered similar if their statistical properties are similar rather than just if they are close in Euclidean data space. We develop a novel VAE architecture to prioritize statistical representations of materials microstructure and the generation of statistically similar microstructure examples from a single location in the latent space. A successful implementation of this architecture would greatly aid materials development and optimization through iterative materials simulations. This novel capability will be demonstrated on both synthetic and natural microstructure datasets.

11:15 AM MT01.03.03
A Flexible Formulation of Value for Experiment Interpretation and Design
Matthew Carbone; Brookhaven National Laboratory, United States

Optimal design of experiments is an outstanding challenge in the materials science community. Standard techniques such as Bayesian optimization can address this challenge as long as the goal of an experimental campaign is maximizing some observable. While useful in a wide variety of cases, it is insufficient to address more epistemic goals, such as thoroughly exploring a sample space when an explicit objective is lacking. In this work, we showcase a formulation of “scientific value,” a scalar representation of local uniqueness. Our method scalarizes arbitrarily high-dimensional data, allowing for the traditional optimization toolbox to be applied to any problem. Intuitively, our method, which we call the Scientific Value Agent, explores regions of space in which observables change rapidly, whilst exploring other areas sufficiently, wasting minimal experimental budget. It is also robust to the cold start problem, and can be utilized with no prior knowledge and next-to-no data. We demonstrate this technique by exploring a variety of simulated and real-world examples, including phase boundaries, autonomously changing the temperature measurement of a ferroelectric material, and analyzing nanoparticle synthesis data. Our method can be seamlessly extended to studies with multiple outputs, or fidelities, and can seamlessly integrate into existing autonomous experimentation frameworks with minimal added effort to the user.

11:30 AM MT01.03.05
Simultaneous Analysis of Wide Angle X-Ray Scattering Data (WAXS) and Extended X-Ray Absorption Fine Structure Spectroscopy (EXAFS) of Very Small Nanoparticles
Markus Winterer and Jeremias Geiss; University of Duisburg-Essen, Germany

Although experiments investigating the atomistic structure of disordered materials are today facile through modern instruments for X-ray scattering and spectroscopy, it is still a challenge to extract the relevant information especially in case of very small nanoparticles with a diameter smaller than 10 nm. In our contribution we will present recent advances in data analysis of this inverse problem using Reverse Monte Carlo (RMC) analysis [1].

RMC simulations enable the analysis of WAXS data as well as EXAFS spectra via partial pair distribution functions (pPDF) obtained from a physical, structural model. In case of nanoparticles and scattering data this approach suffers from the termination of the pPDFs due to the finite size of the particles. This produces artifacts in the computed scattering intensity due to the long-range probing distance of scattering which are eliminated by using the Debye scattering equation (DSE) for computing the scattering intensity from a particle model. Computational efficiency is provided by binning the distance distribution of atom pairs in the DSE.

Data fusion, i. e. simultaneous refinement of both WAXS data and EXAFS spectra of small nanoparticles, is thus enabled using a mutual structural model. Therefore, this method allows the self-consistent extraction of complementary information on the local structure contained in EXAFS and on the long-range order in WAXS data. We describe this novel method for the nanocrystalline complex oxide LaFeO3 [1]. The results are highly relevant for example for heterogeneous catalysis [2].

The method described can be further developed to additionally include small angle scattering data and provides an interface either via the (atomistic) structural model or the pPDFs to other physics simulation and materials modeling methods such as molecular dynamic (MD) simulations or density functional theory (DFT) modeling.

References:
1:30 PM *MT01.04.01

Campaign Design for Autonomous Experimentation in Materials Research

Beni Muruvanz; AFRL/RXA, United States

The current materials research process is slow and expensive; taking decades from invention to commercialization. The Air Force Research Laboratory pioneered ARES™, the first autonomous experimentation system for materials development. A rapidly growing number of researchers are now exploiting advances in artificial intelligence (AI), autonomy & robotics, along with modeling and simulation to create research robots capable of making research progress orders of magnitude faster than today. We will discuss concepts and advances in autonomous experimentation in general, and associated hardware, software and autonomous methods.

Campaign design for autonomous experimentation or self-driving labs is complex and dependent on research objectives, experimental apparatus, analysis capabilities and decision strategies. Examples of autonomous experimentation campaigns to explore important aspects of campaign design will be given.

2:00 PM DISCUSSION TIME

2:30 PM MT01.04.03

Leveraging Physics and Machine Learning to Predict Battery Aging

Michael J. Kenney1, Maxim Ziatdinov2, Katerina Malollari1 and Sergei Kalinin3; 1Amazon Lab126, United States; 2Oak Ridge National Laboratory, United States; 3The University of Tennessee, Knoxville, United States

A primary concern with lithium-ion battery technology is the performance deterioration over time. Capacity retention, a vital performance measure, is frequently utilized to assess whether these batteries have approached their end-of-life. Machine learning offers a powerful tool for predicting capacity degradation, leveraging both past data and physical knowledge in the form of simulations or phenomenological models. In this study, we showcase the utility of probabilistic machine learning and transformer-based deep learning modeling in battery health prediction. For our probabilistic models, which operate without pre-training, we employ: i) a structured Gaussian process (GP) - an enhanced version of the standard GP that integrates a phenomenological model as a probabilistic prior mean function, and ii) a multi-fidelity GP, augmented by prior-physics-based simulations to boost its predictive power. Concurrently, we deploy time-series transformers pre-trained on existing datasets for forecasting purposes. Our findings juxtapose these models, offering insights into their optimal application scenarios, and the associated codes are open for access.

2:45 PM BREAK

3:15 PM *MT01.04.04

Understanding Complex Crystal Structures and Phase Transitions through Self-Assembly Simulations

Julia Schermechadze; Cornell University, United States

How do atoms come together to form crystal structures? Powerful theoretical and experimental tools exist to elucidate the structure of crystalline materials on multiple length scales. Directly observing the formation of their ordered structures, however, remains supremely challenging. How can we understand the path that a material takes to its crystalline state? We take a general approach toward understanding crystallization across multiple materials families by simulating their self-assembly using simple coarse-grained models, in order to investigate the emergence of long-range order from short-range interactions. In this way, we gain systematic insights into the phenomena that lead to the crystallization into even complex types of order, such as materials with large unit cells or aperiodic crystals. Our goal is to use these insights to find ways to tailor crystallization pathways and to create new materials. In this talk, I will discuss the broad spectrum of structural phenomena captured with particles that interact via simple isotropic pair potentials, which we apply to study crystal growth and solid–solid phase transformations. Our work promises to establish new pathways to materials design through simulations, which explicitly incorporate and explore phase transformation kinetics.

3:45 PM MT01.04.06

Programming Soft Materials with JAX-MD

Chirs Xu, Xiu Du1,2, Ella King3,2, Qian-Ze Zhu2, Samuel S. Schoenhoff1 and Michael Brenner2; 1University of Hawai‘i at Mānoa, United States; 2Harvard University, United States; 3Simons Foundation, United States; 4OpenAI, United States

Soft Materials are ubiquitous in everyday life and are crucial in many different forms of revolutionary technologies. One property of Soft Materials is their ability to self-assemble into intricate structures from a finite set of building blocks with continuously tunable parameters. This giant design space of building blocks is a double-edged sword: on one side it provides researchers infinite possibilities to design building blocks for targeted functions, while on the other side it might take forever to search the design space. Here, we propose a new inverse design method that captures both interaction and geometry of building blocks. By enabling rigid body functionalities in JAX-MD, an end-to-end differentiable molecular dynamics engine, we can create soft materials model with components that are simple enough to design yet powerful enough to capture complex materials properties. In this talk, I will discuss the implementation of the methods alongside examples to showcase its potential applications.

4:00 PM MT01.04.07

Representation-Space Diffusion Models for Generating Periodic Materials

Anshuman Sinha, Shuyi Jia and Victor Fung; Georgia Institute of Technology, United States

Generative models hold the promise of significantly expediting the materials design process when compared to traditional human-guided or rule-based methodologies. However, effectively generating high-quality periodic structures of materials on limited but diverse datasets remains an ongoing challenge. Here we propose a novel approach for periodic structure generation which fully respects the intrinsic symmetries, periodicity, and invariances of the structure space. Namely, we utilize differentiable, physics-based, structural descriptors which can describe periodic systems and satisfy the necessary invariances, in conjunction with a denoising diffusion model which generates new materials within this descriptor or representation space. Reconstruction is then performed on these representations using gradient-based optimization to recover the corresponding Cartesian positions of the crystal structure. This approach differs significantly from current methods by generating materials in the representation space, rather than in the Cartesian space, which is made possible using an efficient reconstruction algorithm. Consequently, known issues with respecting periodic boundaries and translational and rotational invariances during generation can be avoided, and the model training process can be greatly simplified. We show this approach can provide competitive performance on established benchmarks compared to current state-of-the-art methods.

SESSION MT01.05: Machine Learning and Simulations V

Session Chairs: Aditi Krishnapriyan and Wennie Wang

Wednesday Morning, April 24, 2024
Room 320, Level 3, Summit

8:30 AM *MT01.05.01

Combining Data, Physics and Machine Learning for Accelerating Materials Computations

Boris Kozinsky and Albert Muselein; Harvard University, United States

Discovery and understanding of next-generation materials requires a challenging combination of the high accuracy of first-principles calculations with the ability to reach large size and time scales. We pursue a multi-tier method development strategy in which machine learning (ML) algorithms are combined with exact physical symmetries and constraints to significantly accelerate computations of electronic structure and atomistic dynamics. First, density functional theory (DFT) is the cornerstone of modern computational materials science, but its current approximations fall short of the required accuracy and efficiency for predictive calculations of defect properties, band gaps, stability and electrochemical potentials of materials for energy storage and conversion. To advance the capability of DFT we introduce non-local charge density descriptors that satisfy exact scaling constraints and learn exchange functionals called CIDER [1]. These models are orders of magnitude faster in self-consistent calculations for solids than hybrid functionals but similar in accuracy. On a different level, we accelerate molecular dynamics (MD) simulations by using machine learning to capture the potential energy surfaces obtained from quantum calculations. We developed NeqQP [2] and Allegro [3], the first deep equivariant neural network interatomic potential models, whose Euclidean symmetry-preserving layer architecture achieves state-of-the-art data efficiency and accuracy for simulating dynamics of molecules and materials. In parallel, we implement autonomous active learning of interactions in reactive systems, with the FLARE algorithm that constructs accurate and uncertainty-aware Bayesian force fields on-the-fly from a molecular dynamics simulation, using Gaussian process regression [4]. These MD simulations are used to explore long-time dynamics of phase transformations and

heterogeneous reactions.


This work was supported by DOE Office of Basic Energy Sciences Award No. DE-SC0022199 and Department of Navy award N00014-20-1-2418 issued by the Office of Naval Research; the NSF through the Harvard University Materials Research Science and Engineering Center Grant No. DMR-2011754, NSF OAC # 2118201, the Camille and Henry Dreyfus Foundation, and Bosch Research.

9:00 AM *MT01.05.02
Not as Simple as We Thought: A Rigorous Examination of Data Aggregation in Materials Informatics

Taylor D. Sparks1,2; Federico Ottomano3; Giovanni De Felice2 and Vladimir Gusyev2; 1University of Utah, United States; 2University of Liverpool, United Kingdom

Recent Machine Learning (ML) developments have opened new possibilities for materials research. However, due to the underlying statistical nature, the performance of ML estimators is heavily affected by the quality of training datasets, which are severely limited and fragmented in the case of materials informatics. Here, we investigate whether state-of-the-art ML models for property predictions can benefit from the aggregation of different datasets. We probe three different aggregation strategies in which we prioritize training size, element diversity, and composition diversity by using novelty scores from the DiSCoVeR algorithm. Surprisingly, our results consistently show that both simple and refined data aggregation strategies lead to a reduction in performance. This suggests caution when merging different experimental data sources. To guide the size increment, we compare the use of DiSCoVeR, which prioritizes chemical diversity, with a random selection. Our results show that targeting novel chemistries is not beneficial in building a training dataset.

9:30 AM *MT01.05.03
Leveraging Fragment-Based Representations in Active Learning and Reinforcement Learning Frameworks for Materials Design

Daniel Taber; Texas A&M University, United States

This talk will focus on the development and application of two types of materials design. First, we will focus on developing reinforcement learning methods that are used to accelerate the design of functional materials, including radical-based polymers and organic optoelectronic materials. In our first demonstration of the reinforcement learning scheme, we show that this framework can integrate with quantum chemistry calculations in real-time, and through a careful design of the learning curriculum, we are able to find a diverse set of molecules with desired singlet and triplet energy levels. Second, we will describe our work on developing representations for predicting the polymer physics of disordered polymers at a much lower computational cost than current coarse-grained methods. One advantage of the new representation is that it avoids specifying the longest chain of the bond in advance. In addition, this representation works well with a set of highly charged sequences, uncovering new insights to the fundamental interactions and scaling behavior of these systems. We will then discuss the compatibility of this representation with reinforcement learning methods.

9:45 AM MT01.05.04
Physics Supervised Deep Learning-Based Optimization (PSDLO) with Accuracy and Efficiency

Hanging Jiang and Xiaowen Li; Westlake University, China

Identifying efficient and accurate optimization algorithms is a long-desired goal for the scientific community. At present, a combination of evolutionary and deep-learning methods is widely used for optimization. In this paper, we demonstrate three cases involving different physics and conclude that no matter how accurate a deep-learning model is for a single, specific problem, a simple combination of evolutionary and deep-learning methods cannot achieve the desired optimization because of the intrinsic nature of the evolutionary method. We begin by using a physics-supervised deep-learning optimization algorithm (PSDLO) to supervise the results from the deep-learning model. We then intervene in the evolutionary process to eventually achieve simultaneous accuracy and efficiency. PSDLO is successfully demonstrated using both sufficient and insufficient datasets. PSDLO offers a new perspective for solving optimization problems and can tackle complex science and engineering problems having many features. This new approach to optimization algorithms holds tremendous potential for application in real-world engineering domains.

10:00 AM BREAK

10:30 AM *MT01.05.05
End-To-End Differentiability and Tensor Processing Unit Computing (TPU) to Accelerate Materials’ Inverse Design

Mathieu Bauchy; University of California, Los Angeles, United States

Numerical simulations have revolutionized material design. However, although simulations excel at mapping an input material to its output property, their direct application to inverse design has traditionally been limited by their high computing cost and lack of differentiability. Here, taking the example of the inverse design of a porous matrix featuring a target sorption isotherm, we introduce a computational inverse design framework that addresses these challenges. First, we adopt end-to-end differentiability to build a differentiable forward numerical simulation. Thanks to its differentiability, the forward simulation is used to directly train a backward deep generative model, which outputs an optimal porous matrix based on an arbitrary input sorption isotherm curve. Second, this inverse design pipeline leverages the power of tensor processing units (TPU)—an emerging family of dedicated chips, which, although they are specialized in deep learning, are flexible enough for intensive scientific simulations. This approach holds promise to accelerate the inverse design of novel materials with tailored properties.

11:00 AM *MT01.05.06
Accelerated Development of Materials Using High-Throughput Strategies and AI/ML

Surya R. Kalindii; Georgia Institute of Technology, United States

The dramatic acceleration of the materials innovation cycles is contingent on the development and implementation of high throughput strategies in both experimentation and physics-based simulations, and their seamless integration using the emerging AI/ML (artificial intelligence/machine learning) tools. This talk presents recent advances made in the presenter’s research group, including: (i) a novel information gain-driven Bayesian framework that identifies the next best step in materials innovation (i.e., the next experiment and/or physics-based simulation to be performed) that maximizes the expected information gain towards a specified target (e.g., optimized combination of material properties, refinement of a material constitutive response), (ii) computationally efficient versatile material structure analyses and statistical quantification tools, (iii) formulation of reduced-order process-structure-property models that enable comprehensive inverse solutions needed in materials design (e.g., identifying specific compositions and/or process histories that will produce a desired combination of material properties), and (iv) high throughput experimental protocols for multi-resolution (spatial resolutions in the range of 50 nm to 500 microns) mechanical characterization of heterogeneous materials in small volumes (e.g., individual constituents in composite material samples, thin coatings or layers in a multilayered sample). These recent advances will be illustrated with case studies.

11:30 AM MT01.05.07
MACE-MP: A Foundation Model for Atomatic Materials Chemistry

Janosh Rebesail; Lawrence Berkeley National Laboratory, United States

Machine-learned force fields have transformed the atomistic modelling of materials by enabling simulations of ab initio quality on unprecedented time and length scales. However, they are currently limited by: (i) the significant computational and human effort that must go into development and validation of potentials for each particular system of interest; and (ii) a general lack of transferability from one chemical system to the next. Here, using the state-of-the-art MACE architecture we introduce a single general-purpose ML model, trained on a public database of 150k inorganic crystals, that is capable of running stable molecular dynamics on molecules and materials. We demonstrate the power of the MACE-MP-0 model - and its qualitative and at times quantitative accuracy - on a diverse set problems in the physical sciences, including the properties of solids, liquids, gases, chemical reactions, interfaces and even the dynamics of a small protein. The model can be applied out of the box and as a starting or "foundation model" for any atomistic system of interest and is thus a step towards democratizing the revolution of ML force fields by lowering the barriers to entry.

11:45 AM MT01.05.08
Machine-Learning Solar Cell Efficiency from a Dataset of Continuum Simulations

Andrea Crovetto; Technical University of Denmark, Denmark

Power conversion efficiency limits of solar cells based on ideal semiconductors are well known as a function of the semiconductor’s band gap energy (Shockley-Queisser limit and their derivatives). However, it is notoriously difficult to estimate the maximum photovoltaic (PV) efficiency potential of real-world materials featuring a number of unavoidable imperfections. In this contribution, I will show that this problem can be addressed by integrating a dataset of 30,000 drift-diffusion (continuum) simulations with machine learning to estimate the PV efficiency of a generic, non-ideal PV material. With this data-driven approach, and unlike any previously reported method, a generalized effect of, e.g., finite carrier mobilities and doping...
differences on the maximum PV efficiency can be modeled.

Importantly, the simulation dataset is not static but instead new data can be collected in a closed-loop fashion, depending on how the machine learning model performs with the available data at a given time. Furthermore, the relevant solar cell physics is incorporated into the model at various stages of our workflow, resulting in a favorable trade-off between statistical generality and physical understanding.

The relevancy of the machine-learned PV efficiency is demonstrated on a sample of 16 PV materials of current research interest. The method can immediately be applied to experimentally synthesized or computationally examined materials at any development level, as long as seven of their bulk material properties (the basic descriptors) have been determined by experiment of first-principles calculations.

**SESSION MT01.06: Machine Learning and Simulations VI**

**Session Chairs:** Aditi Krishnapriyan and Taylor Sparks

**Wednesday Afternoon, April 24, 2024**

Room 320, Level 3, Summit

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**1:30 PM • MT01.06.01**

**Harnessing Materials Imperfections: Case Studies of ‘Defects’ in Materials for Energy Sustainability**

Wenjin Wang, University of Texas at Austin, United States

We present work in the Wang Materials Group (https://wangmaterialgroup.com) in understanding and harnessing defects in materials for energy sustainability applications that leverage and/or are inspired by aspects of machine learning. Our goal is to elucidate and predict the materials properties at the microscopic level using first-principles calculations, drive the exploration of novel materials platforms, and create strategies that directly couple to/guide experiments. Here, we present on two such case studies on next-generation memory and storage applications and electrocatalysts.

Memristors are an emerging memory technology that can help meet the capacity and energy efficiency demands. Non-volatile resistive switching (NVRs) between high- and low-resistance states has been broadly observed in a variety of two-dimensional materials. As atomically thin systems, two-dimensional materials are promising as the active switching layer for two-terminal vertically stacked memristor devices. We examine one particular mechanism of NVRs based on the formation and dissolution of point defect complexes to describe the switching energetics and switching processes. In this talk, we will present our efforts in leveraging automated calculations to screen for defects capable of inducing NVRs in two-dimensional materials and extract materials-based scaling relationships for the switching energy.

In the second case study, we turn to the investigation of structure and catalytic activity relationships in electrocatalysts. Low-temperature electrocatalysis of water is at the forefront of strategies that could help realize a clean hydrogen economy. The (oxy)hydroxides are scientifically significant as electrocatalysts that electrochemically form on many pre-catalyst surfaces in the amorphous state. Interestingly, amorphous electrocatalysts have been reported to consistently outperform crystalline ones. Our goal is to connect the structural disorder in amorphous electrocatalysts to mechanisms in enhancing the electrocatalytic activity. We will discuss the considerations to appropriately describe the electronic and atomic structure in using point defects and genetic algorithms to understand local structural disorder.

**2:00 PM • MT01.06.02**

**Anion Charge Distribution Effects of Lithium Diffusion in Polymer Electrolytes Using End to End Force Field Parameterization through Machine Learning**

Pablo A. Leon and Rafael Gomez-Bombarelli; Massachusetts Institute of Technology, United States

Solid polymer electrolytes (SPEs) are seen as promising alternatives to conventional liquid electrolytes in lithium battery systems due to their low density, mechanical compliance, and low flammability but are challenged by lower ionic conductivity. Molecular dynamics (MD) simulations can be used to guide the design of novel SPEs by allowing quantitative determination of separable anion and cation diffusions as well as local solvation environments. Classical potential MD simulations update molecular conformations by the net force on each atom due to covalent and nonbonded interactions. However, these classical potentials require materials- and local environment-specific parameters such as nonpolarizable point charges on each atom that have historically been meticulously hand-tuned across decades.

In this work, we explore the effects of using distinct anion charge distributions based on minimum energy Lithium-ion specific interactions on solvation and conductivity in polymer electrolyte simulations. An in-house, machine learning-based workflow, named AuTopology, was used to autonomously learn the interatomic potential parameters of unique atomic environments for two different classical models from DFT forces as training data. In particular, the effect of machine learning regularization and chemistry-informed training data selection on resulting polymer-ion system behavior is highlighted. The learned harmonic OPLS model and anharmonic PCFF+ model parameters were then used to equipulate condensed-phase simulations at a variety of experimentally-relevant concentrations. These simulations were allowed to run for hundreds of nanoseconds to determine the individual anion and cation diffusivities and resulting conductivities. Using this framework and an in-house database of molecular conformations, we have been able to reproduce wB97XD3-level DFT forces from trained OPLS force fields within 5.5 kcal/mol-A. Lithium solvation environments and ion diffusivities were found to match legacy parameterizations to the same order of magnitude.

**2:15 PM • MT01.06.05**

**Elucidating Structural Heterogeneity of Amorphous Materials with X-Ray Absorption Spectroscopy and Machine Learning**

Hyuna Kwon, Yu-Ting Hsu, Wonseok Jeong, Wenyu Sun, Liwen Wan, Michael Nielsen and Yuan Anh Pham; Lawrence Livermore National Laboratory, United States

The ability to precisely determine the atomic structure of functional materials would have a transformative and broad impact on a broad range of emerging technologies, from energy storage and conversion to ion-selective membranes. In this talk I will summarize our recent activities in integrating atomistic simulations, data science, and spectroscopic measurements to elucidate structure and chemical heterogeneities in disordered systems. I will show how machine learning potential is used to efficiently explore the vast conformational space of amorphous carbon nitrides and to identify the local structural motifs of the systems. Density functional theory simulations were used to establish a correlation between the local structure motifs and X-ray absorption spectroscopic signatures, which then serves as the basis for interpreting and extracting chemical content from experimental data. Beyond predicting the chemical content, I will also discuss a strategy to predict the three-dimensional atomic structure of amorphous systems from X-ray absorption spectroscopy via a generative diffusion model. Using amorphous carbon as a case study, it is found that the generative model exhibits a remarkable scale-agnostic property, enabling the generation of large-scale atomic structures, while being able to accurately predict the atomic structure from targeted spectroscopy. The methods developed here are general and can be broadly applied for inverse design of functional materials.

**3:30 PM BREAK**

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**3:30 PM • MT01.06.04**

**Uncertainty Quantification in Machine Learning Models of Materials Properties**

Dane Morgan¹, Ryan Jacobs¹, Lane Schultz¹, Vidit Agrawal¹, Shixin Zhang¹, Glenn Palmer², Ben Blaizek³, Arianna Courtas¹ and KJ Schmidt¹;¹University of Wisconsin--Madison, United States; ²Duke University, United States; ³The University of Chicago, United States

Machine learning models are being increasingly used to predict an enormous range of materials properties. Such models are typically trained on computed and/or experimental data that has strong biases in terms of the sampled systems, potentially leading to models with limited accuracy and very specific domains. It is therefore of increasing importance to establish effective practices for uncertainty quantification of machine learning models used for materials properties. In this talk we share an approach that divides uncertainty quantification into separate challenges of error and domain determination, which together provide a strong framework for practical uncertainty quantification. This approach leads to uncertainty quantification that can guide users whether prediction on any given test data point is likely to be appropriate, and if it is appropriate, what accuracy might be expected. For determining errors, we demonstrate that, when properly calibrated, ensembles of models fit to bootstrap sampling of training data can provide robust and easily accessible estimates of test data point residuals[1]. For determining domain, we demonstrate that a kernel density estimate of training data density in feature space can be used to identify regions of feature space with inadequate sampling and therefore likely to be out of domain. Assessing any domain determination strategy is difficult as there is no unique ground truth for a test data point being in or out of domain. To manage this problem we propose a set of criteria for ground truth based on matching chemical intuition and expected large residuals and residual estimation errors with being out of domain. We show that a kernel density approach can generally categorize new test data points as in/out of domain with good accuracy (e.g., max F1 scores of about 80% or better) when using any of these criteria. Finally, we discuss how these methods can be trivially integrated into model fits through the MAST-ML² package and how such uncertainty aware models can be easily hosted in the cloud through the Foundry³ service.

X-ray absorption spectroscopy (XAS) is a premier materials characterization technique, which is element specific and sensitive to the local chemical environment. However, the physical information in XAS, in particular, x-ray absorption near-edge structure (XANES), is encoded in the spectral function in an abstract form. First principles calculations are widely used to unravel the complex structure-spectrum relationship. However, this approach requires a great deal of expertise and is computationally expensive. These drawbacks limit the scope of XAS modeling for complex systems and in real-time analysis. To address this challenge, data-driven XAS analysis methods emerge, which take advantage of the fast developing machine learning tools for spectral interpretation.

Successful examples show that machine learning models can be used to accelerate XAS simulations and identify the physical origin of spectral trends in a statistically salient way.

In this study, a semi-supervised machine learning method for the discovery of structure-spectrum relationships is developed and then demonstrated using the specific example of interpreting XANES spectra. This method constructs a one-to-one mapping between individual structure descriptors and spectral trends. Specifically, an adversarial autoencoder is augmented with a rank constraint (RankAAE). The RankAAE methodology produces a continuous and interpretable latent space, where each dimension can track an individual structure descriptor. As a part of this process, the model provides a robust and quantitative measure of the structure-spectrum relationship by decoupling intertwined spectral contributions from multiple structural characteristics. This makes it ideal for spectral interpretation and the discovery of descriptors. The capability of this procedure is showcased by considering five local structure descriptors and a database of XANES spectra. This method constructs a one-to-one mapping between individual structure descriptors and spectral trends. Specifically, an adversarial autoencoder is augmented with a rank constraint (RankAAE). The RankAAE methodology produces a continuous and interpretable latent space, where each dimension can track an individual structure descriptor.

In our work, we introduce a physics-informed robust analysis of XANES spectra, striking a balance between reconstruction and descriptor-specific information. Our method, the Multitasking Algorithm for Variational Auto Encoder (MAVEN), achieves a disentangled, interpretable latent space through multi-objective optimization, focusing on reconstruction, denoising, autoencoding, and descriptor mapping. MAVEN stands out for its ability to disentangle and interpret latent space variables, offering a unique generative capability within the autoencoder framework. We’ve also developed a methodology to quantify the level of disentanglement achieved, rooted in information theory principles. We show the utility of MAVEN by interpreting experimental XANES of palladium and palladium hydride nanoparticles. These are renown for their lattice expansion, which MAVEN distinguishes from particle size effects via coordination number analysis. The comparison of trends from the MAVEN algorithm to those obtained from extended x-ray absorption fine structure (EXAFS) spectral analysis using Demeter software indicates MAVEN’s potential for high-fidelity real-time analysis of local structures. Our discussions will explore the applications of this technique in bimetallic nanoparticles systems and assess its effectiveness on experimental XANES spectra.

The thermodynamics of alloy components determine material structures, properties and hence the processability and performance matrices of engineering alloys. Incorporating grain boundaries in thermodynamic models is not a simple task: grain boundary defects in polycrystals occupy a wide 5-dimensional configuration space, imposing a computational barrier in evaluating thermodynamic data across the chemical space. This complexity calls for a combination of recent advances in data science approaches and computational materials science. This talk will first discuss an isotherm approach in modeling equilibrium solute behavior at grain boundaries and show that relevant spectral thermodynamic quantities can be extracted from atomistic simulations. Then, data-science and machine-learning enabled accelerated models are presented to understand the work to many alloy systems. Finally, a full-spectral case study of a binary alloy system with the inclusion of rapid estimations of dilute segregation energies, solute-solute interactions at grain boundaries and excess vibrational entropy of segregation is presented. These accelerated models open opportunities to construct an embedded alloy grain boundary atlas, which ultimately can assist in alloy design.

Learning Grain Boundary Thermodynamic Spectra in Polycrystals
Christopher A. Schuh1,2, Nutth Tuchinda1, Thomas Matson2 and Malik Wagh1; 1Northwestern University, United States; 2Massachusetts Institute of Technology, United States.

The thermodynamics of alloy components determine material structures, properties and hence the processability and performance matrices of engineering alloys. Incorporating grain boundaries in thermodynamic models is not a simple task: grain boundary defects in polycrystals occupy a wide 5-dimensional configuration space, imposing a computational barrier in evaluating thermodynamic data across the chemical space. This complexity calls for a combination of recent advances in data science approaches and computational materials science. This talk will first discuss an isotherm approach in modeling equilibrium solute behavior at grain boundaries and show that relevant spectral thermodynamic quantities can be extracted from atomistic simulations. Then, data-science and machine-learning enabled accelerated models are presented to understand the work to many alloy systems. Finally, a full-spectral case study of a binary alloy system with the inclusion of rapid estimations of dilute segregation energies, solute-solute interactions at grain boundaries and excess vibrational entropy of segregation is presented. These accelerated models open opportunities to construct an embedded alloy grain boundary atlas, which ultimately can assist in alloy design.

Artificial Neural Network Interatomic Potentials Developed for Grain-Boundary Modeling in Al2O3 Ceramics
Katsumuki Matsunaga1,2, Tatsuya Yokoi1 and Yu Ogura1; 1 Nagoya University, Japan; 2 Japan Fine Ceramics Center, Japan.

Excellent structural and functional properties of ceramic materials often originate from their grain boundaries and interfaces. Therefore, it is essential to obtain in-depth understanding of electronic and atomic structures of the grain boundaries for materials design. However, crystal structures of ceramic components such as oxides are generally low symmetry and thus contain many atoms, so that a great number of atoms should be inevitably handled in the grain boundary modeling. This often makes it difficult to systematically treat the grain boundary structures at the first-principles level. In the present study, artificial neural network interatomic potentials trained by first-principles data were developed for Al2O3, which is a representative ceramic oxide, and applied for their grain boundaries. Grain boundary structures thus obtained were compared with experimental STEM images to verify accuracy of the potentials. On the basis of the calculated grain boundary structures, first-principles calculations were again applied to investigate specific electronic structures of the grain boundary cores that are closely related to the grain boundary properties. Some other examples such as extension to multicomponent systems for the segregated grain boundaries will also be discussed.

On Neural Networks for Grain Boundary Dynamics
Fadi Abdeljawad1; Malek Alkaayali2 and Milad Taghizadeh; 1 Lehigh University, United States; 2 Clemson University, United States.

Nearly all structural and functional materials are polycrystals; they are composed of differently oriented crystalline grains that are joined at grain boundaries (GBs). Such interfaces play a critical role in controlling many engineering and functional properties. Understanding GB physics is, therefore, a key aspect of materials discovery and design efforts. Owing to their local atomic environments, GBs provide preferential sites for alloying elements to occupy. Indeed, the direct manipulation of GB chemical states has been found to influence a host of materials properties and processes, such as cohesion and fracture resistance, transport, electrochemical response, electrical conductivity, and processability during advanced manufacturing techniques. Of
Machine Learning Derived Periodic Table for High Entropy Alloys

Machine Learning of Defect Kinetics for Multi-Principal Element Alloys

Neural Network of Defect Kinetics for Multi-Principal Element Alloys

Electronic Moment Tensor Potentials (eMTPs): a class of machine-learning interatomic models and a generalization of the classical MTPs, reproducing both the electronic and vibrational degrees of freedom, up to the accuracy of ab initio calculations (Srinivasan et al., 2023). Following the original polynomial interpolation idea of the MTPs, the eMTPs are defined as polynomials of vibrational and electronic degrees of freedom, corrected to have a finite interatomic cutoff. Practically, an eMTP is constructed from the classical MTPs fitted to a training set, whose energies and forces are calculated with electronic temperatures corresponding to the Chebyshev nodes on a given temperature interval. The eMTP energy is a Chebyshev interpolation of the classical MTPs. With eMTPs, one can access the temperature-dependent electronic and vibrational free energies and the coupling between the two, separately.

The performance is demonstrated on two classes of systems: (1) refractory Nb and TaVCrW high-entropy alloy, and (2) equiatomic Nickel-Titanium (NiTi) shape-memory alloy (SMA). The refractories demonstrate a significant electronic, vibrational, and coupling contribution to the free energy, all of which get captured accurately by performing a thermodynamic integration (Jung et al., 2022) to the eMTPs. We are able to reach full density-functional theory accuracy in thermodynamic properties all the way to the melting point without any further ab initio calculations.
The NiTi SMA is considerably more challenging to model owing to several energetically competing phases (body-centered cubic B2, monoclinic B19\textsuperscript{\textordmasculine}, orthorhombic B19 and base-centered orthorhombic B33). We train an eMT model to obtain the thermodynamic phase stability including all relevant contributions. The experimentally observed low-temperature martensitic (B19\textsuperscript{\textordmasculine}) and high-temperature austenitic (B2) phases get entropically stabilized. Both the vibrational and electronic contributions also significantly affect the B2-B19\textsuperscript{\textordmasculine} phase transformation, bringing the behavior much closer to experiments. The eMT-thermodynamic integration approach enables us to analyze the accuracy of different exchange correlation functionals and \textit{ab initio} parameters. Lastly, to investigate kinetic effects, we perform large-scale molecular dynamics simulations using the eMT to model the stress-induced and temperature-induced phase transformation.

### References

1. Srivasan P., Demuria D., Grabowski B., Shapeev A.V.: preprint at research square https://doi.org/10.21203/rs.3.rs-2643432/v1, 2023
The liquidus curve captures the high-temperature eutectics, peritectics, congruent melting and incongruent melting regions of a phase diagram. Being able to predict liquidus curves would enable an \textit{ab initio} guidance of materials synthesis temperatures, as well as the design of materials stable under high-temperature operation conditions. Liquidus curves are available in databases like Thermodata or SGTE, but the available chemical spaces in these databases lag far behind computational materials discovery efforts. Direct simulation of liquid free energies across broad chemical spaces is probably infeasible (even using machine-learned interatomic potentials) given the wide range of temperatures and compositions that must be sampled. Here, we present a CALPHAD-inspired approach to reference liquidus curves from experimental ASM phase diagrams to DFT convex hulls from the Materials Project. Using this technique, we fit non-ideal liquid mixing free-energies on a 50x50 matrix of binary alloy phase diagrams. Using very simple machine-learning models, we can then predict liquid free energies in novel chemical spaces, including ternary or quaternary + spaces, at a computational cost low enough to be integrated with high-throughput DFT databases like the Materials Project. Our technique predicts liquidus curves, intermetallic melting temperatures, and three-phase invariant points (eutectics and peritectics) with surprisingly good accuracy, despite the known magnitude of formation energy errors in DFT convex hulls.

### References


### 4:30 PM MT01.08.08

**Machine Learning and Monte Carlo Simulations of The Gibbs Free Energy of The Fe-C System in a Magnetic Field**

Ming Li\(^1\), Luke Wirth\(^2\), Ajinkya Hire\(^3\), Stephen Xie\(^1\), Michele Campbell\(^4\), Dallas Trinkle\(^1\) and Richard Hennig\(^1\); University of Florida, United States; \(^2\)University of Illinois at Urbana-Champaign, United States; \(^3\)KBR, Inc., Intelligent Systems Division, NASA Ames Research Center, United States; \(^4\)University of California-Merced, United States

To model the thermodynamics and kinetics of steels in response to high magnetic fields requires knowledge of the magnetic Gibbs free energy, which involves millions of energy evaluations for the potential energy landscapes as a function of the applied field in the configurational space. Although sufficiently accurate, density-functional theory (DFT) calculations would result in high computational cost, hindering its direct application.

To address this challenge, we take advantage of the ultra-fast force field (UF3) method \(^1\), a machine-learning potential that combines effective two- and three-body potentials in a cubic B-spline basis with regularized linear regression, to approximate the DFT energy landscape. We assembled a database by performing DFT calculations using the Vienna Ab initio Simulation Package (VASP). This DFT database focuses on the information of the energies and forces as a function of magnetic field for a series of bcc and fcc Fe(C) structures, throughout which both structural and magnetic configurations are varied. The UF3 potentials are trained on this database to quickly evaluate the energies of ensembles based on the structural and spin configurations, and the accuracy of the resulting UF3 models predicting energies and forces is validated.

Subsequent Monte Carlo simulations take place with these machine learning models implemented. Thermodynamic integration is utilized to combine the simulations at different temperatures to achieve the magnetic Gibbs free energy models for the two Fe(C) phases as a function of temperature, atomic fraction of carbon, and magnetic field. Our calculations aim to investigate the origin of the experimentally observed shift in the transition temperature of tens of kelvins under an applied field of 10 T \(^2\).

\(^1\) Xie, S.R., Rupp, M., and Hennig, R.G., npj Comput Mater 9, 162 (2023)


### 4:45 PM MT01.08.09

**Engineering Relative Stability in Four Dimensions with The Generalized Clausius-Clapeyron Relation**

Jiadong Chen and Wenhao Sun; University of Michigan, United States

Sequential learning algorithms based on Bayesian optimization are routinely deployed for materials stability optimization in high-parameter spaces. We anticipate these optimization methods would perform better if they were built upon stronger priors, for example, as derived from the fundamental thermodynamics underlying the equilibrium behavior of materials. Here, we present a thermodynamics-based technique to optimize the relative stability of a material in a high-dimensional thermodynamic space, based on a new derivation of a generalized high-dimensional Clausius Clapeyron relation. Using this thermodynamic infrastructure, we design several pathways to enhance the relative acid stability of Mn-oxides versus its dissolved states for potential electrochemical catalyst application. We construct a 4-D Fourier diagram with pH, redox potential \(E\), particle radius \(1/R\) and a chemical potential \(\mu_H\) as axis. By exploring the gradients of the high-dimensional phase boundaries, we derive first-principles insights that nano-sizing \((1/R)\) and certain doping ions \((\mu_H)\) can stabilize some metastable Mn-oxides polymorphs, where \(1/R\) decreases acid stability and \(\mu_H\) increases it. Our high-dimensional thermodynamic framework is a general method to engineer relative stability in parameter spaces that leverage multiple forms of thermodynamic work.

### 5:00 PM MT01.09.01

**Rapid Discovery of Lightweight Cellular Crashworthy Solids for Battery Electric Vehicles using Artificial Intelligence and Finite Element Modeling**

Edward J. Michaud\(^1,2\) and Dayakar Penumadu\(^1\); Volkswagen Group of America, United States; \(^1\)The University of Tennessee, Knoxville, United States

Battery electric vehicles (BEVs) offer significant environmental benefits over traditional internal combustion engine (ICE) vehicles, including zero tailpipe emissions and improved energy efficiency. Despite this, typical BEV batteries can weigh up to 500kg, substantially heavier than a conventional vehicle's engine and fuel tank. This makes BEVs great candidates for lightweighting, offering improvements in driving range, acceleration, handling, and overall efficiency. At the same time, these batteries must be protected from side-impact even further than a conventional ICE vehicle.

In this study, we aim to leverage computational modeling and artificial intelligence (AI) methods to lightweight the battery's protective structures beyond capabilities achievable by a typical human. Specifically, we focus on the methods necessary to train an artificial intelligence architectire such that models can be rapidly generated and validated hundreds to thousands of times. Ultimately, this research will contribute to the development of more efficient and sustainable BEVs, which can help to mitigate climate change and reduce the environmental impact of transportation while maintaining or improving safety standards.

### 5:00 PM MT01.09.02
Finally, we will apply the DPMD force field to an ionic liquid and perovskite interface system, which is virtually impossible to simulate from using traditional force fields. Experiments have

Recently, ab-initio molecular dynamics (AIMD) based DeePMD (DPMD) potential has not only improved computational accuracy and speed but has also overcome the limitations of traditional

results demonstrate a square-root dependence of the etching yield on the incident energy. Furthermore, we observe modifications at the topmost surface, where the ratio of Si to N is 1:1. This

computationally prohibitive for large-scale simulations. Recent advances in machine-learning potentials (MLPs) have demonstrated their efficacy in simulations involving surface catalysis,

Molecular Dynamics Simulation of HF Etching of Amorphous Si$_3$N$_4$ Using Neural Network Potential Changho Hong, Sangmin Oh and Seungwu Han; Seoul National University, Korea (the Republic of)

Molecular Dynamics Simulation of HF Etching of Amorphous Si$_3$N$_4$ Using Neural Network Potential Changho Hong, Sangmin Oh and Seungwu Han; Seoul National University, Korea (the Republic of)

Dry etching plays a key role in the fabrication of semiconductor devices. Recently, the requirement of high aspect ratios (40–60) of deep-trench structures and the introduction of through-silicon vias for 3D circuit integration demand precise etching control. Traditional macroscale models, such as the level set and Monte Carlo-based methods, have been employed to predict the outcomes of process parameter optimization. However, phenomenological fitting of model parameters can result in inaccurate predictions of feature profiles due to the omission of detailed chemical processes. Molecular dynamics (MD) simulations can offer a close look into atomic processes in ion etching, overcoming the trial-and-error approaches for parameter determination in macroscopic simulation models. Classical potentials are an option but have limitations in both availability and accuracy. Density functional theory (DFT), although highly accurate, is computationally prohibitive for large-scale simulations. Recent advances in machine-learning potentials (MLPs) have demonstrated their efficacy in simulations involving surface catalysis, physical sputtering, and surface oxidation processes. However, application of MLPs for etching reactions between ions and solid-state materials is currently lacking. This is attributed to the complexity of predicting chemical reaction pathways, which creates challenges in constructing training sets for MLPs.

In this study, we investigate the mechanisms underlying Si$_3$N$_4$ etching by HF ions using MD simulations driven by a neural network potential (NNP). The NNPs are trained using SIMPLE-NN package. The training set is constructed through manual curation of relevant atomic environments and an iterative training process. The basic constituents of atomic configurations are both crystalline and amorphous bulk structures, as well as their slab counterparts. Additionally, guided MD is employed to sample the chemical reactions between HF molecules and the Si$_3$N$_4$ substrate; here, hydrogen and fluorine are displaced toward nitrogen and silicon respectively based on the assumption of bond preference. Alongside guided MD, high-temperature MD of a slab is used to facilitate the sampling of diverse local atomic environments that may emerge during energetic ion collisions. Using manually curated training sets, NNPs are iteratively validated and refined. This refinement is achieved by incorporating structures from NNP trajectories that exhibit significant energy discrepancies when compared against DFT calculations. Utilizing this optimized NNP, we conduct etching simulations on 4 nm$^2$ amorphous Si$_3$N$_4$ substrates over a 5 ns timescale, and analyze characteristics such as etching yield and surface modification. Our results demonstrate a square-root dependence of the etching yield on the incident energy. Furthermore, we observe modifications at the topmost surface, where the ratio of Si to N is 1:1. This ratio is intriguingly similar to observations from experimental studies utilizing different reactive plasma species. The primary etch products at normal incidence are SiF$_2$, SiF$_4$, N$_2$, and H$_2$. This behavior is attributed to chemical sputtering, in which the surface is significantly modified by incoming reactive species, becoming susceptible to chemical etching. In contrast, at high angles of incidence, the surface remains largely unmodified, with the primary etch products being lower-coordinated molecules of Si and N, along with N$_2$ molecules. This suggests that under these conditions, the etching is more affected by physical sputtering. Our methodology offers a cost-efficient approach to achieving DFT-level accuracy in MD simulations, thereby elucidating etching mechanisms and contributing to the optimization of the etching process.

Deep Potential Model for Analyzing Enhancement of Lithium Distributions at Ionic Liquid and Perovskite (BaTiO$_3$) Interface Ansong Park, Sangdeok Kim, Chanui Park, Woonjae Kang, Seungtae Kim and Won Bo Lee; Seoul National University, Korea (the Republic of)

Recently, ab-initio molecular dynamics (AIMD) based DeepMD (DPMD) potential has not only improved computational accuracy and speed but has also overcome the limitations of traditional force-field-based methods. In this study, we will discuss the technical details and considerations for utilizing this deep learning-based force field, particularly in multi-component systems such as ionic liquids. We will compare the results of structural and dynamical properties calculated from traditional force fields, scaled charge force fields, polarizable force fields, and DPD force fields. Finally, we will apply the DPDMD force field to an ionic liquid and perovskite interface system, which is virtually impossible to simulate from using traditional force fields. Experiments have
shown that the hybrid solid electrolyte (HSE), consisting of nanoscale perovskite particles mixed with an ionic liquid (IL), exhibits excellent flame retardancy, thermal stability, and improved ionic conductivity compared to pure IL electrolyte. We will analyze the structural and dynamical differences induced by the perovskite interface in comparison to bulk ionic liquid using DPD-MD field simulations.

5:00 PM MT01.09.08  Autonomous AI generator for Machine Learning Interatomic Potentials Bowen Zheng and Grace Gu; University of California, Berkeley, United States

Machine learning interatomic potentials (MLIPs), which predict the system potential energy given an atomic configuration, have profoundly improved the accuracy and efficiency of molecular simulations. Learning from high-fidelity quantum chemistry-based data while interfacing with classical simulation frameworks, MLIPs inherit the quantum-level accuracy and the efficiency of classical molecular dynamics, achieving the best of both worlds. In recent years, MLIPs have witnessed great research efforts and various types of MLIPs have been proposed, tested, and documented. However, the development of MLIPs has largely been a manual, ad hoc process. Additionally, effective MLIPs are either scattered in online repositories such as Git-Hub or provided as supplementary materials of publications, making them difficult to locate and retrieve when needed. Here, we aim to create an autonomous AI generator for MLIPs, which consists of a Searcher, a Trainer, and an Evaluator. Given a request, for example, “generate an MLIP for Indium phosphide system”, the Searcher is first up to the task, looking for available MLIPs online via web scraping or APIs. If such MLIPs do not exist, the Trainer then performs the following tasks in sequence autonomously: select an MLIP template (such as a neural network or a SNAP MLIP, upon request or by certain criteria), generate DFT-MD training trajectories, and train the MLIP. For an MLIP returned either by the Searcher or the Trainer, the Evaluator calculates various accuracy metrics such as the mean absolute errors (MAEs) and R-squared values. It is also viable to request training multiple types of MLIPs and compare their performances. Lastly, we propose a large language model (LLM)-based agent named ChatMLIP which accepts textual user requests and delivers appropriate responses. By way of AI, the present work may accelerate the development of MLIPs and potentially benefit boarder research fields like carbon capture, protein engineering, drug discovery, among others.

5:00 PM MT01.09.10  Benchmarking, Visualization and Hyperparameter Optimization of UF3 to Enhance Molecular Dynamics Simulations Pawan Prakash, Ajinkya Hire and Richard Hennig; University of Florida, United States

Ab initio methods offer great promise for materials design, but they come with a hefty computational cost. Recent advances with machine learning potentials (MLPs) have revolutionized molecular dynamics simulations by providing high accuracies approaching those of ab initio models but at much reduced computational cost. Our study evaluates the ultra-fast potential (UF3), employing linear regression with cubic B-spline basis for learning effective two- and three-body potentials. On benchmarking, UF3 displays comparable precision to established models like GAP, MTP, NNP(Behler Parrinello), and qSNAP MLPs, yet is significantly faster by two to three orders of magnitude. A distinct feature of UF3 is its capability to render visual representations of learned two- and three-body potentials, shedding light on potential gaps in the learning model. In refining UF3’s performance, a comprehensive sweep of the hyperparameter space was undertaken, emphasizing finer granularity in zones indicative of optimal performance. This endeavor aims to provide insights into the smoothness of the UF3 hyperparameter space, and offers users a foundational default set of hyperparameters as a starting point for optimization. While our current optimizations are concentrated on energies and forces, we are primed to broaden UF3’s evaluation spectrum, focusing on its applicability in Molecular Dynamics simulations. The outcome of these investigations will not only enhance the predictability and usability of UF3 but also pave the way for its broader applications in advanced materials discovery and simulations.

5:00 PM MT01.09.11  Generating Statistically Equivalent Thermal Spray Coatings Using Bayesian Optimization David Montes de Oca Zapain, Anh Tran, Nathan W. Moore and Theron Rodgers; Sandia National Laboratories, United States

Thermal spray deposition is an inherently stochastic manufacturing process used for generating thick coatings of metals, ceramics and composites. The generated coatings exhibit complex internal structures that affect the overall properties of the coating. The deposition process can be adequately simulated using rules-based process simulations. Nevertheless, in order for the simulation to accurately model particle spreading upon deposition, a set of pre-defined rules and parameters need to be calibrated to the specific material and processing conditions of interest. The calibration process is not trivial given the fact that many parameters do not correspond directly to experimentally measurable quantities. This work presents a protocol that automatically calibrates the parameters and rules of a given simulation in order to generate the synthetic microstructures with the closest statistics to an experimentally generated coating. The protocol starts by quantifying the internal structure using 2-point statistics and then representing it in a low-dimensional space using Principal Component Analysis. Subsequently, our protocol leverages Bayesian optimization to determine the parameters that yield the minimum distance between synthetic microstructure and the experimental coating in the low-dimensional space. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy National Nuclear Security Administration under contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government. SAND No. SAND2023-10921A

5:00 PM MT01.09.12  Anisotropic Assembly of Nanoparticles Explored Through Molecular Dynamics Simulations, Global Optimizations and Machine Learning Methods Yilong Zhou1,2, Tsungyeoh Tang3, Sigbjorn L. Bore3, Francesco Paesani2 and Gaurav Arya2; 1Lawrence Livermore National Laboratory, United States; 2Duke University, United States; 3University of California, San Diego, United States

Novel applications of polymer nanocomposites often demand anisotropic organization of nanoparticles (NPs) in polymers. However, achieving unique anisotropic assemblies of NPs in polymers is challenging since NPs tend to self-assemble into three-dimensional close-packed aggregates. In this work, we tackle this challenge of achieving anisotropic NP assembly in polymers through a combination of molecular dynamics (MD) simulations, global optimization, and machine learning. First, we present a new strategy for assembling NPs into anisotropic architectures in polymer matrices, which leverages the interfacial tension between two mutually immiscible polymers forming a bilayer and differences in the relative miscibility of polymer grafts with the two polymer layers to confine NPs within 2D planes parallel to the interface. Through coarse-grained (CG) MD simulations, we demonstrate this strategy, showcasing the assembly of NP clusters, such as trimers with tunable bending angle and anisotropic macroscopic phases, including serpentine and branched structures, ridged hexagonal monolayers, and square-ordered bilayers. The above MD simulations are however inefficient for determining the equilibrium structures of NP assemblies, particularly those involving many particles or complex unit cells. To address this issue, we adapt the efficient Basin-hopping Monte Carlo algorithm to locate the global minimum energy configurations of NPs at interface, allowing us to explore the full breadth of NP structures possible at interface and uncovering many unique NP structures. While exploring the assembly of polymer-grafted NPs at polymer interfaces using explicit CG MD simulations, we observe that many-body effects play an important role in the formation of quasi-1d structures. However, explicit modeling of the polymer grafted and melt chains is highly computationally expensive, even using CG models. We thus introduce a machine learning approach to develop an analytical potential that can describe many-body interactions between polymer-grafted NPs in a polymer matrix. The developed potential reduces the computational cost by several orders of magnitude and thus allows us to explore NP assembly at large length and timescales. Overall, the anisotropic NP structures discovered in this study hold significant potential for applications in various fields, including plasmonics, electronics, optics, and catalysis, where precise and anisotropic NP arrangements within polymers are essential for achieving desired functionalities.


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

5:00 PM MT01.09.13  Differentiable Gaussian Process Force Constants Keerati Keeratikarn and Jarvist M. Frost; Imperial College London, United Kingdom

The finite temperature properties of matter requires understanding thermal motion. In crystals this can be described by representing the collective excitation of the centre of mass motion as a phonon. Phonon energies (Energies) in the harmonic approximation come from the second order force constants (FC) of the potential energy surface (PES). The standard approach is to use a finite displacement method (FDM). Anharmonic contributions (required for finite thermal conductivity) require higher order force constants. FDM-based calculations scale poorly both with the size of the system and the order of the force constants[1]. As an alternative approach, we can use a more sophisticated surrogate potential energy surface model [2].

Gaussian processes (GPs) are a supervised machine learning method which can describe an arbitrary
function. GPs are naturally Bayesian (probabilistic). Our reference data is the electronic structure from which conditions the model (training) [3, 4].

Due to the underlying Gaussian form of a GP, the model is infinitely differentiable [5, 6]. This allows the model to be trained directly on forces (the derivative of energy), reducing the number of calculations required for a given accuracy of PE evaluation [7-9]. This differentiation can be extended to compute the second and the third derivative of PESs (harmonics and cubic anharmonic FCs) by using automatic differentiation (AD). By performing linear operations between arbitrary derivative orders of the GP, the covariance functions among PESs, forces and those FCs can be calculated.

We implement this method in the Julia language, in our GPPC.jl package. We first use our technique of anharmonic property calculations of Si, NaCl and PdTe which their atomic environments are represented on atomic Cartesian coordinates. To impose their space group symmetry, phonon coordinate representations are then used to describe the environment of these three materials resulting in faster convergence of anharmonic properties. To further impose a three-dimensional rotation symmetry, we aim to use an SO(3) representation (such as spherical harmonics) with our GP method to achieve accurate FCs with less data [3, 10]. We compare our results to standard approach of FDM (in Phono3py.py) [2] and cluster expansion (HiPhive.py) [11].

References


5:00 PM MT01.09.14
Understanding The Interplay between Anion Dynamics and Proton Conduction in Solid-Acid Compounds Using Machine Learning Molecular Dynamics Menghang (David) Wang1, Cameron J. Owen1, Grace Xiong2, Jingxuan Ding1, Yu Xie1, Simon L. Batzner3, Albert Musaelian1, Anders Johansson1, Nicola Molinari1, Ni Zhan1, Ryan P. Adams3, Sossina M. Haile2 and Boris Kozinsky1; 1Harvard University, United States; 2Northwestern University, United States; 3Princeton University, United States

Solid acid materials play a pivotal role as electrolytes for intermediate temperature hydrogen fuel cells. However, our current understanding of the relevant atomic motions that govern proton conduction remains incomplete, necessitating further investigation in different solid acid compounds. It is imperative to explore the atomic-scale correlation between anion and proton dynamics to design novel solid acid compounds with high proton conductivity.

In the superprotonic phase, solid acid proton conductors exhibit intricate behaviors, characterized by local proton hops in the O-H...O bond and anion reorientation. These phenomena comprise a two-step process necessary for long-range proton motion. Existing computational studies treat anion and proton dynamics as independent processes, while we find strong correlations between anion and proton dynamics in both CdHPO4 (CDP) and CsDIO4 (CHS) from machine learning molecular dynamics over nanosecond timescales. Achieving a nanosecond timescale is crucial to comprehensively study the diffusive regime. We observe that not all anion reorientations contribute to long-range proton motion, underscoring its multifaceted role in superprotonic behavior. Additionally, the contribution of anion reorientations to long-range proton motion exhibits distinctive characteristics in CDP and CHS. Furthermore, we confirm a significant O-H reorientation preceding the long-range proton motion, substantiating a previously hypothesized but unverified process. Our approach leverages machine learning interatomic force fields (MLFFs) developed through uncertainty-aware active learning [1] and equivariant neural networks [2]. By combining ab-initio precision with simulations of thousands of atoms over nanosecond timescales, our MLFFs support our findings on the correlations of anion dynamics and the long-range proton transfer with sufficient statistics.

This work bridges crucial knowledge gaps in the superprotonic behavior of solid acid proton conductors and has the potential to inform the design of advanced solid acid compounds for renewable energy technologies.


5:00 PM MT01.09.16
Do Computed Grain Boundary Energies Depend on Interatomic Potentials? Universal Trends Employing EAM-X Yasir Mahmood1, Murray Daw1, Michael Chandross2 and Fadi Abdeljawad3; 1Clemson University, United States; 2Sandia National Laboratories, United States; 3Lehigh University, United States

It is well established that grain boundaries (GBs) greatly influence the observable properties of a wide range of engineering and functional materials. Classical atomistic simulations employing the Embedded Atom Method (EAM) have emerged as a powerful technique to simulate GB phenomena. However, folded into such simulations is the dependency of GB structure and properties on the particular choice of EAM parameters. To address this question, we follow a direction of investigation that has not been generally explored, namely we simplify the EAM function space to a small but efficient set of parameters, called EAM-X [1]. Then, we study a set of GBs with various geometries and calculate their energies in the complete EAM-X parameter space. We find that variations in GB energy with EAM parameters can be larger than variations due to GB geometry; an effect that has not been quantified before. The atomistic data are used to determine a fit of the GB energy in EAM-X parameter space, which can be used to obtain boundary energies in real FCC elements by selecting corresponding points in this parameter space. We find that generally there is a moderate correlation between GB energy and shear modulus, and we discuss the relationship to prior work along this parameter space. We work highlights the need to consider sensitivity to details of empirical potentials when performing quantitative studies of GB physics. SNL is managed and operated by NT&ES under DOE NNSA contract DE-N40003525 (SAND2022-1056.4).


5:00 PM MT01.09.17
Atomic Modeling of Bulk and Grain Boundary Diffusion for Solid Electrolyte Li3PS4Cl Accelerated by Machine-Learning Interatomic Potentials Yongliang On1, Yuki Ikeda2, Sergiy Divinsky3 and Blazej Grabowski2; 1University of Stuttgart, Germany; 2University of Münster, Germany; 3University of Iowa, United States

Li3PS4Cl is a promising candidate for the solid electrolyte in all-solid-state lithium-ion batteries. For applications, this material is in a polycrystalline state with many grain boundaries (GBs) rather than an idealized single-crystal state. Atomatic simulations of Li3PS4Cl with GBs, however, remain rare due to high computational cost. In this study, machine-learning interatomic potentials, specifically moment tensor potentials (MTPs) [1], are employed to accelerate the simulations while preserving the ab-initio accuracy. In the initial stage, energies and forces of a small number of configurations are generated under the ab-initio framework. MTPs are then fitted to the ab-initio data, and active learning techniques are used to further stabilize the MTPs. The usage of MTPs enables molecular dynamics (MD) simulations in larger system sizes (up to 20,000 atoms) and longer time scales (several ns). Two tilt GBs $\Sigma[110]//(1-12)$, $\Sigma[110]//(1-11)$ and one twist GB $\Sigma[001](100)$ are focused on, all of which show relatively low GB energies and an enhanced ionic conductivity for Li compared to bulk. Diffusion mechanisms specific to each GB are analyzed. This research offers new insights into the design of solid electrolytes through GB engineering and emphasizes the importance of considering GBs for materials modeling.

The application of Open Large Language Models (LLMs) in material science is revolutionizing the traditional methodologies employed in Named Entity Recognition (NER), classification, and information extraction tasks. This study aims to explore the expansive capabilities and performance limitations of LLMs in the realm of material science, underlining their role in the creation of automated databases via Retrieval-Augmented Generation (RAG) pipelines and probing their behavior through the examination of activation functions. LLMs are increasingly being used to automate the extraction of valuable insights from the expansive corpus of material science literature. They demonstrate high efficiency in NER tasks, effectively identifying and categorizing terminologies, material properties, and synthesis parameters. These capabilities extend to classification tasks, where LLMs can sort documents or data points based on pre-defined categories, such as material type, structural characteristics, or application domains. Despite these promising features, LLMs are not without their limitations. One critical issue pertains to their tendency to produce spurious or “hallucinated” outputs. To mitigate this, our study incorporates ensemble methods and evaluates the outputs through metrics like F1-score for classification tasks and ROGUE-L score for text generation tasks. The RAG pipeline is a notable advancement, developing the database creation process by combining the strengths of both retrieval and generation modules. We particularly focus on the application of RAG in creating a high-throughput, structured database of material structure-processing parameters. The RAG pipeline leverages LLMs to encode text documents into a large vector database. Queries, specified in natural language, are transformed into vector embeddings, followed by a vector similarity search. The output is then aggregated and structured, serving as a robust database for further scientific research.

To deepen our understanding of how LLMs perform in understanding the database entries, we also investigate the activation functions within these neural networks. By scrutinizing how different layers and nodes respond to specific input types, we gain valuable insights into the model's interpretability and reliability. This examination allows us to optimize the model's performance further and provides a diagnostic tool for understanding the complexities inherent in LLMs. In conclusion, this study offers a comprehensive evaluation of the utility and limitations of Open Large Language Models in material science. It elaborates on their role in automating complex NER, classification, and information extraction tasks, their implementation in RAG pipelines for database creation, and the insights gained from analyzing their activation functions. As material science stands to gain significantly from these advancements, understanding and optimizing LLMs can pave the way for more efficient and accurate research methodologies.

Nikita Fedik
5:00 PM
MT01.09.20
Developing and Optimizing an Ultra-Fast Force Field (UF3) for Modeling The Crystalization of Amorphous Silicon Nitride
Jason B. Gibson1, Tesia Janicki2, Ajinkya Hire2, Christopher Bishop3, J. Matthew D. Lane3 and Richard Henning2; 1University of Florida, United States; 2Sandia National Laboratories, United States

Crystallization of amorphous silicon nitride, as observed experimentally, can alter material properties in microelectronics process conditions as a layer-stacked component. Understanding the crystalization mechanism mandates a multi-scale approach in which quantum simulations inform atomistic simulations, which further inform continuum scale simulations and subsequently, experimental work. This talk will detail the progress and challenges faced in developing an Ultra-Fast Force Field (UF3) specifically designed to bridge quantum and atomistic simulations for the Si-N material system. The UF3 integrates effective many-body potentials within a cubic B-spline framework with regularized linear regression, creating a fast and interpretable machine-learned energy model. This model will cover the energy requirements of the MLPS training data, it needs to be diverse enough to avoid overfitting to Si3N4 stoichiometry, while maintaining enough specificity to prevent unneeded generalizations across the entire Si-N compositional range. Following this, we leverage the interpretability of UF3's 3/3-body terms to understand the MLPS' behavior and identify areas for improvement. The presentation will conclude by detailing the simulation results that were used to validate the MLP and an analysis of the simulated crystallization results of the final MLP.


5:00 PM
MT01.09.21
Navigating Transition Path Sampling with Machine Learning Potentials: Insights and Challenges
Vineeth Venugopal and Elsa O; Massachusetts Institute of Technology, United States

In the realm of molecular dynamics, capturing elusive transitions and unveiling potential energy landscapes is a paramount pursuit. Reactive events that lead a system from state A to state B through a transition path are often masked by an ensemble of energetically similar pathways. Transition path sampling (TPS) emerges as a potent tool to uncover these paths, although their infrequency in simulations due to high-energy requirements and limited statistical occurrence remains a challenge.

Machine learning potentials offer a promising avenue to model and discern these intricate transition paths, opening the door to new possibilities. The question that arises is: how do we select the right model and data? Diverse machine learning potentials, such as HIPNN and ANI, have been shown to yield varying transition paths during sampling. An illustration is found in our exploration of alanine dipeptide, a system with multiple degrees of freedom. Intriguingly, even when accuracy metrics like mean absolute error (MAE) and root mean square error (RMSE) align, these static metrics assessed on a portion of the dataset may not suffice to identify the superior model. They serve as preliminary benchmarks, rather than comprehensive tests of model performance. One avenue toward superior performance emerges through active learning sampling in the transition region. Our demonstrated approach significantly bolsters accuracy, reducing energy errors and capturing the required degrees of freedom. However, the path to progress is paved with caution when selecting transition paths for machine learning modeling. We emphasize this point using the example of azobenzene, a seemingly uncomplicated system with limited degrees of freedom, yet it poses a significant challenge for electronic structure calculations. Machine learning results may appear in perfect alignment with easily calculable paths, but this can be misleading if the unique open-shell nature of the transition state is overlooked. Establishing reliable benchmarks for machine learning, particularly in the context of transition path sampling, remains an intricate and ongoing endeavor. Armed with these lessons of caution, our aim is to cultivate a deeper understanding of how to assess the accuracy of machine learning models in dynamical processes.

5:00 PM
MT01.09.22
ChemChat | Conversational Expert Assistant in Material Science and Data Visualization
Tim Erdmann; Sarathkrisnha Swaminathan, Stefan Zecevic, Brandi Ransom and Nathan Park; IBM Research, United States

In recent decades, remarkable advancements have been made in the field of computational chemistry and machine learning (ML), yielding a plethora of sophisticated tools and artificial intelligence (AI) models. Despite their potential, these resources have yet to be fully harnessed due to their steep learning curves and their tendency to operate in isolation. Furthermore, the need for capabilities in programming and ML constitute access barriers to targeted communities—with multiple degrees of freedom. Intriguingly, even when accuracy metrics like mean absolute error (MAE) and root mean square error (RMSE) align, these static metrics assessed on a portion of the dataset may not suffice to identify the superior model. They serve as preliminary benchmarks, rather than comprehensive tests of model performance.

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5:00 PM
MT01.09.23
N-Body Fourier-Sampled Kernel for Machine Learning Potential
Alexandre J. Dézepie1,2, Anruo Zhong3, Clovis Lapointe1, Alexandra Goryaeva1, Jerome Creuze2 and Mihai-Cosmin Marincă1; 1ICMMO, France; 2ICMMO, France

Irradiation induces the formation of vacancy and interstitial defects in crystalline materials, which can aggregate into larger clusters. The structure and mobility of self-interstitial clusters remain a long-standing unresolved problem. For the past 60 years, the scientific community has regarded the formation of interstitial clusters in metallic materials as an accumulation of mono-interstitials that, through diffusion, can aggregate into 2D dislocation loops with a well-defined Burgers vector, progressively growing to observable nanoscale sizes. Recently, we have shown that interstitial clusters in face-centered cubic (FCC) metals can aggregate into 3D objects with a well-defined Burgers vector, progressively growing to observable nanoscale sizes. This has been demonstrated using a combination of moleculardynamics simulations. Studying the recombination mechanism of atomic scale
defects into dislocations, as well as dislocation maturation, necessitates the development of new interatomic potentials. Machine learning potentials offer a compelling solution for atomistic simulations. To achieve this, we will systematically explore the complex energetic landscape of these clusters at 0 K. To investigate the mechanism governing the formation of compact clusters within FCC and BCC crystals, we conducted a series of simulations based on the newly developed interatomic potential. The kinetics of these processes were delineated through extensive molecular dynamics simulations at finite temperatures in Fe, Ni, and Al. Furthermore, we assessed the relative stability of these clusters through free energy calculations [5]. Lastly, we are actively engaged in the pursuit of intermediate states within the recombination mechanism of these nanophases. To achieve this, we will systematically explore the complex energetic landscape of these clusters at 0 K.


Data-Driven Crystal Growth Using Flux-Method Process Informatics Tetsuya Yamada1,2 and Katsuya Teshima1,2,1 Shinshu University, Japan; 2Shinshu University, Japan

Cellulose nanocrystals (CNCs) are rod-like nanoparticles with that exhibit a unique combination of attractive characteristics for many applications: abundance, renewability, biocompatibility, desirable mechanical and chemical properties, and cheap production potential. Given these desirable properties, a broad spectrum of applications has been demonstrated in the literature for CNCs, from biocomposites to composites, and from adhesives to sensors. Among the obstacles to the commercial utilization of CNCs is producing consistent quality, optimizing process parameters and relating characterization protocols. Particle size and particle size distribution are particularly important when optimizing performance in any given application, for example as a rheology modifier for polymer blends, polymer-modified bitumen processing, drug delivery systems, or heat exchangers.

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reduce these costs, Finite Element (FE) simulations are used to assess the cathodic current output. However, these simulations use the cathodic polarization curves as boundary conditions, which can only be discerned by performing experiments. Therefore, a protocol to accelerate the assessment of the cathodic current output for different chemistries under in-service environmental conditions is desirable. In this work, we develop an active learning protocol to minimize the total costs associated with performing the experiments and the simulations. We first calibrate a low-cost gaussian process surrogate model for the cathodic current output as a function of the environmental and geometric parameters that characterize the galvanic cell. The surrogate model is calibrated on a dataset of FE simulations, and it is used to calculate an acquisition function that identifies specific additional inputs with the maximum potential to improve the current predictions. The identification of additional inputs for further exploration is accomplished with the help of a staggered two-step workflow – (i) the influence of the geometric parameters are marginalized to identify the best configuration of environmental conditions for discerning the polarization curves, following which (ii) the geometric inputs best capable of refining the current predictions are identified. We demonstrate the efficacy of this protocol by minimizing the number of simulations necessary to obtain accurate predictions of the current output of a AA7075-SS304 galvanic couple. The protocols developed and demonstrated in this work provide a powerful tool for screening various forms of corrosion under in-service conditions. This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy National Nuclear Security Administration under contract DE-NA0003525. The views expressed in this article do not necessarily represent the views of the U.S. Department of Energy or the United States Government. SAND2023-11065A

5:00 PM MT01.09.28
Exploring Multi-Type Crosslinked Architectures in Polymer Materials Using Graph Neural Networks
Conner Leavitt and Mehdi Zanjani; Miami University, United States

Crosslinked polymer networks provide a promising route for developing novel material composites with a variety of applications in areas such as aerospace and biomedicine. These systems are typically made up of different combinations of backbone polymer chains and crosslinking agents of different kind. Understanding the relationship between the polymer network architecture and its properties is an important topic for design and development of new generation of polymer composites with on-demand functionality. While the study of crosslinked polymer networks has so far been mainly limited to systems with one or two types of crosslinkers, the existing synthesis techniques can readily be extended to devise more complex polymer networks with a larger number of crosslinkers and backbone chain type. However, the high-dimensional parameter space associated with such complex systems makes it difficult to predict the resulting architectures and properties of the materials developed through experimental trial and error.

In this work, we explore new designs for crosslinked polymer materials with multiple types of backbone chains and crosslinkers using a computational framework established based on graph theory (GT) and graph neural networks (GNNs). We demonstrate that including three or four types of backbone polymer chains can improve the mechanical behavior of the polymer composite provided that suitable structural features are established. We develop a graph representation of various polymer networks where edge graph features are defined according to the nature of crosslinking in the system, i.e. covalent or noncovalent bonds. We use a GNN framework to investigate the relationship between experimentally-controlled structural parameters, such as crosslinker density and type, and GT-based structural descriptors, such as graph connectivity and Wiener index. Following this step, we develop another GNN framework to study structure-property relationships using GT-based descriptors and mechanical properties obtained from Molecular Dynamics (MD) simulations. The trained GNNs will be used to predict the behavior of new potential structural morphologies in order to identify 'best-performing' configurations. The results of this work are aimed to be utilized for future experimental development of new crosslinked polymer composites.

9:00 AM *MT01.10.01
The LAMMPS Particle Simulation Package: Bringing Together Innovative Physics Models, Machine-Learning Interatomic Potentials and Extreme-Scale Computing Resources
Aidan P. Thompson; Sandia National Labs, United States

The molecular dynamics method (MD), as implemented in the LAMMPS[1] particle simulation code, is a powerful tool for explicitly sampling the phase space distribution of hundreds or billions of physically and chemically interacting atoms. It provides a wealth of information on how particular microscopic interactions lead to a vast range of emergent behaviors on much larger length and time scales, complementing theory and experiment. The overall usefulness of the method is sensitive to how well the chosen interaction potential approximates the true physical and chemical conditions. Over many decades, this has driven the emergence of many prominent interaction potentials that provide a good tradeoff between accuracy and cost. At the one extreme of minimal complexity are well-established models for simple fluids (Lennard Jones particles), polymer melts (FENE chains), and metals (EAM). In the case of chemical reacting systems, both organic and inorganic, the ReaxFF reactive potential has proven quite effective. More recently, relatively expensive machine-learning (ML) potentials have been found to approach the accuracy of very expensive quantum methods. These are trained to reproduce the energy and forces of many small configurations of atoms obtained from quantum electronic structure calculations e.g. Density Functional Theory. Examples of ML potentials implemented in LAMMPS include Behler-Parrinello, GAP, SNAP[2], the Atomic Cluster Expansion (ACE)[3], and ALEGRO. In this talk, I will give a general overview of LAMMPS capabilities, as well as the those the LAMMPS-integrated FitSNAP software [4] for generating quantum-accurate machine-learning interatomic potentials. I will describe several recent scientific applications of LAMMPS that combine innovative physics models, machine-learning interatomic potentials, and extreme scale computing resources.


9:30 AM *MT01.10.02
Demystifying High Temperature/Pressure Material Synthesis through Physics-Informed Machine Learning
Rebecca K. Lindsey; University of Michigan, United States

Design, discovery, and synthesis of new materials is a notoriously challenging problem, due largely to the massive associated design space and complex underlying phenomena. Simulations can provide a powerful means of navigating this problem space by providing both a capability for pre-screening and extracting otherwise inaccessible atomistically-resolved information on the underlying phenomena, but efforts are often limited by a lack of models exhibiting the necessary balance of accuracy and computational efficiency. In this presentation, we discuss recent efforts to overcome these challenges through development and targeted application of ChIMES, a physics-informed machine-learned interatomic model (ML-IAM) and supporting computational framework. We will present recent efforts to construct models across various materials and application domains, including electronic materials and structural properties. The overall usefulness of the method is sensitive to how well the ChIMES-learned and trained model approximates the true physical and chemical conditions. As a result, we will also develop an active learning protocol to minimize the total costs associated with performing the experiments and the simulations. We will present a protocol for reducing costs to approximately 1% of the original cost.

10:00 AM BREAK

10:30 AM MT01.10.03
Molten Salt Crystallography studied by Machine-Learned Potentials
Zhao Fan1, Michael Whitaker1, Piotr P. Zarzycki2, and Mark Asta1,2; 1Lawrence Berkeley National Laboratory, United States; 2University of California, Berkeley, United States

Molecular dynamics (MD) simulations based on accurate interatomic force-fields are employed to calculate solid-liquid phase diagrams and investigate mechanisms of crystalization at the atomic level. The work is motivated by the potential relevance of molten salts in the context of lithium extraction. We report on the development of efficient and robust machine learning (ML) potentials for three unary salts (LiF, NaF and KF), three binary mixtures (LiF-NaF, LiF-KF and NaF-KF) as well as the ternary mixture of LiF-NaF-KF in the framework of Atomic Cluster Expansion and with the training datasets generated using density functional theory (DFT) with the strongly constrained and appropriately normalized (SCAN) functional. We demonstrate that simulations based on these potentials produce properties consistent with DFT and available experimental data, including lattice constant, liquid density, melting point and latent heat of melting. The phase diagrams for the three binary mixtures and the ternary mixture calculated based on our ML potentials will be presented. In addition, we discuss results of simulations for homogeneous crystal nucleation, with focus on the crystallization pathways and role of metastable polymorphs. These studies are enabled by the attention paid in the potential development to accurate description of competing crystal phases, such as those with wurzite, zinc blende and CsCl-prototype structures. The atomic-level mechanism of homogeneous melting of the rocksalt structure of LiF, NaF and KF will also be illustrated.
Rational Design of Machine-Learned Interatomic Potentials

11:00 AM

Megan J. McCarthy; Sandia National Laboratories, United States

The predictive capability of a molecular dynamics simulation is determined by how accurately the chosen interatomic potential (IAP) captures a material’s bonding characteristics. Integrating machine learning techniques into IAP development has led to powerful improvements in that accuracy, while also introducing new levels of complexity to the training process. The choice of model (hyper)parameters, training set structures, validation tests, and whether and how to use tools such as active learning is frequently a material-specific, highly empirical process. To accelerate development and usage of machine-learned IAPs, new approaches to promote reproducibility and rational design of IAP are needed, ideally ones that are consistent with FAIR (Findable, Accessible, Interoperable, Reusable) research practices. In this talk, I will discuss promising developments in this area, amongst them software tools and techniques our group has developed while training machine-learned IAPs for multicomponent, chemically-complex materials used in extreme environments.

11:30 AM

In Search of a More Perfect Forcefield: Considerations and Strategies for Parameterizing Complex Interatomic Potentials for Molecular Dynamics

Aravind Krishnapoorthy; Texas A&M University, United States

Molecular Dynamics (MD) simulations are an increasingly vital tool to understand molecular processes in a variety of material systems across mechanical, materials, and biological engineering. MD simulations require parameterized interatomic forcefields that capture complex interatomic interactions in materials. However, forcefield parameterization is a non-trivial global optimization problem involving quantification of forcefield variables in large-dimensional search spaces.

In this talk, we will discuss our recent work to parameterize reactive and non-reactive interatomic potentials and will identify opportunities for improving these through newly developed algorithms and software for performing multi-objective and global optimization, as well as schemes inspired by AI and ML training. Using EZFF, a Python package for parameterization of several types of interatomic forcefields using single- and multi-objective optimization techniques, we will discuss a meta-analysis of the performance of forcefields for complex multi-phase materials generated using different strategies such as force-matching, energy-fitting and direct parameterization against dynamical properties. Approaches for parameterization of new forcefields against sparse ground truth data from experiments or expensive simulations will also be analyzed.
account for the variety of lattice structures, on-the-fly training was employed for precise training set generation. The trained SGP yielded good agreement with DFT on predictions of structural, thermodynamic, and vibrational properties. Insights were gained from the generated P-T diagram and free energy composition analyses. The verified SGP training strategy is also employed in the phase stability prediction of BₓO. Factors affecting the phase stability of BₓO, including defect concentration and elemental composition, were investigated using SGP interatomic potentials implemented in large-scale MD simulations. We anticipate this computational approach will aid in understanding the phase transition of complex crystals in future studies.

2:45 PM MT01.11.05
Benchmarking Anharmonicity in Machine Learned Interatomic Potentials Sasanka Bandi\textsuperscript{1}, Chao Jiang\textsuperscript{2} and Chris A. Marianetti\textsuperscript{1}; \textsuperscript{1}Columbia University, United States; \textsuperscript{2}Idaho National Laboratory, United States

Machine learning (ML) approaches have recently emerged as powerful tools to probe structure-property relationships in crystals and molecules. Specifically, ML interatomic potentials have been shown to predict ground state properties with near density functional theory (DFT) accuracy at a cost similar to conventional interatomic potential approaches. While ML potentials have been extensively tested across various classes of materials and molecules, there is no clear understanding of how well the anharmonicity of any given system is encoded. Here, we benchmark popular ML interatomic potentials using third and fourth order phonon interactions in fluorite crystals. An anharmonic hamiltonian was constructed from DFT using our highly accurate and efficient irreducible derivative methods, which was then used to train three classes of ML potentials: Gaussian Approximation Potentials, Behler-Parrinello Neural Networks, and Graph Neural Networks. We evaluate their anharmonicity in not only reproducing anharmonic interaction terms but also in observables such as phonon linewidths and lineshapes. We then present the results of the models trained on a DFT dataset, showing good and reasonable agreement with the DFT computed third and fourth order interactions, respectively. Finally, we discuss strategies to leverage anharmonic terms in the training procedure to improve the accuracy of ML interatomic potentials.

3:00 PM BREAK

3:30 PM MT01.11.06
Data-Driven Approaches to Facilitate Inorganic Materials Discovery and Synthesis Chris Bartel; University of Minnesota, United States

Machine learning is playing an increasingly prominent role in computational materials discovery. Recent advances in (universal) machine learning interatomic potentials allow practitioners to optimize the structure and compute the energy of inorganic crystals for arbitrary material compositions. These computed energetics can then be used as inputs to the convex hull analysis to determine if a hypothetical material is thermodynamically stable against potential competing phases. While stability is an important property for a candidate material, it does not determine if or how that material can be made in the lab. Whereas stability (at some set of conditions) is an intrinsic property of a material, synthesizability is not a similarly straightforward binary – it depends on experimental choices such as precursors, temperature, synthesis approach, etc. This talk will discuss recent efforts to use machine learning in the context of synthesis “recipe” generation, assessment, and optimization.

4:00 PM MT01.11.07
Robust Machine Learning allows Accurate Modeling of Thermodynamics of Catalysts and Bulk Materials Daniel Schwolke-Koda; UCLA, United States

Recent advances in machine learning (ML) interatomic potentials (IPs) allow density functional theory (DFT) calculations to be bypassed with models that balance high accuracy and relatively low computational cost. However, MLIPs can be unreliable in regions of the configuration space not represented in the training data, which often hinders their use as universal predictors when modeling high-complexity systems. In this talk, I will describe how understanding robust generalization in ML can improve the development of next-generation ML models for materials simulation. First, I will demonstrate how extrapolation in atomistic systems can be rigorously defined in a model-free approach, thus without surrogate metrics such as variance of predictions. Then, I will describe how deep learning theory can be used to improve the generalization of MLIPs. These results are used to model several problems in materials simulation, from the thermodynamic of phase transformations to coverage effects in catalysis. In combination with automated workflows for combinatorial data generation, robustness in ML models can help drive the field towards the development of universal MLIPs towards length and time scales not accessible by ground truth calculations.

4:30 PM MT01.11.08
General Protocol for Training Machine Learning Interatomic Potentials for Ionic Liquids and Battery Solvents Zachary A. Goodwin, Nicola Molinari, Julia Yang, Albert Musaelian, Simon L. Batzner and Boris Kozinsky; Harvard University, United States

We develop machine learning force fields (MLFFs), based on the equivariant graph neural networks with NeqGP/Allegro [1,2], for representative ionic liquids and conventional battery solvents. As capturing the complex intermolecular interactions are subtle, and the dynamics of these electrolytes/solvents are quite slow, training a potential for these systems is not always straightforward. We develop a general, automatable protocol for training MLFFs for complex, multicomponent liquids, which efficiently samples representative structures, to collect diverse, uncorrelated molecular configurations for training. This approach is shown to yield reliable simulations in the NVT ensemble, but not always in the NPT ensemble, where we find densities significantly lower than expected from our DFT calculations. We develop an approach to remedy this issue, and test it on a number of electrolytes/solvents to ensure it is a robust method. In addition, we study the question of model transferability, the effect of long-range interactions and uncertainty of the model.


4:45 PM MT01.11.09
Deep Learning-Assisted Analysis of Molecular Dynamics Simulations of LiTFSI/PYR\textsubscript{14}TFSI Ionic Liquid Electrolyte Chansui Park, Sangdeok Kim, Anseong Park, Seungtae Kim, Woojin Kang and Won Bo Lee; Seoul National University, Korea (the Republic of)

Over the past decades, significant research has been conducted to understand microscopic behavior of ionic liquid electrolytes (ILEs) through molecular dynamics (MD) simulations. The development of polarizable force fields is one of the most remarkable achievements as they predict structural and dynamical properties of ionic liquid-based systems very accurately. However, even with the help of polarizable force fields, one cannot analyze atomic dynamics of a system in detail because most of the properties are evaluated by “averaging” individual atomic or molecular properties. A deep learning technique called Graph Dynamical Networks (GDNets) has been suggested to learn atomic scale dynamics from MD simulations. GDNets trains local environments around a specific target atom and classify them into states in an unsupervised manner. The classification model is trained in the direction where the VAMP loss decreases. The classification results are combined with conventional analysis techniques to calculate state-wise properties which can describe the system according to each state. Using this method, we analyzed MD trajectories of LiTFSI/PYR\textsubscript{14}TFSI ILE with a range of lithium mole fractions, where the trajectories were generated under the APPLE&P polarizable force field. Li\textsuperscript{+} ions were treated as target atoms and classified into 3 local configurational states. State-wise radial distribution function, coordination number, spatial distribution function were defined and calculated to identify each state. The identified states were a Li\textsuperscript{+} ion coordinated by 2 and 3 TFSI\textsuperscript{-} ions, and a cluster composed of multiple Li\textsuperscript{+} and TFSI\textsuperscript{-} ions. Also, a transition matrix based on the Markov state model was generated from the classification results. With this matrix, dynamical properties of the states and transitions between states were measured to reveal which state or transition dynamics is faster than others. Finally, a design rule for ILEs with faster Li\textsuperscript{+} ion conduction was suggested.

SYMPOSIUM MT02

Battery Manufacturing—Emerging Opportunities in Data-Driven Experimentation, Analysis and Modeling
The harnessing of data driven methods for materials design in battery manufacturing, demands the linking of data associated with the fundamentals of materials chemistry through to battery performance. A critical limitation of applying current informatics methods is that available data captures only small parts of the materials information spectrum. In this presentation we explore approaches to address this issue to track linkages between multiscale data regimes that allows one to explore connections between crystal chemistry to device performance.

As the world embarks on widespread decarbonization, the supply chain crunch for batteries has become front and center around the world. In the United States, the issues are widespread, from material availability to the lack of cell and pack manufacturing. Recycling, which could bridge the supply gap, is still in its early stages. With the expected growth in the storage market, tactical approaches to solve the challenges will not suffice. What is needed is a comprehensive strategy that brings a holistic approach to solve the battery supply chain issues. This includes the search for alternative materials to the presently-constraints materials (such as nickel, cobalt, and lithium), examining opportunities for clean extraction of battery minerals, and recycling. In addition, an important part of the strategy is to examine leapfrogging materials and manufacturing methods that can enable deep decarbonization of transportation and grid sectors. The talk will examine the status of battery technology, and the opportunities for enabling widespread electrification with a sustainable and secure supply chain.

Rechargeable batteries are among the critical technologies in the decarbonization effort of increasingly expanded transportation and power grids. The demand for safer, longer-lasting, durable energy storage continues to fuel the need for battery innovation. This need, in turn, requires designing new materials, understanding how they function, and developing scalable processes to manufacture them. Electric vehicles (EVs) powered by lithium-ion batteries (LIBs) at scale. To some extent novel electrode active materials can leverage the well-established manufacturing knowledge of lithium-ion batteries. However, several materials synthesis and performance challenges for electrode materials must be addressed for them to mature from lab to industrial scale. We employ natural language processing (NLP) tools to extract challenges from battery literature in the performance and synthesis of active battery materials. The tools also systematically review corresponding mitigation strategies. These selected mitigation strategies are then evaluated among a broad set of pre-existing lab-proposed mitigation strategies. These derived insights enable engineers in research and industry to navigate a large number of proposed strategies.
Batteries continue to see rapid advancement both in materials selection and in emerging use cases. In all cases as new options for battery use and design arise there is a need to validate performance and to understand failure modes. Traditionally validation processes would require years of testing and immense use of resources to reach acceptable certainty that a new battery would function in an intended use case. Recent emergence of the use of combining failure mode analysis with machine learning and other advanced data analytics provides the opportunity to dramatically reduce the time needed for validation and to more quickly bring new discoveries and uses cases from the bench top to the consumer.

In this discussion several different approaches to reducing the time needed for performance validation will be discussed. This includes both the importance of appropriate and targeted data collection as well as the data analytic methods that can support rapid validation. The key to both the advanced analytics and data collection is the need to ensure a link to physical processes which aids in battery failure mode identification. The link also allows extended data sets to be generated using different modeling or synthetic data approaches to be used for enhanced training purposes.

Using a combination of experimental and synthetic data it will be shown that enhanced predictions are possible and that the time and resources needed to make predictions can be dramatically reduced. As an example set different predictions for graphite/NMC batteries used in standard and fast charge conditions will be highlighted.

3:30 PM *MT02.02.03
Data-driven Research for Aqueous Organic Redox Flow Batteries Wei Wang, Pacific Northwest National Laboratory, United States

Aqueous organic redox active materials have recently shown great promise as alternatives to transition metal ions as energy-bearing active materials in redox flow batteries for large-scale energy storage due to their structural tunability, cost-effectiveness, availability, and safety features. However, development to date has been limited to a small palette of aqueous soluble organics. This presentation will provide an overview of a data-driven approach to accelerate the discovery and development of aqueous organic redox-active molecules for flow batteries, including database curation, structure-property correlation, and automated property characterization and performance testing developed in PNNL’s ARES (Automated Robotics for Energy Storage) lab.

Reference: P. Gao, etc. “SOMAS: a platform for data-driven material discovery in redox flow battery development”, Scientific Data, 9, 740, 2022
Y. Liang, etc “High-throughput solubility determination for data-driven materials design and discovery in redox flow battery research” Cell Reports Physical Science 4, 101633, 2023

4:00 PM *MT02.02.06
High-Throughput Approach to High Energy Lithium-Ion Cell Roadmap Development Gang Cheng, Ye Zhu, Ran Devanayanagam and Hui Wang; Wildcat Discovery Technologies, United States

As EV adoption has grown, there has been an increased focus in the battery industry on the development and implementation of high-nickel cathodes from 80% Ni to now 95 and above with increasing Si% in the anodes. These materials can deliver improved energy density relative to today’s materials but suffer from poor lifetime and durability. Variations in electrode composition can impact the performance of the material. This presentation highlights Wildcat high-throughput strategy that can accelerate implementation of high-nickel cathodes paired with high Si% of anodes in applications. The presentation focuses on approaches other than compositional changes to the high nickel NMC/Si-C cells to improve cycle life in high-loading electrodes.

SESSION MT02.05: Circular/Green Battery Manufacturing and Recycling
Session Chair: Shailesh Upreti and Feng Wang
Wednesday Morning, April 24, 2024
Room 321, Level 3, Summit

10:30 AM MT02.05.02
3D Printed Flexible Lithium-Ion Batteries with Improved Cycling Performance Xin Hu1,2, Yimin Chen1,2, Baozhi Yu1,2 and Ying Chen1,2; 1Deakin University, Australia; 2ARC Research Hub for Safe and Reliable Energy, Australia

3D printing technology, one of the additive manufacturing techniques, has shown remarkable promise in creating flexible and tailor-made high-performance batteries, which are in high demand for the upcoming era of intelligent and widespread energy usage. Nonetheless, a notable performance disparity, particularly in terms of cycling stability, still persists between 3D-printed electrodes and traditional counterparts, severely constraining the practical utility of 3D-printed batteries. This presentation discusses the development of a range of 3D-printed electrodes based on thermoplastic polyurethane (TPU) using fused deposition modeling for high-performance, flexible, and customizable lithium-ion batteries. The TPU-based electrode filaments are produced in significant quantities through a straightforward extrusion method. Consequently, the electrodes are printed with precision, offering excellent dimensional accuracy, flexibility, and mechanical stability. Notably, 3D-printed TPU-LFP electrodes demonstrate an impressive capacity retention of 100% after 300 cycles at 1C, representing one of the most robust cycling performances among all reported 3D-printed electrodes. This exceptional performance can be attributed to the outstanding stress-absorbing characteristics of the TPU-based electrodes, which effectively accommodate the volume changes during cycling and thus substantially prevent the collapse of the 3D-printed electrode structures. These findings not only open up new possibilities for creating adaptable and flexible batteries but also pave the way for bridging the performance gap between 3D-printed and traditional lithium-ion batteries.

10:45 AM *MT02.05.03
Sustainable LiFePO4 and LiMnFe1-xPO4 (x=0.1 to 1) Cathode Materials for Lithium-Ion Batteries: A Systematic Approach from Mine to Chassis Atiyeh Nekahi, Anil Kumar Madikere Raghunatha Reddy, Karim Zaghib, Xia Li, Sixu Deng and Michel L. Trudeau; Concordia University, Canada

We conducted a comprehensive literature review for LiFePO4 (LFP) and LiMnFe1-xPO4 (x=0.1 to 1) (LMFP)-based lithium-ion batteries (LIBs), focusing primarily on electric vehicles (EVs), which account for approximately 90% of LIB consumption. Although numerous individual research studies exist, a unified and coordinated review that covers the subject from mine to chassis is notably absent. Accordingly, our review encompasses the entire LIB development process, starting with I) initial resources, including lithium (Li), iron (Fe), manganese (Mn), and phosphorous (P), their global reserves, mining procedures, and their demand in LIB production. Then, we examined II) the main Fe- and Mn-containing precursors of Fe3+, Fe4+, Fe5+, Fe6+, Fe7+, and MnO2, focusing on their preparation methods, employment in LIBs, and their effect on the electrochemical performance (EP) of the final active cathode materials (ACMs). These two steps are followed by III) utilizing these precursors in synthesizing ACMs. Specific attention is paid to the pioneering synthesis methods in olivine production lines, particularly hydrothermal liquid-state synthesis (LSS), molten-state synthesis (MSS), and solid-state synthesis (SSS). Afterward, we described IV) electrode engineering and design and optimization of electrolytes and V) the production of cells, modules, and packs. Finally, V) our review underscored the challenges associated with the widespread utilization of olivines in LIBs, emphasizing safety, cost, energy efficiency, and carbon emission. In conclusion, our review offers a comprehensive overview of the entire trajectory involved in the fabrication of LFP/LMFP-based LIBs, spanning from the initial elements in the mine to the assembly of final packs that power EVs.

11:15 AM *MT02.05.04
Circular Manufacturing of Next-Generation Lithium-ion Battery Cathode Materials with R2R Molten Salt Electrodeposition Heng Yang; Xerion Advanced Battery Corporation, United States
For the past few years, Xerion has been developing a roll-to-roll (R2R) molten salt electrodeposition technology (DirectPlate™) for circular manufacturing of lithium-ion battery cathodes. Cathode materials such as LiCoO₂, Li(Ni,Mn)O₂, and Li,Mn₂O₄ are demonstrated with good electrochemical properties. DirectPlate™ cathodes are distinctly different from conventional slurry-cast electrodes combining several notable properties: they are very dense with less than 10% porosity, free of additives (carbon and polymer binder), and their crystal orientation can be accurately controlled, enabling high-rate operation at or beyond state-of-the-art areal capacity loading (3-4 mAh/cm²). As Li⁺ diffusion primarily occurs through the single crystalline domains aligned vertically to the current collector, DirectPlate™ LiCoO₂ cathodes deliver good electrochemical properties in a solid-state cell without the need to infiltrate electrolyte into the cathode.

We further demonstrate that end-of-life DirectPlate™ cathodes can be efficiently re-lithiated and repaired with a short molten salt treatment; or they can be upcycled into another cathode material with a completely different composition. Finally, we demonstrate that the DirectPlate™ cathode can be employed as a redox membrane for direct lithium extraction from various lithium-containing solutions. Integrating the collective mineral refinement, electrode fabrication and recycling capabilities into the R2R DirectPlate™ platform enables next-generation circular battery manufacturing with much lower energy and environmental cost.

SESSION MT02.06: Data-Driven Battery Optimization and Health Prognosis
Session Chairs: Eric Dufek and Alejandro Franco
Wednesday Afternoon, April 24, 2024
Room 321, Level 3, Summit

1:45 PM *MT02.06.02
AI Performance and Health Prognosis for Degradation-Aware Battery Development Noah H. Paulson, Joseph Kubal, Logan Ward, Saurabh Saxena, Wenquan Lu and Susan Babinec; Argonne National Laboratory, United States

Battery development requires extensive experimental trials ranging from benchtop materials discovery, to scale up trials, to full production optimization, incurring costs that may exceed hundreds of millions of dollars. One principal barrier to a more efficient and accelerated development process is the requirement to consider the degradation of batteries with use, the experimental evaluation of which requires 12 to 18 months of laboratory cycling experiments to reach failure. Physics-based simulations of battery degradation are rapidly advancing, but the diversity and complexity of coincident degradation mechanisms precludes the complete replacement of experimental trials. Data-driven methods, however, do not require exhaustive description of degradation mechanisms, and in recent years have shown strong performance in predicting battery degradation and remaining useful life (RUL). In this presentation, we share recent work in predicting battery RUL from limited cycling for a dataset of 300 Li-ion pouch cells representing 6 cathode chemistries and a variety of anode and electrolyte compositions. RUL prognosis was performed with a mean absolute error of ~100 cycles for a model trained on all available cathode chemistries, and useful predictions were made for unseen chemistries. Furthermore, we present timeseries prognosis of a multivariate battery state of performance and health including capacity, energy, efficiency, resistance, and open circuit voltage quantities.

2:15 PM MT02.06.03
Harnessing AI: Accurate Predictions of Battery Capacity Fade and Battery Cycle Life Jordan Crivelli-Decker1, Marc Cormier2, Shivang Agarwal3, Ty Soure1, Steffen Ridderbusch1, Dan Zhao1, Stephen Glazier2, Brian Wee1, Don Fiander2 and Angie Xiao1; 1SandboxAQ, United States; 2Novonix, Canada

Predicting battery degradation is pivotal for advancing materials and screening protocols in battery design, utilization, testing, and recovery. This enables better battery management and maintenance of the desired performance characteristics over an extended period including both up and downstream manufacturing processes such as material selection, design qualification, technology/cell selection (battery management), and warranty, etc. However, traditional models and machine learning techniques often fall short in capturing these characteristics.

Lithium-ion cells typically show a gradual capacity degradation up to a certain point, known as the knee-point, beyond which the degradation accelerates rapidly, leading to the cell's End-of-Life. SandboxAQ’s collaboration with NOVONIX has resulted in a robust method to predict long-term cell capacity fade from early-life cycling data. The approach begins with extracting early-life current, voltage, and capacity data collected on NOVONIX’s world-class Ultra-High Precision Coulometry (UHPC) cycler systems. Electrochemically relevant metrics are then combined with advanced feature engineering and sophisticated data transformations are employed to construct features conducive for machine learning.

Proprietary machine learning and deep learning models were trained on several comprehensive, but limited datasets. Despite limited training data, these models demonstrate a remarkable ability to accurately classify the cells with and without catastrophic failure at a given point in time, predict the cycle number at which 80% of cell’s initial capacity remains, and estimate the remaining useful life of the cell, which provides key indicators of cell health and longevity.

One of the standout features of these models is their flexibility. They are designed to seamlessly incorporate new data as it becomes available, ensuring that the predictions remain relevant and accurate over time. This approach not only provides a more cost and time-efficient alternative to long-term experiments traditionally used to estimate battery life but also opens avenues for more dynamic and responsive battery management strategies.

In summary, our solution leverages AI to rapidly make accurate, physics-based, end-of-life predictions using early-life electrochemical data. We leveraged comprehensive manufacturing cell data to deliver custom machine learning and deep learning models that were able to reliably predict cycle life only from high fidelity early-life data. The models are designed to easily integrate any future data, offering a cheap and efficient alternative to lengthy benchtop experiments.

3:00 PM BREAK

SESSION MT02.07: Data-Driven Materials and Process Design I
Session Chairs: Deyu Lu and Noah Paulson
Wednesday Afternoon, April 24, 2024
Room 321, Level 3, Summit

3:30 PM *MT02.07.01
Data-Driven Battery Analysis with Machine Learning: From Laboratory to Field Application Wei Han Li; RWTH Aachen University, Germany

Machine learning has emerged as a pivotal force within the battery industry, spanning research endeavors from the material level to the system level, encompassing both production processes and practical applications. Recent advancements in machine learning and data-driven methodologies have enabled innovative solutions for complex problems, particularly those scenarios where conventional physics-based models have fallen short.

In my talk, I will delve into our latest endeavors in the realm of data-driven battery analysis, encompassing both laboratory experimentation and real-world application in electric vehicles and stationary energy storage systems. Our research is centered on the development of deep learning models designed to augment and denoise CT images for in-depth battery electrode analysis. Additionally, we are actively engaged in harnessing machine learning and statistical learning techniques to scrutinize data from various testing and field sources, thereby improving aging diagnostics in the cloud.

This talk aims to offer a comprehensive overview of the diverse array of machine learning approaches employed in battery-related analyses while also shedding light on the unique challenges faced and the abundant prospects awaiting exploration.

4:00 PM MT02.07.02
Incorporating Domain Knowledge in Statistical Machine Learning to Efficiently Navigate Parameter Space and Test Durability for Energy Storage Maher Aljalalvani; Marcus M.
This work underscores the potential of data-driven approaches in expediting the discovery of high-performance electrolytes for lithium metal batteries. Although crystalline LiMO₃ (M=Nb, Ta) coatings show substantial enhancements in the battery electrochemical performances, there exists an apparent contradiction between the low Li-ion conductivity of crystalline LiMO₃ coating and the good rate capabilities achieved in these cells. This contradiction needs to be well understood to optimize the functional properties of the electrolyte reactivity, and to guide the design of new high-performing electrolytes. In this two-part presentation, we introduce machine learning methods and workflows that enable us to predict electrolyte performance, guide the design of new high-performing electrolytes, and extract important scientific insights.

In the first part, we introduce a novel workflow that combines principles of feature engineering, feature selection, and machine learning model assessment. This workflow allows us to extract promising strategy for improving CE, its inherent complexity makes performance prediction and electrolyte design challenging. In this two-part presentation, we introduce machine learning methods and workflows that enable us to predict electrolyte performance, guide the design of new high-performing electrolytes, and extract important scientific insights.

In the first part, we introduce a novel workflow that combines principles of feature engineering, feature selection, and machine learning model assessment. This workflow allows us to extract promising strategy for improving CE, its inherent complexity makes performance prediction and electrolyte design challenging. In this two-part presentation, we introduce machine learning methods and workflows that enable us to predict electrolyte performance, guide the design of new high-performing electrolytes, and extract important scientific insights.

Exploring Secondary Phase Formation at The Solid-Electrolyte/Cathode Interface using Machine-Learning Interatomic Potential Wonseok Jeong, Brandon Wood and Liwen Wan; Lawrence Livermore National Laboratory, United States

This work was sponsored by the Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office and was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. A portion of this research was performed using computational resources sponsored by the Department of Energy's Office of Energy Efficiency and Renewable Energy and located at the National Renewable Energy Laboratory.

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1. Solomon Oyakhire, Xin, F.
2. Zeyu Deng, Yuheng Li and Pieremanuele Canepa; 1 National University of Singapore, Singapore; 2University of Houston, United States

Exploring Secondary Phase Formation at The Solid-Electrolyte/Cathode Interface using Machine-Learning Interatomic Potential Wonseok Jeong, Brandon Wood and Liwen Wan; Lawrence Livermore National Laboratory, United States

All-solid-state Li-ion batteries are attractive next-generation energy-storage devices, offering improved safety, energy density, and durability compared to conventional Li-ion batteries. A critical challenge in these batteries is the occurrence of side reactions at the solid-electrolyte/cathode interface, particularly at elevated temperatures during co-sintering. These reactions have the potential to result in the undesired formation of secondary phases that impede the transport of lithium ions. The dynamic formation of these secondary phases at the atomic scale and the conditions governing their emergence remain unclear.

In this work, we explore the nucleation and evolution of secondary phases, such as La-Co-O₃, at the interface between the LiₓLa₂Zr₂O₇ (LLZO) solid electrolyte and the LiCoO₂ (LCO) cathode. Our investigation comprises three main components that employ atomistic simulations driven by a machine-learning potential (MLP) for accelerated and comprehensive analysis.

Firstly, we utilize a crystal structure prediction algorithm in conjunction with an MLP to accelerate the identification of potential secondary phases that may form at the interface. Secondly, we conduct MLP-driven metadynamics simulations to investigate the relationship between local structural features and the energy landscape associated with the nucleation of secondary phases. This exploration helps us understand the conditions leading to the formation of bulk-like secondary phases. Finally, we perform large-scale MLP molecular dynamics simulations to directly observe the formation of secondary phases in a model interface structure.

Through this multi-level investigation, we offer a holistic understanding of the formation of secondary phases at the LLZO/LCO interface. This insight is critical for understanding battery degradation resulting from interface reactions.

This work was sponsored by the Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office and was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. A portion of this research was performed using computational resources sponsored by the Department of Energy's Office of Energy Efficiency and Renewable Energy and located at the National Renewable Energy Laboratory.

4:55 PM MT02.07.05
Data-Driven Electrolyte Design for Lithium Metal Batteries Solomon Oyakhire,1,2, Sang Cheol Kim1, Yi Cui1 and Stacey F. Bent1; 1Stanford University, United States; 2University of California, Berkeley, United States

Enhancing Coulombic efficiency (CE) plays a pivotal role in facilitating the adoption of high-energy-density lithium metal batteries. While liquid electrolyte engineering has emerged as a promising strategy for improving CE, its inherent complexity makes performance prediction and electrolyte design challenging. In this two-part presentation, we introduce machine learning methods and workflows that enable us to predict electrolyte performance, guide the design of new high-performing electrolytes, and extract important scientific insights.

In the first part, we introduce a novel workflow that combines principles of feature engineering, feature selection, and machine learning model assessment. This workflow allows us to extract insights that guide the design of five new, high-performing electrolytes. Leveraging simple features, such as elemental composition that encodes pertinent physics within the electrolytes, we constructed interpretable models using linear regression, random forest, and bagging techniques. Through the results derived from these interpretable models, we identified crucial electrolyte features that are instrumental in achieving high battery efficiency. One such feature is the atomic fraction of oxygen in the solvent, highlighting the significance of reducing solvent oxygen for achieving high Coulombic efficiency (CE). Equipped with this insight and a few others, we formulated five new electrolyte compositions with fluoroine-free solvents, one of which attains a high CE of 99.70%.

In the second part, we employ data segmentation along with machine learning methods to discern crucial performance descriptors within distinct electrolyte efficiency classes. Through this approach, we made a surprising discovery. Common electrolyte performance descriptors like lithium morphology, ionic conductivity, solid electrolyte interface chemistry, and lithium-electrolyte reactivity, do not explain performance variations in Coulombic efficiency beyond Electrolyte Efficiency (CE) of 98%. By utilizing new machine learning model assessment techniques, interpretable machine learning models, correlation analysis, and rigorous spectroscopy and electrochemistry characterizations, we unveil the pivotal role of galvanic corrosion in accounting for performance disparities within high CE (>98%) electrolytes.

This work underscores the potential of data-driven approaches in expediting the discovery of high-performance electrolytes for lithium metal batteries.

SESSION MT02.08: Poster Session
Session Chairs: Deyu Lu and Feng Wang
In the field of battery material science, the use of advanced imaging techniques is paramount for a comprehensive understanding of electrode materials. Computed Tomography (CT) has become an invaluable tool, offering insights into the internal structures of battery components. However, the challenges of low-contrast materials and small feature sizes inherent to battery electrodes necessitate innovative approaches for image enhancement and feature extraction. In this study, we explore the application of a machine learning approach, i.e., UNets, for enhancing CT images and employ a Variational Autoencoder (VAE) for feature extraction and clustering.

Our focus centers on a graphite-silicon composite electrode, chosen due to its relevance in battery materials and the complex imaging challenges it presents. Notably, the smallest features, such as carbon black and chipped graphite flakes, exist at nanometer scales, contributing to a heterogeneous structure. Moreover, the materials, including graphite and carbon black binder, share similarities in their core charge numbers, leading to low signal contrast, making their distinction challenging.

The study primarily addresses three key aspects:

**Image Enhancement:** We utilize UNets to enhance CT images of the graphite-silicon composite electrode. These neural networks excel in denoising and super-resolution, improving the visibility of small features and enhancing the overall image quality. The application of UNets leads to clearer, more informative images, aiding researchers in the analysis of battery materials in a faster way.

**Feature Extraction:** Through the implementation of a VAE, we perform feature extraction and clustering on the CT images. This technique enables the identification and isolation of important structural features within the electrode, offering insights into the material's composition and distribution. The extracted features can be instrumental in understanding the electrode's behavior during battery aging.

**Applications:** We discuss the practical applications of enhanced CT images and feature extraction in battery material science. The enriched images facilitate the accurate characterization of small-scale structures and the spatial distribution of materials within the electrode. This information can be used in the development of battery materials and manufacturing processes, contributing to enhanced performance, safety, and longevity.

Our study underscores the potential of utilizing cutting-edge image enhancement techniques and feature extraction methods in battery material science. By enhancing the quality of CT images and extracting relevant features, researchers can gain deeper insights into the intricate structures of battery electrodes. This research bridges the gap between imaging technology and materials science, offering valuable tools for advancing the development and manufacturing of high-performance batteries.

5:00 PM MT02.08.03

A Novel Machine Learning Approach for Surface Roughness Quantification and Optimization of Cast-On-Strap Lead-Antimony Alloy via Two-Point Correlation Function

Nasir K. Allam

American University in Cairo, Egypt

Surface roughness has a negative impact on the materials’ lifetime. It accelerates pitting corrosion, increases effective heat transfer, and increases the rate of effective charge loss. However, controlled surface roughness is desirable in many applications. The automotive lead-acid battery is very sensitive to such effects. In our case study, the cast-on-strap machine has the largest effect on the surface roughness of the lead-antimony alloy. In this regard, statistical correlation functions are commonly used as statistical morphological descriptors for heterogeneous correlation functions. Two-point correlation functions are fruitful tools to quantify the microstructure of two-phase material structures. Herein, we demonstrate the use of the two-point correlation function to quantify surface roughness and optimize lead-antimony poles and straps used in the lead-acid battery as a solution to reduce their electrochemical corrosion when used in highly corrosive media. However, we infer that this method can be used in surface roughness mapping in a wide range of applications, such as pipes submerged in seawater as well as laser cutting. The possibility of using information obtained from the two-point correlation function and applying the simulated annealing procedure to optimize the surface micro-irregularities is investigated. The results showed successful surface representation and optimization that agree with the initially proposed hypothesis.

5:00 PM MT02.08.04

First-Principles Investigations of FeP@Graphene as Anode Material for Sodium-Ion Batteries

Qi-Jing Hong

National Central University, Taiwan

In recent years, numerous strategies have been proposed to tackle the challenges of large volume changes and capacity decay in conversion-type electrodes. Most studies have focused on experimental investigations, and only a few have centered on simulation studies. This research aims to apply density functional theory to study FeP and its modifications, which are one of the most widely recognized conversion-type electrodes in experimental studies due to its low cost and high theoretical capacity. Experiments have shown that combining FeP with graphene (FeP@graphene) can be a promising way to alleviate the volume variation issue. Furthermore, Cu doping in FeP has been reported to enhance conductivity and capacity. The calculation results of the partial density of states (PDOS) did not exhibit substantial differences between models with and without Cu doping in FeP, but the adsorption energy of a single Na atom was significantly lower in the Cu doped system. Analyses of electron density difference maps (EDDM) and partial atomic charges are performed to further discern the distinctions between FeP@graphene with and without Cu doping. Climbing image-nudged elastic band (CI-NEB) calculations are conducted to investigate the diffusion behavior of Na in the FeP@graphene structure.

SESSION MT02.09: Data-Driven Materials and Process Design II

Session Chairs: Eva Allen and Feng Wang

8:00 AM *MT02.09.01

Data-Driven Analysis on The Dynamics and Heterogeneity of Particle Network in Composite Electrodes of Li-Ion Batteries

Kejie Zhao

Purdue University, United States

We use a data-driven approach to assess the heterogeneous electrochemistry and mechanics in composite cathodes. We visualize the morphological defects at multi-scales ranging from the macroscopic composite, particle ensembles, to individual single particles. Particle fracture and interfacial debonding are identified in a large set of tomographic data. The mechanical damage of active particles is highly heterogeneous. The difference originates from the polarization of the electrolyte potential, various local conducting environments, and thus the non-uniform distribution of the activation energy for the charge transfer reaction. We model the kinetics of intergranular fracture and interfacial degradation to assess the heterogeneous mechanical damage in composite electrodes using microstructure-informed mechanics modeling. We quantify the influence of the mechanical damage on the metrics of battery performance. More interestingly, the interfacial failure conducts the network and redistribute the electrochemical activities that render a dynamic nature of electrochemistry and mechanics evolving over time in the composite electrodes.

8:30 AM MT02.09.02

Navigating Phase Diagram Complexity to Optimize The Robotic Synthesis of Battery Cathodes and Solid-State Electrolytes

Radenko Chen

and Wenhao Sun

University of Michigan, United States

There are a plethora of computationally-predicted battery 'wonder' materials, but only a limited number of them can be successfully synthesized. Efficient synthesis recipes are essential to accelerate the realization and manufacturing of theoretically-predicted electrodes. Oftentimes the solid-state synthesis of multicomponent oxide electrodes is impeded by undesired byproduct phases, which can kinetically trap reactions in an incomplete non-equilibrium state. We present a thermodynamic strategy to navigate high-dimensional phase diagrams in search of precursors that circumvent low-energy competing byproducts, while maximizing the reaction energy to drive fast phase transformation kinetics. Using a robotic inorganic synthesis laboratory, we perform
4:45 AM MT02.09.03
Cathode Upcycling for Direct Recycling Using a Rapid Coprecipitation Approach Eva M. Allen1, Jessica Macholz1, Feng N. Wang1, Mansi Porwal2, Tim Fister1, Denis Keane1, Michael Guise1, Viktor Nikitin1, Jordi Cabana2 and Albert Lipson1; 1Argonne National Laboratory, United States; 2University of Illinois at Chicago, United States; 3Northwestern University, United States

In line with carbon neutrality goals by 2050, the Li-ion battery market has surged. To enhance battery sustainability and circularity, direct recycling methods aim to recover intact cathode materials. However, end-of-life cathode materials are typically 15-20 years old and often have lower energy density compared to current cathode materials. In response, we have developed a rapid coprecipitation process to boost energy density by converting low Ni-compositions, LiNi0.33Co0.33Mn0.33O2 (NMC111), into higher Ni-compositions (NMC622). This process forms a Ni-rich coating that diffuses into the core, increasing compositional homogeneity upon high-temperature reutilisation. Our technology leverages existing infrastructure, offering low capital cost and minimal additional chemical input. Through ex-situ tomographic transmission X-ray microscopy (TXM) and XANES, we quantify Ni:Co:Mn elemental ratios and Ni valence state, confirming that elemental content events at the secondary particle level, but elemental gradients remain at the primary particle level upon reutilisation. Ex-situ high-resolution and in-situ wide-angle X-ray diffraction reveals a significant difference in the reutilisation process. These findings can guide further improvements in synthesis for increased initial capacity and retention.

9:00 AM MT02.09.04
In Situ Insights into Cathode Calculation: A Multimodal Assessment of the Crystallization Process of LiNiO2 Akhil Tayal1, Pallab Barai2, Hui Zhong1, Xiaohui Qu1, Jianming Bai1 and Feng N. Wang2; 1Brookhaven National Laboratory, United States; 2Argonne National Laboratory, United States

Calculation is a crucial step in the solid-state synthesis of metal oxides, finding applications not only in manufacturing of cathode materials for batteries but also across various industrial sectors. However, the inherent complexity associated with the process, involving elusive kinetic intermediate, hindering in-depth understanding and predictive control over the production of high-performance metal oxide materials. In this presentation, we report our in-situ analysis of the crystallisation process of LiNiO2, a potential high-performance cathode for Li-ion battery, to assess the course of crystallization and phase progression vs temperature and time. The composition phase evolution diagrams derived from quantitation Rietveld analysis over in-situ XRD patterns, extracted with multivariate curve resolution (MCR) fitting of the ex-situ XAS data, simulated with a phase-field-based continuum model, and constructed by using a cosimilarity balanced automated data analysis as an in-line tool for process monitoring, are examined individually and compared with each other to draw new insights over the calculation process in order to establish optimized processing parameters.

9:30 AM MT02.09.05
PyBOP: A Python Framework for Battery Model Optimisation and Parameterisation Brady Planden, Nicola Courtier and David Howey; University of Oxford, United Kingdom

To maximise the benefits of battery models, we need to parameterise them accurately from materials and electrochemical data. However, this remains a significant challenge [1] due to the need for expert knowledge in experimental data acquisition, processing, and system identification. In response, we introduce a systematic software framework, PyBOP [2], to establish and formalise novel parameterisation workflows for various continuum battery models. We present initial results from synthetic open-source battery datasets for benchmarking our model parameter identification efforts, comparing traditional deterministic methods with advanced Bayesian inference techniques. We will also highlight PyBOP's capabilities for optimising cell design by discussing an electrode optimisation study on high-voltage LNMO cathode and silicon-graphite composite anode cell. Throughout this work, we demonstrate PyBOP's ability to accommodate different levels of proficiency in model parameterisation and optimisation, including illustrative workflows tailored towards researchers or industrial users.

10:00 AM BREAK

SESSION MT02.10: A/ML for Materials and Process Modeling I

9:30 AM MT02.10.01
Nanoscale structures in battery cathodes from theory, ML, and microscopy/spectroscopy experiments Maria K. Chan; Argonne National Laboratory, United States

The determination of nanoscale structural evolution in battery materials during synthesis and cycling is of paramount importance to understand battery performance and degradation. The integrated use of first principles density functional theory (DFT) modeling, machine learning (ML), together with microscopy (e.g. STEM), diffraction/scattering, and spectroscopy (e.g. XANES and EELS) measurements, has enabled more in-depth understanding of such structural evolution. In this talk, we will discuss how this combination of techniques has allowed us to determine oxygen instability and reactivity, map local cation and defect concentrations, and determine intermediate phases in lithium battery cathode materials.

11:00 AM MT02.11.01
Tackling Ion Transport and Interfacial Evolutions in Solid-State Batteries through "Intelligent" Machine-Learning Zeyu Deng1, Abhishek Panchal2, Xie Weihang1, Sai Gautam Gopalakrishnan1 and Pyerre maneume Canepa2,1; 1National University of Singapore, Singapore; 2University of Houston, United States; 3Indian Institute of Science, India

Computational material science is crucial to establishing a firm link between complex phenomena occurring at the atomic scale and macroscopic observations of functional materials, such as energy materials for solar cells, fuel cells, and rechargeable batteries. Storing and distributing green energy is central to the modernisation of our society. Rechargeable batteries, including lithium (Li)-ion batteries, contribute substantially to shifting away from oil and other petrochemicals. The 2019 Nobel Prize in Chemistry awarded to John Goodenough, Stanley Whittingham, and Akira Yoshino resulted in the Li-ion battery as a mainstream technology powering millions of portable devices, electric vehicles, and stationary applications. Commercial Li-ion batteries suffer from stability issues. All-solid-state batteries utilizing solid-electrolyte "membranes" separating the distinct chemistries of the electrode materials appear to be a safer alternative. Commercial Li-ion batteries must be designed in a scalable manner. All-solid-state batteries and their devices are expected to have a higher energy density, better cycle stability, and lower risk of thermal runaway.

11:30 AM MT02.10.02
Robust Machine Learning Inference from X-Ray Absorption Near Edge Spectra through Featureization Yinning Chen1,2, Chi Chen3, In-Hui Hwang1, Michael J. Davis1, Wanli Yang3, Chengjun Sun1, Shyue Ping Ong2 and Maria K. Chan1; 1Argonne National Laboratory, United States; 2University of California, San Diego, United States; 3Lawrence Berkeley National Laboratory, United States

Machine learning (ML), used in conjunction with materials modeling, is reshaping the way that researchers analyze and interpret materials characterization data by greatly accelerating the process and providing underlying physics.[https://link.springer.com/article/10.1557/s43577-022-00446-8]. One notable application is the extraction of essential materials properties, such as oxidation states and structural information, from X-ray absorption spectroscopy (XAS) data. Traditional ML models typically utilize raw spectral intensities as the model input, with limited understanding on how to transform the spectral spectra to potentially boost model performance. In this presentation, we will compare and assess the effectiveness of both reduced-dimensional features and complete representations to discover the optimal representation of x-ray absorption near edge structure (XANES) data. Our system of interest is LiNi0.5Mn0.5O2 (NMC), a large-scale experimental validation of our precursor selection principles. For a set of 35 target quaternary oxides with chemistries representative of intercalation battery cathodes and solid-state electrolytes, we perform 224 reactions spanning 27 elements with 28 unique precursors. Our predicted precursors frequently yield target materials with higher phase purity than when starting from traditional precursors. Robotic laboratories offer an exciting new platform for data-driven experimental synthesis science, from which we can develop new fundamental insights to guide both human and robotic chemists.
typical cathode material for Li-ion batteries. This material presents challenges in studying detailed changes during electrochemical cycling due to the complexity arising from transition metal mixing. We will evaluate various input transformations for XAS through regression and classification tasks to demonstrating how such feature engineering improves prediction accuracy and interpretability of ML models. Furthermore, we will discuss model validation using unseen experimental datasets, illustrating the transferability and robustness of the feature. A thorough explanation will also be provided to elucidate why certain features outperform others, aiding in the data analysis of experimental spectra [arXiv preprint arXiv:2310.07049].

Acknowledgement

This work is supported by the U.S. Department of Energy (DOE) Office of Science Scientific User Facilities project titled “Integrated Platform for Multimodal Data Capture, Exploration and Discovery Driven by AI Tools”. M.K.Y.C. acknowledges the support from the BES SUPEE Early Career award. Work performed at the Center for Nanoscale Materials and Advanced Photon Source, U.S. Department of Energy Office of Science User Facilities, was supported by the U.S. DOE, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. We also acknowledge the support provided the Data Infrastructure Building Blocks (DIBBS) Local Spectroscopy Data Infrastructure (LSDI) project funded by National Science Foundation (NSF), under Award Number 1640899. MID was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences operating under Contract Number DE-AC02-06CH11357.

11:45 AM MT02.10.05

Atomic Modeling of Chemomechanics at Electrified Interfaces Veerendra Naralasetti, Himanshu Shekhar and Aravind Krishnamoorthy; Texas A&M University, United States

As the world moves to a more electrified future, addressing several mechanical and tribological challenges in electric systems ranging from electrical energy storage to electric vehicle powertrains requires a more fundamental understanding of chemomechanics of electrified interfaces. More detailed insights into the reactivity of surfaces under mechanical contact are needed to design novel materials/lubricants that are needed to improve the efficiency of electro-mechanical systems. In this study, we performed ab initio density functional theory (DFT) calculations and reactive molecular dynamics (RMD) simulations to understand the surface reactivity and evolution of tribolayers in surfaces under electrified and non-electrified contact. Atomistic simulations of Polyalphaolein (PAO) lubricants on naturally-oxidized steel surfaces reveal the formation of amorphous non-stoichiometric iron-carbide tribolayers that are non-protective and contribute to surface wear, consistent with experimental observations. Reactive MD simulations, performed using a specially parameterized ReaxFF forcefield, were used to predict surface passivity and tribological performance at extreme conditions of temperature, pressure and electrification encountered near asperities in surfaces under mechanical loading and thus derive new design rules for surface structures and lubricants for electrified applications.

SESSION MT02.11: AI/ML for Materials and Process Modeling II

Session Chairs: Deyu Lu and Feng Wang

Thursday Afternoon, April 25, 2024
Room 321, Level 3, Summit

1:30 PM MT02.10.02

Designing 2D Janus MXene Zr2CXT (X = O, S, Se, and Te) for Lithium-Ion Batteries using Computational Approaches Yu-Ting Lin and Szu-Chia Chien; National Central University, Taiwan

Lately, 2D MXenes have drawn significant attention owing to their potential applications in energy storage, optoelectronics, sensors, etc. Among various types of 2D MXenes, transition metal carbides with a general chemical formula of M\textsubscript{n+1}X\textsubscript{n}T\textsubscript{n} where M represents a transition metal atom, such as Ti, V, and Zr, X represents a C or N atom, and T represents the surface termination atom including O, S, Se, and Te, have become promising materials for electrodes in Li-ion batteries (LIBs) due to its high electrical conductivity and low diffusion barrier\textsuperscript{1,2}. Through chalcogen functionalization, the MXenes with higher capacity and relatively low diffusion barrier energy can be obtained\textsuperscript{3,4}. On the other hand, by functionalizing different surface elements on the two opposite sides of a single layer MXenes, distinct materials properties can be linked together, facilitating the realization of versatile functions and the expansion of various applications. Janus Zr-based MXenes, Zr2CXT, was recently found to possess excellent structural, elastic, electronic, and optical properties\textsuperscript{5,6}, making them promising materials in LIBs applications. It is of great interest to search for potential Janus 2D Zr2CXT for broader applications. However, precise control of the functionalization on the MXenes surface by experimental methods is indeed very challenging. Therefore, this work aims to apply density functional theory (DFT) calculations to explore the promising Janus Zr-based MXenes for electrode materials in Li-ion batteries. Various Zr\textsubscript{2}C\textsubscript{T}X\textsubscript{X} with surface atoms, including O, S, Se, and Te are studied. The essential properties of suitable anode materials, such as the dynamical stability, electronic properties, and diffusion barrier, are calculated. Furthermore, the adsorption energy of the Li on the Zr\textsubscript{2}C\textsubscript{T}X surface is also calculated, as well as the capacity. It is anticipated that this work will provide insights into designing good 2D Janus MXenes for LIBs applications.

References


1:45 PM MT02.10.03

AI-assisted X-ray absorption spectral analysis: Data reproducibility, database, and machine Learning Deyu Lu; Brookhaven National Laboratory, United States

X-ray absorption spectroscopy (XAS) is a premier element-specific experimental technique widely used for materials characterization in battery research. XAS encodes rich local structural and chemical information around X-ray absorbing species, however such information is convoluted in a abstract form, making it very difficult and time consuming to analyze. In this talk, we will discuss the emerging opportunities in AI-assisted XAS analysis, which leverages first-principles theory, high-throughput computing and data analytics. Specifically, we will highlight key areas in this approach, including pipelines to ensure data quality and reproducibility, spectral database development, and machine learning applications. The AI-assisted analysis pipeline can enable real-time feedback in high-throughput studies and autonomous experimentation.

2:00 PM MT02.11.02

Graph Neural Networks for Accurate Prediction of Ionic Transport Properties of Solid-State Electrolytes Cibrán López Álvarez\textsuperscript{1,2}, Edgardo Saucedo\textsuperscript{1,2} and Claudio Cazorla\textsuperscript{1,2};
\textsuperscript{1}Polytechnic University of Catalonia, Spain; \textsuperscript{2}Barcelona Research Center in Multiscale Science and Engineering, Spain

In the pursuit of energy-efficient and environmentally friendly energy storage devices, solid-state electrolytes (SSE) have emerged as promising candidates due to their substantial stability and performance. The discovery of new materials with enhanced ionic transport is essential for the advancement of SSEs. To address this challenge, we introduce a novel approach based on Graph Convolutional Neural Networks (GCNNs) to predict the ionic diffusion coefficient of materials in large datasets such as the Materials Project database.

Our GCNN model is trained on a large and diverse database of density functional theory ab initio MD (DFT-AIMD) simulations\textsuperscript{[1,2]}, comprising several families of SSE and tens of millions of atomic configurations, what allows extracting valuable insights from the underlying crystallographic and structural relationships.

The predictive power of our GCNN-based approach is demonstrated through extensive validation on the dataset, showcasing its ability to accurately forecast the electrolyte behavior of both known and yet to discover materials. The integration of GCNNs into the materials discovery pipeline holds great promise for the development of next-generation SSEs technologies, introducing here a framework which allows predicting on any desired dataset.

The scripts resulting from this study have been made publicly available as a Python package, that is user-friendly and easily adaptable\textsuperscript{[3]} to any desired target database.
Beyond Predictions: An Interpretable Machine Learning Approach for Battery Performance Forecasting

Ozgur Kahvecioglu, Xiaoping Wang, Mark Wolfman, Tim Fister, Juan C. Garcia, Hakim Iddir, Krzysztof Pupek and Venkat Srinivasan; Argonne National Laboratory, United States

Rapid electrification of the automotive industry requires the synthesis of battery cathode materials at large scale, where the high temperature calcination is considered to be the most energy consuming and expensive process. Oxidation and lithiation of the transition metal cathode precursors occur at elevated temperatures (around 700°C – 1000°C) during the calcination process. The various physicochemical processes that occur during the calcination process can be summarized as dehydration, oxidation, lithiation, layering, and sintering induced grain growth. Transport of reactants, removal of reaction byproducts, and maintaining uniformity of temperature within the reaction zone, are of significant importance for successful scale-up of the calcination processes. A multiscale computational methodology is developed, where the kinetics of chemical reactions are extracted at the smaller length scale, and the mass and energy transport related issues are addressed at the larger length scale. Collaboration with in situ characterization using X-ray diffraction (XRD) techniques provide experimental data required for the model development activities. Atomicistic simulations are conducted to extract further insights regarding the energetics of the evolution of different phases during the high temperature calcination process. Overall, the developed modeling capability is able to help with the optimization of calcination protocols during their scale up procedure.

2:45 PM BREAK

3:15 PM MT02.11.04
Beyond Predictions: Machine Learning Methods, Data and Automation for Sustainable Electronics

Amina El Malki, Mohamed Ati, Mark Asch, Alejandro A. Franco; 1,2; 1Research Institute of Industrial Science & Technology, Korea (the Republic of); 2POSCO NEXT Hub, Korea (the Republic of)

This presentation will discuss our recent study on the application of machine learning to predict the electrochemical behavior of batteries, a key aspect in the field of battery management systems and fast charging technologies. In a distinct departure from existing utilization-based degradation models, this research offers a fresh perspective that emphasizes material-focused performance prediction.

The core of this study is the extensive analysis of data from tens of thousands of charge-discharge cycles of Li-rich layered oxide in a single cell setup. This approach allows for a more focused study of material properties, while avoiding the complexities often introduced by cell configurations. A key achievement of the research is the application of deconvolution techniques to extract intrinsic material properties from the extensive dataset, a critical step in achieving improved prediction accuracy and understanding of material properties.

An integral part of this research is the detailed monitoring of these intrinsic properties over time. This enables not only broad trend predictions, but also a detailed understanding of the electrochemical behavior of the material. In addition, insights into the material's elemental composition ratios contribute to both performance prediction and a deeper understanding of its intrinsic properties.

The study demonstrates a high accuracy of over 98% in predicting battery performance, confirming the efficiency of the machine learning models and the robustness of the dataset. In addition, the research extends its applicability beyond LLO materials, suggesting its potential across different battery materials. This broad relevance underscores the significant impact of the study on battery material design and performance optimization.

In summary, this research represents a significant advancement in the application of machine learning to battery performance prediction. By focusing on intrinsic material properties and leveraging an extensive, detailed dataset, the study not only achieves high prediction accuracy, but also establishes a scalable model for materials analysis in battery technology. The methods and results introduced can lead to more efficient, reliable, and adaptable energy storage solutions for future battery technology.

3:30 PM MT02.11.06
Machine Learning Workflow to Track Degradation Mechanisms in Industrial Lithium Ion Battery Cells

Amina El Malki, Mohamed Ati, Mark Asch and Alejandro A. Franco; 1,2, Mohamed Ati, Mark Asch and Alejandro A. Franco; 1,2, 3LAMFA, CNRS UMR 7352, Université de Picardie Jules Verne, France; 3POSCO NEXT Hub, Korea (the Republic of)

The degradation of lithium-ion battery (LiIB) cells is a complex process resulting from the interaction of multiple phenomena. Understanding LiIB cell aging requires tracking measurable effects of different degradation mechanisms, known as degradation modes. These include the loss of active material in the electrodes, loss of lithium inventory, and conductivity loss. The aging mechanisms are directly correlated with electrochemical cycling protocols and operation conditions of the LiIB cell, such as parameters related to the type and rate of current in the charge and discharge, voltage cutoff conditions, temperature, break periods, state of charge, and cycle number.

Using machine learning techniques to uncover the interrelations between aging conditions/protocols and mechanisms can trigger tremendous progress in designing battery management systems capable of extending cell lifetime in Electric Vehicles (EV) applications [1]. In this work, we introduce a novel workflow that combines various machine learning techniques with electrochemical LiIB cell state of health diagnostic analysis, facilitating the discovery of the impact of a broad set of cycling conditions/protocol parameters on aging modes [2]. This approach allows for deriving the possible aging mechanisms that might manifest in each distinct condition.

While numerous studies have employed machine learning techniques on LiIB cell datasets, they often focus on a limited number of cycling stressors (e.g., C-rate for charge and discharge), and the datasets typically originate from tests conducted in academic laboratories. In this study, a comprehensive industrial dataset, encompassing a broad range of cycling conditions and protocols to simulate real-world usage of LiIB cells in Electric Vehicles (EVs), is utilized. We explore how more than 10 stressors impact the aging modes of cells and identify the predominant degradation mechanisms based on cycling conditions. The analytical capabilities of our machine learning tool are demonstrated through various application examples, and strategies for mitigating aging in automotive applications are discussed. Finally, we consider how our machine learning workflow holds the potential to propel current battery management systems in EVs to the next level.


Autonomous Experimentation for Materials Research

The current materials research process is slow and expensive; taking decades from invention to commercialization. The Air Force Research Laboratory pioneered ARESTM, the first autonomous experimentation system for materials development. A rapidly growing number of researchers are now exploiting advances in artificial intelligence (AI), autonomy & robotics, along with modeling and simulation to create research robots capable of making research progress orders of magnitude faster than today. We will discuss concepts and advances in autonomous experimentation in general, and associated hardware, software and autonomous methods.

We will distinguish between non-iterative AI/ML approaches that use large data sets (e.g., CNN, LLM) and small data, iterative approaches that strive to identify & confirm scientific hypotheses using AI reasoning.

We consider the impact of autonomous experimentation on human scientists and the scientific enterprise: Changing roles for humans and robots, expectations. In the future, we expect autonomous experimentation to revolutionize the research process, and propose a “Moore’s Law for the Speed of Research,” where the rate of advancement increases exponentially, and the cost of research drops exponentially. We also consider a renaissance in “Citizen Science” where access to online research robots makes science widely available.

Polybot: Accelerating Electronic Polymer Discovery through AI/ML and Automation

The increasing demand for flexible, wearable, and smart electronics has propelled the exploration of electronic polymers. To unleash their full potential, understanding the complex relationships between processing, structure, and properties is crucial, along with the development of scalable methods for producing high-quality thin films and devices. This task is particularly challenging due to the intricate interactions between processing parameters, including solution formulation, rheological behavior, and post-treatment procedures. In this presentation, we introduce Polybot, an advanced Autonomous Materials Acceleration Platform (MAP) that seamlessly integrates AI/ML, robotics, and automated characterization techniques for expediting the discovery and optimization of electronic polymers. Polybot exemplifies its prowess through closed-loop studies, demonstrating simultaneous enhancements in polymer processability and performance within a high-dimensional experimental parameter space. Furthermore, we delve into the intriguing realm of small data, addressing the integration of literature-derived insights and physics-based simulations within MAPs. Our discussion will illuminate both the challenges and the promising prospects associated with this integration, showcasing how it enriches the efficiency and robustness of the materials discovery process.

High-Throughput Structural Investigation of Block Copolymer and Conjugated Polymer Co-Assemblies

Conjugated polymers (CPs) have garnered much interest as semi-conducting materials for organic electronics. The properties of conducting polymers can be affected from induced long-range order. Block copolymers (BCPs) are commonly used as templating materials due to their ability to self-assemble into many crystalline structures. Blending structure directing BCPs and relatively rigid CPs may lead to materials with enhanced properties due to the formation of highly ordered structures. Thus, it is essential to understand the phase behavior of these co-assembled blends. The shape and order of these structures are also affected by many parameters including temperature, concentration, molecular weight, side chains, shear, etc. High-throughput characterization and analysis will be required to effectively investigate these factors. To demonstrate this, hydrogel blends of BCP polyethylene oxide-polypropylene oxide-polyethylene oxide and conjugated polyelectrolyte poly[3-(potassium-4-butanoate)thiophene-2,5-diy]] were prepared at varying concentrations with an open-source liquid handling robot. The polymer blends were structurally characterized through high-throughput small angle x-ray scattering (HT-SAXS), utilizing a custom cartridge system that can enable thousands of measurements per day at a synchrotron. In addition, various temperatures and shear conditions were applied to the polymer blends to produce monolithic oriented gels and measured via small angle neutron scattering (SANS). A statistical analysis tool, autophasesmap, was developed in our group to automatically generate phase maps that provide a hierarchical summary of the HT-SAXS experiments. This is accomplished by measuring the similarity between sampled profiles and data-based template functions and clustering the profiles based on this similarity. Multiple ordered phases of the polymer blends were then identified through the presence and position of Bragg peaks in 1D profiles and Bragg spots in 2D profiles.

Development of a High-Throughput Electrochemical Device for Data-Driven Electrolyte Materials Discovery

Data-driven research in the field of electrolyte discovery for energy storage applications is growing rapidly. However, current characterization techniques struggle to analyze large numbers of samples accurately and efficiently. To address these limitations, we propose an innovative electrochemical measurement system to integrate with robotic platforms. This high-throughput system provides highly reliable and repeatable conductivity measurements, facilitating fast screening of battery materials and establishing materials-electrochemical property relationships. Our research contributes to advancing electrolyte materials for energy storage and demonstrates the potential of high-throughput characterization technologies in accelerating materials discovery.
Accelerated Development of Ga2O3 Thin-Film Epitaxial Growth by AI Approaches with FAIR Data in NOMAD

Artificial intelligence (AI), when paired with laboratory automation, can greatly accelerate materials optimization and scientific discovery. For example, it can be used to efficiently map a phase-diagram with intelligent sampling along phase boundaries, or in "retrosynthesis" problems where a material with a target structure is desired but a synthetic route is not known. These AI approaches are especially promising in soft matter and polymer physics, where design parameters (e.g. chemical composition, MW, topology, processing) are vast and where properties and function are intimately tied to molecular design features. However, for AI algorithms to operate efficiently in these spaces, they must also be "encoded" with relevant domain expertise specific to the problems being tackled. This talk will cover recent advances in hardware and software tools for accelerated materials optimization for polymers and soft matter systems. Finally, it will outline remaining challenges in practical implementations and identify future opportunities for research.
We present the implementation of this use case in NOMAD (nomad-lab.eu) [5] and discuss the functionalities developed to digitize the entire data lifecycle in crystal growth and epitaxy, with the ultimate goal of FAIR data for materials growth. We developed and deployed Electronic Laboratory Notebooks (ELN) to document all relevant synthesis procedures. We will show how structured data opens up the potential to facilitate and automate data management, and the sustainable application of AI-based analytics, dedicated to process optimization in synthesis.

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The exploration of coherent phonons demands flawless interfaces to circumvent phonon phase disruptions and inter-phonon interactions, a formidable challenge to achieve in practice. Van der Waals (vdWs) heterostructures, created through the precise layering of diverse two-dimensional materials, offer an optimal foundation for vdW heterostructures while evaluating few candidates without missing optimal results.

In this study, we explore the thermal conductivity distribution of graphene/WSe₂ heterostructure in a candidate space of tens of thousands by employing SLEPA and atomistic Green’s functions. Though analysis, we identified two factors that have a significant negative impact on the thermal conductivities of heterostructures: the average distance of WSe₂ from the center of the heterostructure and the presence of specific sequences, such as ‘1 0 0 1’, where ‘0’ represents graphene and ‘1’ represents WSe₂. Moreover, by using mode-resolved atomistic Green’s function (AGF), the underlying mechanism under these factors is investigated. The findings reveal that, as the average distance of WSe₂ from the center of the heterostructure decreases, there is an increase in the transmission of high-frequency phonons at oblique angles. Additionally, an increase in the number of ‘1 0 0 1’ leads to higher transmission of low-frequency phonons that are normally incident on the heterostructure. These factors can suppress phonon transmission across a broad spectrum of frequencies and angles of incidence, leading to the optimized heterostructure with remarkably low thermal conductivity.

In Material Informatics, material exploration via high-throughput experiments has gained traction. This study used a specially equipped combinatorial sputtering system and thermoreflectance method to explore amorphous materials with TC ~0.1 W/mK. There is a significant demand for solid-like thermal insulation materials combining mechanical strength, which can be applied to heat-mediated sensing devices and heat shields. Amorphous materials are promising candidates for dense thermal insulator since the disordered structure strongly suppresses propagation of the vibrational modes. Their metastable nature can result in varied structures depending on the fabrication process. For instance, our prior research demonstrated that TC of amorphous Si (a-Si) and Ge (a-Ge) films varies with the deposition temperature during sputtering. This implies that amorphous structures can be modulated using sputtering process parameters (PP). Due to challenges in identifying structures, optimizing properties of amorphous materials has not been studied much. In this study, while treating the structure and the composition as a black box, we use the sputtering parameters as the explorable variables and TC as the target variable to be minimized through Bayesian optimization. This high-throughput experiment also works as a materials screening process to identify interesting materials for the characterization analysis. It allows efficient experimental data accumulation on the relationships between the thermal conductivity and the characteristics of amorphous. As a further objective of this study, we also plan to implement machine learning to interpret the gathered data and enhance our comprehension of heat transfer in amorphous materials, which is not yet fully understood.

Samples were prepared using Combinatorial Sputter Coating System (COSCSSOCS), which can deposit the target material with four arbitrarily controlled PPs: mixed gas composition, total gas pressure, sputtering power, and sample-target distance. The multiple holders enabled automatic deposition of 14 samples under a unique set of PPs, in a single batch. We prepared 40 of a-SiOₓ (35 of a-SiNₓ and 12 of a-SiGeNₓ) films with a thickness between 30-200 nm and measured the TC. Here, a-SiOₓ and a-SiNₓ were measured by frequency-domain thermoreflectance (FDT) and a-SiGeNₓ was measured by time-domain thermoreflectance (TDTR). Moreover, for the a-SiNₓ, deposition was performed under 26 new conditions, as suggested by Bayesian optimization.

32 out of the 40 a-SiOₓ films exhibited similar TC ranging from 0.6 to 0.9 W/mK except for the remaining 8 films with TC between 1.4-2.2 W/mK, likely due to contaminations of iron from the deposition chamber during sputtering. In contrast, a-SiNₓ exhibited TC ranges from 0.6 to 1.5 W/mK with a wide-tailed distribution. This indicates the broader TC modulation range for a-SiNₓ compared with a-SiOₓ. Among 26 of a-SiNₓ films prepared under the same conditions as a-SiOₓ, deposition was performed under PPs suggested by Bayesian optimization, the one with the lowest TC achieved 0.5 W/mK. This result ensures the efficacy of our strategy to reduce TC. For a-SiGeNₓ films, the lowest TC was 0.2 W/mK, lower than the reported TC of similar materials like a-Ge₃Sb₅S₁₆ (0.4 W/mK). TDTR also confirmed decreases in speed of sound as Sn content increases which contributes to the TC reduction. As a result, a-SiGeNₓ emerges as a promising candidate for further optimization. Various characteristics like density and structure, beyond merely composition, might be modulated through the depositions across diverse PPs.

To enhance the experimental throughput, we employed the masking mechanism of COSCSSOCS for multipoint deposition on a single substrate in a single deposition batch. This experimental scheme should facilitate data accumulation on the order of 100 samples per single deposition batch. We are currently continuing our material exploration in the a-SiGeNₓ system and will report on these results in our presentation.

Data-driven material science has the potential to transform the way we design and develop materials. This emerging field represents a significant departure from traditional trial-and-error methods and empirical approaches that have characterized materials science for decades. Experiments in this area involve a multidimensional parameter space, making analysis challenging and time-consuming. Finding predictive empirical relations that allow for precise control over various aspects of the synthesis process has posed a challenge to human cognitive abilities alone. This becomes even more complex when combining datasets from different labs or from different scientists due to the lack of established standards for data models and methods to capture the large number of experimental details, including elaborate workflows and a large diversity of instruments for characterization. It requires a radical shift in how information is handled and research is performed. Experiment data must be complemented with its rich-metadata context, also covering ontologies and workflows according to the FAIR (findable, accessible, interoperable, reusable) principles [1].

Opening new perspectives towards finding structure, correlations, and novel information with data-analysis and AI tools, therefore, is intimately connected to the challenge of integrating this information into a FAIR infrastructure [2].
a model that allows pushing forward their development and optimization, especially in terms of PV performance. However, the intrinsic complexity of TFPV materials and devices requires approaching their research in a holistic way. This involves the performance of a holistic characterization approach which presents three main challenges: 1) performing a systematic combinatorial characterization (using different characterization techniques) of materials and devices, 2) automating characterization (data acquisition) for generating a statistically relevant amount of information (big data), 3) generating automatized, fast, and multidimensional data processing strategies.

In this work, an approach to solve these three challenges is presented through the creation of a modular and highly customizable automatized characterization platform and methods that provide a fast, holistic, and non-destructive characterization of complex material and devices. The above-mentioned challenges are faced up by the platform in the following way:

1) Systematic heterogeneous characterization – integrating dedicated sensors for the evaluation of composition, morphology, crystal structure, thickness, and optoelectronic parameters by different techniques (X-ray fluorescence, Raman, photoluminescence and UV-Vis-NIR reflectance spectroscopies, visual imaging, elastic light scattering, I-V, EQE, electroluminescence).

2) Automatize data acquisition – developing dedicated software and protocols for systematic and automatized data acquisition and a data storage structure for efficient data analysis.

3) Automatized and fast multidimensional data processing – developing flexible methodologies and algorithms to automate data conditioning and processing using statistical and AI-assisted data analysis using machine learning algorithms to accelerate the big data analysis and identify correlation patterns and processes to push forward the development of the TFPV technologies.

A real case for the accelerated research of Cu$_2$ZnSnS$_4$-based TPV (CZTSe) devices is then used as practical example for the proposed platform. More than 20 samples (with 5x5 cm$^2$ size) are systematically studied as the initial step for large-scale production of CZTSe based PV devices. The devices have Glass/Mo/MoSe$_2$/CZTSe/CdS/i-ZnO/ITO structure and small controlled and non-controlled fabrication processes variations are included in the samples. Each samples is discretized in 3x3 mm$^2$ individual solar cells (up to 196 cells per sample), which allows achieving a complete data library that aids obtaining a considerable amount of cell-by-cell information to implement statistically relevant analyses. A systematic characterization combining optical and optoelectronic techniques as described above is performed in each cell. The analysis of the data obtained allows correlating the physicochemical properties of the TFPV materials with variations in device performance. This knowledge provides key information for the development of new materials and layers properties, their interrelations and, finally, the current technology limitations. This information is strongly relevant for the future development of the CZTSe technology towards high efficiencies and its future industrialization. Moreover, the proposed platform opens a way for the development of a process monitoring tool for controlling the production of TFPV devices that is easily adaptable to other optoelectronic technologies.

SESSION MT03.04: Poster Session: Machine Learning, Data, Software
Session Chairs: Keith Butler, Shijing Sun and Jie Xu
Tuesday Afternoon, April 23, 2024
Flex Hall C, Level 2; Summit

5:00 PM MT03.03.04
PV-VISION: An Deep Learning based Package for Automated Solar Module Inspection Xin Chen$^{1,2}$ and Anubhav Jain$^1$; $^1$Lawrence Berkeley National Lab, United States; $^2$University of California, Berkeley, United States

Solar photovoltaic (PV) modules are susceptible to manufacturing defects, mishandling problems or extreme weather events that can limit energy production or cause early device failure. Trained professionals use electroluminescence (EL) images to identify defects in modules, however, field surveys or inline image acquisition can generate millions of EL images, which are infeasible to analyze by rote inspection. We developed an open-source computer vision package PV-VISION to automatically process the EL images using deep learning models, covering automatic image preprocessing, cell defect detection and crack feature extraction. We demonstrated the functions of PV-VISION on two tasks: investigating fire impacts on solar farms by inspecting 2.4 million cells and quantifying crack growth in solar modules under mechanical aging tests. We anticipate that PV-VISION can offer a supportive platform for researchers in the solar field, facilitating a more efficient and data-driven approach to EL image analysis.

5:00 PM MT03.03.05
SynthVANet for Effective Prediction of Vertically Aligned Nanocomposite Synthesis Jianan Shen, Tinghan Yang, Jiayi Liu, Benson Tsai, Yizhi Zhang, Chang Liu, Shiyu Zhou, Nirali Bhatt, Zedong Hu, Elizabeth Quigley, Jialong Huang, Jennifer Neville and Hayian Wang; Purdue University, United States

The creation of self-assembled vertically aligned nanocomposite (VAN) thin films via a one-step pulsed laser deposition process has garnered tremendous research interests due to their multifunctionality and unique features such as vertical strain control and anisotropic structure. However, synthesizing VAN structures poses significant challenges, often requiring a trial-and-error approach because of their complex mechanics. To address this, we have developed an AI-driven tool to help guide the synthesis of VAN efficiently. This method automatically extracts data from published literature via a large language model (LLM), ChatGPT, combined with lab-collected data to create a comprehensive database. The crystal-graph-based neural network, SynthVANet, utilizes this database for binary classification of VAN and non-VAN structures, achieving high accuracy as validated by precision, recall, and F1 scores. Overall, this model aims to offer researchers a means to assess the probability of success associated with their growth recipes, significantly reducing experimental time and costs.

5:00 PM MT03.03.06
Optimization of Bistable Clamp for Aerospace Thermal Systems Russell Laudone, Matthew Nakamura and Joseph Brown; University of Hawaii at Manoa, United States

Large spacecraft, launch vehicles, and hypersonic craft use a thermal protection system (TPS) consisting of tiles to mitigate potential thermal hazards while traveling through the atmosphere at high velocities. Historically, these tiles have been attached via silicone adhesive that mates tiles to the craft permanently. The proposed mechanism is a macroscale interlocking bistable compliant clamp that securely houses and rapidly exchanges thermal tiles attached to the TPS. Compliant mechanism design presents a significant learning curve due to large deflections requiring nonlinear mechanics models, and unexplored design space for analysis of deflection of flexible links and mechanisms. Despite their design challenges, compliant mechanisms present many desired characteristics not found in traditional multi-joint rigid-body components, including lower part cost, scalability, precise motion, zero off-gassing, and reduction in weight and friction. Here we report methodology, designs, and results that demonstrate use of optimization techniques to automate revised compliant structures by comparing them against a specified fitness metric. This proposed method is less time-consuming and more efficient than traditional computational or “trial-and-error” methodology and exports parameterized structures in manufacturable file format. This paper's proposed bistable compliant clamp was fabricated in polyactic acid (PLA), assessed with finite element analysis (FEA), and mechanically cycled on a tensile tester. Results identified preliminary performance metrics regarding stress concentrations, retention force, and input force. It was theorized that these metrics depend on geometrical parameters and could be optimized to maximize retention force and minimize input force, while keeping acceptable material-based stress concentrations and bistable characteristics. The design methodology implemented topology optimization techniques to identify potential parameter solutions that improve one or more of the defined performance metrics. Redesigned models were fabricated and tested against the original prototype to validate the algorithm’s ability to enhance mechanisms’ performance. The proposed compliant mechanism serves as a solution for a re-attachable TPS tile system and methodology to optimize compliant structures that do not require expensive equipment in compliant design theory. This result also demonstrates optimal design of unit cells that may be tessellated to form an adhesive metasurface.

5:00 PM MT03.03.07
Machine Learning for Experimental Design of Ultrafast Electron Diffraction Mohammad Shaaban; Texas A&M University, United States

In the field of nanomaterials research, this study presents a groundbreaking approach to overcome the challenges associated with Ultrafast Electron Diffraction (UED) data analysis. We introduce convolutional neural network (CNN) models that enable real-time analysis of UED data, unveiling dynamic material processes and identifying signs of damage. Moreover, Generative Variational Autoencoder (G-VAE) models are introduced to interactively optimize experimental parameters. These machine learning techniques showcase their potential for self-correcting UED experiments and can be readily extended to other characterization methods. By using CNNs to classify UED images and G-VAEs for dimensionality reduction, this study identifies defect formation, lattice distortions, and phase transformations in real-space, offering a transformative shift in materials research. Transfer learning techniques are also demonstrated for practical application on experimental UED patterns, promising advancements in materials science experimentation.
Bayesian Optimization for Customizable Hierarchical Kirigami Piezo-Transmittance Strain Sensor Designs

Jinjin Gu1, Bowen Zheng1, Jihyeon Ahn2, Inkyu Park2 and Grace Gu1; 1UC Berkeley, United States; 2Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The significance of IoT systems incorporating green and sustainable energy sources has grown exponentially. Simultaneously, the demand for sensing systems integrated with low-powered and self-powered capabilities has emerged. Piezo-transmittance strain sensors, which operate on the optical transmittance change induced by mechanical deformation of the functional film, have demonstrated remarkable potential for in self-powered soft sensing applications integrated with solar cells. These sensors are notable for their reliability, rapid response, and long-term stability. While soft sensing systems offer advantages because of their compliance and stretchability, their suitability for vertical sensing platforms varies depending on the mechanical properties of the target objects. Consequently, there is a growing need to develop customized sensor characteristic optimization procedures within this field. The utilization of a kirigami structure in piezo-transmittance sensors addresses two benefits. First, the repeated unit-cell pattern across the film area ensures sensor uniformity. Additionally, it offers design flexibility, allowing for the accommodation of predicted mechanical deformations within the pre-designed structure. In this research, we optimized a hierarchical kirigami-based structure, focusing on sensor sensitivity within different working ranges, as the functional film for piezo-transmittance strain sensors. First, we utilize the results obtained from finite element simulations as a training dataset to build a neural network surrogate machine learning model. This model accepts geometric variables as input and furnishes data regarding the desired performance metrics, thereby substituting the requirement for more costly physical simulations, facilitating the optimization process. The Bayesian optimization and the cross-entropy method were used to optimize the sensor’s geometric structure, and a comprehensive analysis of the geometric factors was conducted through sensitivity analysis. Through sensitivity analysis, we can identify the major geometric factors that affect the sensor's performance. Additionally, in contrast to axiographic behavior, the sensor's performance is better in a simpler model, specifically at hierarchical level 1. Furthermore, through experimental testing, we can validate the superior performance of the designed kirigami piezo-transmittance strain sensors.

Physics inspired Machine Learning of Eliashberg Spectral Function for High-Throughput Screening of Novel Superconductors

Aiinkya Hing, Jason B. Gibson, Benjamin Geisler, Philip Dee, Oscar Barrera, Peter Hirschfeld and Richard Hennig; University of Florida, United States

The Eliashberg spectral function (α²F) is at the core of understanding the electron-phonon superconducting properties of a material. But calculating α²F from ab initio methods for a large number of materials is expensive, impeding the high-throughput search of novel superconductors. With machine learning models gaining prominence over the past decade for material properties, our work harneses this potential for α²F prediction. In this presentation, we will present our expansive database of theoretically calculated high-quality α²F and introduce our state-of-the-art equivariant neural network models trained using it. This talk also elucidates the nuances of training models for predicting continuous properties such as α²F, focusing on innovative physics-inspired node embeddings to bolster model performance. For the α²F-derived properties like the electron-phonon coupling λ, and two moments of the frequency (〈ν0〉, and 〈ν²〉), our base model, relying solely on crystal structure, achieves a Pearson correlation coefficient of 0.3, 0.7, and 0.8. In comparison, integrating moderately expensive node embeddings increases the Pearson correlation coefficients of 0.5, 0.8, and 0.9 on the derived properties. An intriguing power-law relationship between model loss and training dataset size is observed, emphasizing the imperative for community-collaborated expansion of α²F databases.

AI Accelerated Computational Design of The Freeform Solar Cell Structures

Ruosi Guo1,2, Wenqing Wang1,2, Masahito Takakusa2, Kenjiro Fukuda1 and Takao Someya1-2; RIKEN, Japan; 2The University of Tokyo, Japan

Artificial intelligence generated configurations (AIGC) have emerged as a game-changing approach for inverse design, demonstrating remarkable potential in the realm of free-form device structures. This innovation is especially valuable in the context of thin-film solar cell (SC) devices, where patterned meta-surfaces offer the potential to enhance both their electrical and optical properties.

Traditional human-designed periodic meta-surfaces, while effective, are inherently constrained by topological limitations and a limited set of parameters. The advent of free-form design liberates us from these constraints, allowing for the creation of intricate and unconventional shapes, as well as the exploration of a vastly expanded design landscape. This newfound design freedom holds the promise of unlocking unprecedented functional capabilities, potentially surpassing human intuition. Nevertheless, the efficient exploration of this expansive design space presents a significant computational challenge.

One of the primary obstacles to realizing high-throughput free-form designs is the computational cost associated with conventional numerical simulations. In our study, we tackle this challenge head-on by introducing a fully automated system that harnesses the power of high-speed Deep Learning (DL) surrogate solver alongside intelligent configuration optimizer. Compared to standard numerical methods, our DL surrogate model accelerates the prediction of outcomes by 22,700 times, resulting in a 98.47% reduction in computation costs, all while maintaining an average accuracy of approximately 99%.

Our extensive evaluation, encompassing a dataset of 600,000 configurations generated by the intelligent configuration optimizer, has led to the discovery of an optimized SC device design boasting a power conversion efficiency of 17.58%. This performance greatly surpasses the 14.70% baseline efficiency of SC device lacking patterns on the substrate layer. These findings underscore the immense potential of AIGC techniques in efficiently enhancing the performance of photovoltaic devices, paving the way for a brighter future in renewable energy applications.

Machine Learning to Construct Process-Structure-Property Relations of hBN Thin-Films

Dokwan Kook and Satish Kumar; Georgia Institute of Technology, United States

Hexagonal Boron Nitride (hBN) is a 2D material with high in-plane thermal conductivity and low out-of-plane thermal conductivity. Due to its anisotropic properties, hBN films have high potential for the thermal management of next-generation electronics. The thermal conductivity of hBN films depends on the processing conditions and its thickness. The construction of Process-Structure-Property (PSP) relations of hBN film can help in accelerating the synthesis of hBN films with desired thermal properties. Machine learning (ML) techniques can help in utilizing both measurements and simulations to develop reliable PSP relations to guide the synthesis process. In this presentation, we will discuss how Gaussian Process Regression (GPR) can be applied to experimental and simulation data to construct PSP relations. Pulsed laser deposition (PLD) is used for the extraction of experimental data, and molecular dynamics simulations is used for the extraction of simulation data. The PSP relations will be constructed using SEM images as structure data and out-of-plane thermal conductivity as property for various process conditions. A significant challenge is dimensionality mismatch which occurs from the large size of the structural data compared to process conditions and properties, e.g., SEM images are 2D images of a 3D structure, while process conditions or properties are typically 1D. Dimensional mismatch makes the ML model difficult to learn. To resolve this problem, we will apply two-point correlations and principal component analysis. Two-point correlations preserve spatial statistical information of the SEM images. This will allow original structural data from the samples to be converted into similar shapes, allowing the ML model to be trained efficiently. Applying principal component analysis will allow the structure data to be expressed as a linear combination of orthogonal vectors. The data will be represented by the matrix of coefficients of orthogonal vectors, which will be much smaller than an SEM image itself. Experimental data have high fidelity but low quantity, while simulation data can be produced in larger volume. Simulation data will be included with the experimental data during the training of ML model to accelerate PSP relations and the model will identify process conditions corresponding to high thermal conductivities accurately.

MaterialEyes – Looking into Renewable Energy Materials with Theory- and AI-Guided Characterization

Maria K. Chau; Argonne National Laboratory, United States

The understanding and design of materials for sustainability -- such as photovoltaics, optoelectronics, and energy storage materials -- rely on measurements not just of the functional properties, but also of fundamental structural and electronic properties. Data driven approaches such as machine learning (ML) for interpreting these measurements via microscopy and spectroscopy rely on labeled, reliable, balanced training data. We will discuss the use of AI including computer vision and large language models (LLMs) to obtain such training data from literature, and also the use of theory-guided AI approaches to interpret experimental and spectroscopy data. We will also discuss the use of generative AI to understand interfaces and structural evolution in renewable energy materials.
Computational Design of Dual-Atom Catalysts for Sustainable Energy Conversion

Proposal of Bayesian Framework for Inverse Inference to Predict Material Properties from Microstructures

Materials for electronic devices such as organic light emitting diodes need to have tailored optoelectronic properties and be synthetically viable. As devices are composed of organic thin films with different functionality, the optoelectronic properties of materials need to be designed in concert and the role of the interfaces between thin films must be understood. Computational high-throughput screening of molecular excited states can greatly facilitate this complex multi-objective design problem. I will present our recent work on deep machine learning models that are able to predict structure, electronic structure, and excited states of organic molecules and materials in general. Our models predict optical excitations, the fundamental gap, electron affinity and ionization potential with multi-fidelity training for situations where datasets are limited in size and robust out-of-distribution performance is needed, as well as potential implications of pre-training towards developing foundational machine/deep learning models to predict the spatio-temporal evolution of electrochemical interphases. [3]. We also discuss the development of methods like symbolic regression to learn the laws of electrolyte transport [8], the predictions of energy and forces with calibrated uncertainty quantification for interatomic potentials using neural network ensemble models [2]. Finally, we explore different applications with our approach from the design of organic electronics to plasmonic sensors and tailored nanoparticles. [1] Chemical Science, 12, 10755-10764 (2021); 2) Nature Comp. Sci. 3, 139–148 (2023);

11:15 AM MT03.04.08
Proposal of Bayesian Framework for Inverse Inference to Predict Material Properties from Microstructures Satoshi Nouguier1 and Junya Inoue2; 1JAMSTEC, Japan; 2The University of Tokyo, Japan

This presentation introduces a Bayesian framework designed for inverse inference to predict material properties or process parameters from microstructure images. The basic strategy of the proposed framework is the integration of Bayesian inference methodologies with machine learning techniques. This enables us to not only predict target properties but also quantify the uncertainty associated with these predictions. Specifically, our focus lies on the development of a Bayesian framework based on generative networks which recently have received much attention in the field of computational material science. The integration could contribute to the examination of the prediction uncertainty.

In this presentation, we will explain the fundamental concepts of our framework and the outcomes of its application to this specific case study. Our chosen case is the prediction of material properties from artificial dual-phase steel microstructures. Also, we will discuss the comparison between our proposed Bayesian framework and a conventional inference method based on convolutional neural networks. By the end of this presentation, you will gain insights into the novel Bayesian approach and its potential advantages over conventional methods, providing a powerful tool for more robust predictions in the field of computational material science.

11:30 AM MT03.04.10
Physics-Informed Pre-Training of Graph Neural Networks for Materials Property Predictions Shuyi Jia, Fan Shu, Akaash Parthasarathy, Chandreyi Chakraborty and Victor Fang; Georgia Institute of Technology, United States

Pre-training of machine learning models, particularly in the form of self-supervised learning, is now an ubiquitous approach for improving model performance and robustness which has featured prominently in the fields of natural language processing and computer vision. To apply these similar concepts to the materials sciences, new domain-aware pre-training strategies need to be developed. We introduce a series of physics-informed pre-training strategies which align well to materials data and can be applied towards the widely used graph neural network class of machine learning models. We demonstrate the effectiveness of this approach on a wide range of benchmarks across multiple materials systems and properties. We discuss the benefits of pre-training for situations where datasets are limited in size and robust out-of-distribution performance is needed, as well as potential implications of pre-training towards developing foundational models for the materials sciences.

11:45 AM MT03.04.11
Using Domain Specific Languages to Enable Artificial Intelligence for Polymer and Catalyst Design Nathan Park1, Jannis Born2, Matteo Manica2, James Hedrick1, Tim Erdmann1 and Pedro Arrechea1; 1IBM Almaden Research Center, United States; 2IBM Research-Zurich, Switzerland

Traditional research workflows in polymer chemistry, which often rely heavily on trial-and-error, stand to be profoundly reshaped through continued advances in automated experimentation and artificial intelligence (AI). However, the seamless integration of these advances within existing research activities still faces significant hurdles. To overcome these obstacles, we have focused our efforts in key areas which would be impactful for experimentalists. First, we have developed new system-level equipment, both for polymerization in continuous-flow reactors as well as small molecules in flow to bath systems. Second, we show how the use of a domain-specific language (DSL) can solve a host of issues surrounding experimental data representation and management—facilitating more straightforward development of AI models. Finally, we demonstrate how experimental data represented in a DSL can be utilized to develop effective generative models for materials and catalyst design.

SESSION MT03.05: Machine Learning for Computation: High-Throughput Computing
Session Chairs: Keith Butler and Arun Kumar Manodi-Kanakkithodi
Wednesday Afternoon, April 24, 2024
Room 322, Level 3, Summit

1:30 PM MT03.05.01
Computational Design of Dual-Atom Catalysts for Sustainable Energy Conversion Guoxian (Emma) Hu; Georgia Institute of Technology, United States

Dual-atom catalysts (M$_2$M$_2$-N-C) are emerging as promising candidates for electrochemical reactions (e.g., oxygen reduction reaction) which are critical for clean and sustainable energy devices. However, due to the large chemical design space, myriad possible structural configurations, and dynamic structure evolutions of the metal centers under reaction conditions, the design of dual-atom catalysts has been challenging and cost-prohibitive for both experiments and computations. Here, using high-throughput density functional theory (DFT) calculations combined...
with machine learning, we rapidly and efficiently evaluate over 20000 dual-atom catalysts for oxygen reduction reaction. We first generate a DFT database of a subset of the dual-atom catalysts, and validate our computational predictions of the structure, stability, and catalytic activity with experimental data where available. With this benchmarked database, machine learning models based on neural networks were trained and applied to identify promising dual-atom catalysts in the search space which possess higher durability and activity than the state-of-the-art Pt and Fe-N-C single-atom catalysts. Furthermore, additional DFT calculations were performed on selected catalysts to reveal the origin of their improved catalytic performance and establish structure-property-performance relationships. The computational framework developed in this work can be generally extended to other important electrochemical reactions including carbon dioxide reduction reaction and hydrogen evolution reaction for sustainable energy conversion.

1:45 PM MT03.05.02
Sub-Trillion-Scale Atomic Data Integrated Deep Learning Approach for Predicting Thermal Transport Properties of 60,000 Inorganic Perovskites Ming Hu; University of South Carolina, United States

Although first-principles based anharmonic lattice dynamics method coupled with the phonon Boltzmann transport equation has been developed to obtain the phonon properties including lattice thermal conductivity at highest accuracy ever, the costly and time-consuming nature of the required interatomic force constants calculations renders high-throughput infeasible when facing tens of thousands of new materials. Here, a high-dimensional multi-element deep neural network with sub-trillion-scale atomic data is trained, dubbed Elemental Spatial Density Neural Network Force Field (Elemental-SDNNFF), achieving a competitive force root mean square error and a speed-up of 4 to 5 orders of magnitude in comparison to first principles. The effectiveness and precision of the Elemental-SDNNFF approach is demonstrated on a set of 150,000 inorganic crystalline structures spanning 63 elements in the periodic table by prediction of complete phonon properties such as phonon dispersions and lattice thermal conductivity. We then use our trained neural network model to predict and screen full phonon properties of 60,000 single and double perovskite structures. Due to the inherent structural feature of dynamical disorder, the perovskite structures have shown diverse thermodynamic and phonon transport properties. Dynamic stability of all 60,000 perovskite structures is predicted by screening negative frequencies in the Brillouin zone. Four-phonon scatterings and two-channel thermal transport are also analyzed and screened. The underlying mechanism is explained in deep at the electronic level. This study demonstrated that our algorithm is very powerful for predicting phonon properties of large-scale inorganic crystals and is also promising for accelerating high-throughput search of novel phononic materials for emerging applications.

2:00 PM *MT03.05.03
Understanding and Mitigating Bias in Autonomous Materials Characterization and Discovery Jason R. Hatrick-Simpe; University of Toronto, Canada

Since the publication of the Mission Innovation Materials Acceleration Platform, AI is increasingly responsible for driving automated experimental and computational tools. There have been multiple case studies for which autonomy was demonstrated to successfully drive materials optimization or discovery problem and the world of scientific robots has moved from science fiction to reality. However, within the broader AI community it is well known that AI’s carry with them their creators’ biases and this has serious implications on model development and deployment. Using several case studies, I will illustrate how biases can arise in materials science and specific steps that can be taken to remove them. Specifically, I will discuss some of our recent work in (1) reducing human bias in label generation by applying robust statistics to spectroscopic data analysis, (2) identifying and mitigating search space bias through model disagreement, and (3) circumventing the big data bias loop by illustrating how the presence of information redundancy in large computational datasets and (4) how construct an optimally informative dataset for model training.

2:30 PM BREAK

3:30 PM *MT03.05.04
Predicting The Structure and Properties of Bulk and Surface Perovskite Oxides with Machine Learning and Simulations Rafael Gomez-Bombarelli; James K. Darnelwood, Jessica Karaguesian, Jaclyn Lunger, Jiayu Peng and Xiaochen Du; Massachusetts Institute of Technology, United States

Ceramics based on multicomponent oxides are a promising platform for catalysis and electronics. By controlled doping of multiple elements, it may be possible to tune electronic and transport properties of oxide materials towards high performance applications. This opens an exciting and high-dimensional design space for choosing the most promising choices and stoichiometric ratios of elements that fine tune desired properties.

Here we will describe how machine learning models, powered by electronic structure simulations can address property prediction and design in multicomponent space. In particular, we will explore how perovskite oxides, which can support quaternary or even more complex compositions, can be engineered in silico.

We will describe the use of elemental and electronic descriptors to predict whether perovskite oxide materials will exhibit chemical ordering when synthesized, we will evaluate the use of per-site deep learning models to predict atomically-project properties such as magnetic moments of catalytic side activity, the use of machine learning interatomic potentials to relax perovskite structures and to create surface phase diagrams, and the ability of equivariant models to capture symmetry-breaking relaxation and properties from idealized, unrelaxed prototypes.
These tools put together, alongside machine learning models for synthesis planning, will support the development of bottom-up data-driven design pipelines for multicomponent oxide materials with tailored properties.

4:00 PM *MT03.05.05
Fantastical Training Data and How To Generate It Martin Zwijnenburg; University College London, United Kingdom

In an ideal world we would train machine learning models for organic materials on training data generated using coupled-cluster singles-doubles-triples-quadruples or something similar and fully take into account the environment of the molecules. In practice this is impossible considering the number of training points required for most models. As a result, we have to make choices. Even more so when we want our model not to predict ground state energies and/or geometries but excited state properties, such as optical excitation energies or electron affinities/ionisation potentials, as well as to be transferable. Models that could accurately predict excited state properties for a wide range of organic materials would be very useful in virtual high-throughput screening of materials for organic LEDs, photovoltaics and photocatalysts.

In my contribution I’ll discuss our work and that of others on training data generation for excited-state properties of organic materials. I’ll consider which properties to aim for, what the best possible training data might look like and how hybrid schemes based on tight-binding methods calibrated to higher-level methods can be exploited.

4:30 PM MT02.05.06
Experiment Versus Computation, Physics Versus Machine Learning in The Inverse Design of Photovoltaic Materials Andrea Crovetto; Technical University of Denmark, Denmark

As a practical case study to advance methods for the inverse design of photovoltaic (PV) materials, my group has been given the following task for the next 5 years: Identify and synthesize the best PV absorber out of the space of all inorganic materials containing sulfur and phosphorus (phosphosulfides). Within this family of materials ~10 compounds have already been considered as potential PV materials, ~260 have previously been synthesized, ~420 are present in the Materials Project database, and 200,000 phosphosulfide compounds from ternary and quaternary systems are chemically plausible according to charge-neutrality arguments.

To try to solve this puzzle within a 5-year timeframe, we have set up a multi-faceted inverse design platform. This platform includes:

1. High-throughput/medium versatility modular synthesis apparatus for combinatorial growth of any inorganic phosphosulfide thin films, so that there are no excuses for excluding certain elements from experimental work. This includes sulfur- and phosphorus partial pressure control (both at atmospheric and low total pressures), separate chambers for volatile metal incorporation, and creation of perpendicular combinatorial gradients in the metal-to-metal ratio as well as in the S/P ratio.

2. High-throughput characterization apparatus, focusing on the properties that are expected to be correlated with the final PV performance and are difficult to simulate with sufficient accuracy.

3. A tiered approach to material property simulation, with a focus on complementing (rather than reiterating) the information available from experiment. The simulation tools can be roughly divided into first-principles quantum mechanical methods, semiclassical methods, and classical “rule-of-thumb” methods.

4. A data management tool to accommodate both experimental and simulation data.

5. Various artificial intelligence tools to be used both for decision-making in the lab and for understanding complex composition-structure-process-property-performance relationships.

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Vitrimers are a new class of self-healing polymers that can heal by rearranging their molecular structure via dynamic covalent bonds. These polymers offer promise for improving the circular life-cycle and sustainability of various polymeric systems that are used in our day-to-day life ranging from fiber composites to electronics. A recently developed framework called Accelerated ReaxFF, uses the “bond boost” approach to speed up the MD simulations by providing reactive sites in the reactants with boost energy equivalent or slightly larger than the energy reaction barrier to overcome the cross-linking process barrier and form desired products. This approach avoids unwanted high-temperature side reactions while allowing for recombination of high-barrier events. This method can be employed not just for virtual characterization of vitrimer polymers but also to understand the rearrangement reactions in epoxy-acid vitrimer polymer chemistries. Further, using coupled molecular dynamics and machine learning, we design new vitrimer chemistries with targeted applications. This includes collecting a dataset of glass transition temperature of various vitrimer chemistries calculated through molecular dynamics (MD). This dataset is then used to train a latent space and property predictor. Finally, a search is performed within the latent space to uncover vitrimer chemistries with desired properties.

**9:00 AM *MT03.06.03**

**Taming The Complexity of Materials Degradation with Machine Learning**

**Brett M. Savoie**

Purdue University, United States

Limited stability and unacceptable degradation products are common reasons for otherwise promising materials to fail technological translation. The enduring state-of-the-art for establishing these properties essentially remains make-and-break testing, which is costly and provides information only at the end of the materials development process. The complexity of the reaction networks that govern degradation and the difficulty of data analysis pose tremendous obstacles to predictive approaches, however recent advances in automated reaction prediction and machine learning are increasingly making it possible to tractably describe and even predict degradation phenomena. In this talk I will highlight our group’s recent work developing methods for predicting reaction outcomes and how they have been applied to several different materials classes. The second half of the talk will discuss machine learning approaches to the closely related problem of identifying degradation products on the basis of typical spectral information sources.

**9:30 AM *MT03.06.04**

**Materials Cartography: The Role of Materials Representation**

**Steven B. Torrisi**

Toyota Research Institute, United States

Within materials science, practitioners are concerned with modeling length scale that spans many orders of magnitude, presenting differing challenges across the atomistic, mesoscale, and device levels. Moreover, problems where data are scarce pose challenges for applying machine learning in many scientific fields. When designing, training, and applying a model, the representation of input features can be just as important as the target and architecture of the model itself. Finding the appropriate way to represent a material of interest is not always straightforward and remains an active area of research. In this talk, I will highlight recent work which explores the concept of materials representation in applications ranging from materials and device-level informatics to molecular dynamics, highlighting intriguing results as well as lessons learned that may be useful for practitioners in diverse subfields of materials science.

**10:00 AM BREAK**

**10:30 AM *MT03.06.05**

**Learning from Data and Distributions to Accelerate Engineered Materials: Energy, Devices and Materials**

**Rachel C. Kurchin**

Carnegie Mellon University, United States

Whether or not we take an explicitly probabilistic perspective, and whether or not we are using black-box models or traditional physics-based ones, learning from and with distributions (of data, probability, and/or parameters) is an important tool in the data-driven modeler’s toolbox. In this talk, I’ll present two stories from my group’s work emphasizing why this is important. First, I’ll discuss some past and present work in using Bayesian parameter estimation to characterize materials and interfaces in photovoltaic devices. In this work, we use a drift-diffusion model to simulate current-voltage curves with a variety of different materials properties for both the layers and the interfaces within the device. By comparing these simulated curves to measured data we can effectively “invert” the device model to get posterior distributions reflecting our knowledge about the input parameters to the model as a function of measurements corresponding to the output.

Next, I’ll shift to focus on some ongoing work utilizing diffusion models (the same type of machine learning model behind generative image tools such as DALL-E and Midjourney) to generate realistic microstructures of solid-oxide cell electrodes for use in device degradation simulations. A key aspect of validating these models is running their outputs through software that computes measured data we can effectively “invert” the device model to get posterior distributions reflecting our knowledge about the input parameters to the model as a function of measurements corresponding to the output.

**11:00 AM MT03.06.06**

**Algorithmic Design and Implementation of an Automated Synthesis Platform for Rare and Exceptional Materials Discovery**

**Alexandra E. Siemens**

1, Armi Tiihonen1,2, Basita Das1, Eunice Aissi1, Fang Sheng1, Sebastian De Jesus1, Lleyton Elliot1, Sharii Maredia1, James Serdy1, Hamide Kakav1,3 and Tonio Buonassisi1,3

1Massachusetts Institute of Technology, United States

2Aalto University, Finland

3Cukurova University, Turkey

Discovery of exceptional materials with high-performance properties, such as perovskite materials with ideal band gap and high stability, stands as an imperative challenge for developing sustainable electronic devices to tackle decarbonization and address the larger climate crisis. However, these exceptional materials are rare – existing only in narrow hypervolumes of vast and high-dimensional material search spaces, similar to a needle-in-a-haystack. With the rise in self-driving labs, it has become tractable to search larger volumes of these high-dimensional search spaces. However, current high-throughput self-driving labs are limited by their algorithmic performance in discovering needle-in-a-haystack exceptional materials as these labs are often guided using standard Bayesian optimization methods that inherently smooth over these regions containing exceptional materials within the search space. In this contribution, we present the design of DISCO ([Di]covery, [Sy]nthesis, [Ch]aracterization, and [Op]timization), an autonomous and high-throughput platform designed specifically to target the discovery of exceptional materials for sustainable electronic device applications. We highlight the following key contributions of DISCO: (1) design of a zooming-based Bayesian learning with hypervolume penalization to maximize the number of exceptional materials discovered per unit time and (2) vectorization of the predicted exceptional materials for ultra-high-throughput synthesis and automated characterization within high-dimensional materials search spaces. The DISCO platform uses a method of ultra-high-throughput inkjet gradient deposition that synthesizes up to 100 unique material compositions within 10 seconds. Each material gradient is suggested by a custom Bayesian learning algorithm, entitled ZoMBI-Hop ([Z]ooming [M]emory [B]ased [I]ntialization). ZoMBI-Hop drives the discovery of exceptional materials within DISCO by iteratively zooming the search bounds into regions of high-reward, in turn, capturing the true rough, non-convex nature of the needle-in-a-haystack optimum, rather than smoothing it over. Furthermore, ZoMBI-Hop jumps between high-reward basins in the search space, such that once an optimal region has been discovered, then that hypervolume becomes penalized for future iterations, resulting in only new high-reward regions being searched. Using this approach, we demonstrate the targeted discovery of up to 10x more exceptional materials from 60 materials search spaces, relative to previous ZoMBI implementations, given the same number of experiments. Each optimum suggested by ZoMBI-Hop is transformed from a single point into a vector that spans the extents of the search bounds using the angle of highest predicted cumulative reward along the vector. This vectorization of a single point generates a gradient of...
High-Throughput Methods for Lead-Free Halide Double Perovskites: Computation and Experiment


Knowledge of the exact atomic structure is crucial for computational analysis of unknown phases observed in experiments and for discovering novel materials. We previously developed the FANTASTX (Fully Automated Nanoscale To Atomic Structure from Theory and eXperiments) package, a multi-objective evolutionary algorithm to determine atomicistic structure from experimental characterization data. This approach relies on sampling the potential energy landscape of thermodynamically stable structures to find the best match between the simulated phase and observed experimental data. In this work, we develop a method for efficient sampling of candidate structures based on generative modeling.

Achieving effective human-machine interaction hinges on the recognition and response of machines to human emotions. However, the integration of emotions into robotics is a formidable challenge, primarily due to the intricacy and subjectivity of human emotional experiences. To enable the development of cognitive robotics capable of simultaneously perceiving and responding to human emotions, it is essential to make significant strides in emotional sensors driven by artificial intelligence (AI) and machine learning algorithms capable of accurately interpreting and responding to emotional cues. In this study, we introduce a novel approach to multimodal emotion sensing by harnessing non-invasive data collection of physiological indicators, including heart rate pulse, breathing patterns, and voice signatures. We utilize wearable printed organic piezoelectric sensors that offer rapid response times and are highly sensitive to a wide spectrum of force waveforms, frequencies, and pulse-width modulation. The responses obtained from these wearable sensors are fed into a long short-term memory neural network algorithm, achieving remarkable classification in distinguishing various emotional states.

The development of advanced materials requires precise and efficient search through a vast range of possible material candidates and conditions to find the select few which satisfy highly customized or specific experimental goals. We focus on the area of AI-based sequential decision making where, at each step, the next candidate material is suggested based on previous accumulated data. We develop and extend the recently proposed concept of Bayesian Algorithm Execution to allow machines to automatically convert a complex, targeted experimental goal into an adaptive data collection strategy, resulting in substantially improved performance compared to state-of-the-art methods.

Lead-free halide double perovskites have been evaluated up until today. The material class can be enlarged even further by substituting the Pb2+ ion not only with one M1+ and one M3+ ion but with two of each resulting in a total of six ions in the material.[3-5] This adaption increases the number of possible materials immensely and gives rise to the demand for a different approach in material investigation: high-throughput (HTP) screening.

The combination of these strategies is a promising approach towards a HT screening in novel materials discovery and is shown to be applicable on the example of Cs2AgxNa1-xBi1-yInyCl6 and therefore to build up a database. Using machine learning algorithms on this database can lead to a deeper understanding of the coupling between the ion exchange and macroscopic material properties.

Sources:
For example, we can now easily make data-driven tests of well-known rules and heuristics or develop quantum chemistry-based materials descriptors for machine learning approaches. These

Modern opportunities for data-driven chemistry and materials science through automation

We address these bottlenecks and present an integrated, experimental-theoretical workflow that leverages high-throughput, automated experiments, and abstract computational models with

Despite the initial success of AI in closed-loop chemical discovery workflows, there still exist major challenges in their scalable implementation – the major bottlenecks being i) the degree of

Often this process is directed using data-driven optimization strategies.

The full utility of computation in the chemical discovery pipeline is only realized with the close integration of experiment and theory. This could be achieved via closed-loop, experimental-theoretical workflows is also possible and promises further acceleration in the field.

Novel chemical systems are necessary to fully address the major global challenges facing humanity, including the climate emergency, resource scarcity, and energy consumption needs. Traditional chemical discovery initiatives are founded on intuition-guided, “trial-and-error” processes. Here, small, iterative changes to chemical structure and experimental conditions are made by the researcher. This is significantly resource and time intensive; after each small modification, the molecule must be synthesized (often a trial-and-error process in itself) and properties measured. As a result, these workflows are associated with long timescales (~20 years) and high costs. Recently, computation has accelerated this process via atomistic simulations and data-driven approaches. Yet, present applications of computation are largely post-rationalization of experimental observations or high-throughput screening of manually-curated databases of hypothetical systems.

The full utility of computation in the chemical discovery pipeline is only realized with the close integration of experiment and theory. This could be achieved via closed-loop, experimental-theoretical workflows, which are poised to efficiently identify high-performing candidate compounds for target applications. Here, AI-driven theoretical predictions guide high-throughput, automated experiments and these experimental results are used to improve the accuracy of the predictive models in an iterative process, which is repeated until convergence criteria are met. Often this process is directed using data-driven optimization strategies.

Despite the initial success of AI in closed-loop chemical discovery workflows, there still exist major challenges in their scalable implementation – the major bottlenecks being i) the degree of human intervention needed and ii) lack of methods to manage the number and quality of initial data points. This is further complicated by the necessary integration and accommodation of i) varying metadata formats, ii) non-compatible, proprietary characterization software, and iii) hands-on robotic platform calibration and manipulation, among others. Each of which needs to be explicitly addressed to realize coherent, automated closed-loop chemical discovery. Thus, data-driven solutions and supporting software are imperative to seamlessly close-the-loop in experimental-theoretical discovery workflows. We address these bottlenecks and present an integrated, experimental-theoretical workflow that leverages high-throughput, automated experiments, and abstract computational models with data-driven optimization strategies to drive towards viable supramolecular materials for gas storage and separation applications.

We address these bottlenecks and present an integrated, experimental-theoretical workflow that leverages high-throughput, automated experiments, and abstract computational models with data-driven optimization strategies to drive towards viable supramolecular materials for gas storage and separation applications.

In recent years, many protocols in computational materials science have been automated and made available within software packages (primarily Python-based). This ranges from the automation of simple heuristics (oxidation states, coordination environments) to the automation of protocols, including multiple DFT and post-processing tools such as (an)harmonic phonon computations or binding analysis. Such developments also shorten the time frames of projects after such developments have been made available and open new possibilities. For example, we can now easily make data-driven tests of well-known rules and heuristics or develop quantum chemistry-based materials descriptors for machine learning approaches. These tests and descriptors can have applications related to magnetic ground state predictions of materials relevant for spintronic applications or for predicting thermal properties or electronic properties, etc.

Combining high-throughput ab initio computations with fitting, fine-tuning machine learning models and predictions of such models within complex workflows is also possible and promises further acceleration in the field.

In this talk, I will show my latest efforts to link automation with data-driven chemistry and materials science.

Industrial liquid formulations from electronics to nanoparticle coatings to drug delivery vehicles are often strikingly complex, with large numbers of components (10-100), complex multistep processing.
and a wide variety of design requirements for a functional, sustainable, regulatory compliant product. This complexity often precludes physics-informed mapping between component fractions, processing, structure, leaving most formulation design to empirical trial-and-error or design of experiments strategies. I will discuss recent efforts by the Autonomous Formulation Laboratory (AFL) team at NIST to use machine learning driven, highly automated characterization to rapidly and intelligently map formulation phase space using structural characterization tools such as small-angle x-ray and neutron scattering (SAXS/SANS) together with secondary measurements, e.g. optical imaging, UV-vis-NIR and capillary viscometry. Our initial studies have resulted in an order of magnitude reduction in the time needed to map a model phase diagram and rapid cross-learning between model petroleum-based and biobased formulations. Other systems of interest from our personal care, biopharmaceutical, and alternative energy industrial collaborators will also be highlighted, including recent results on multimodal cooperative active learning.

4:00 PM MT03.07.07
A Low-Cost, Closed-Loop Nanomaterials Synthesis Automation Platform Maria Politi, Brenden Pelkie, Blair Subbaraman, Fabio Baum, Kiran Vaddi, Nadya Peek and Lilo D. Pozzo; University of Washington, United States

Conventional nanomaterials synthesis schemes can be labor- and time-intensive, which significantly impedes the pace of new materials discovery and their applications. Semi-automated and fully automated platforms, in combination with data-science principles and artificial intelligence, have become an emerging paradigm for accelerated materials discovery. The combination of high-throughput experimentation and minimal human interactions with the system have allowed faster material synthesis, characterization, and analysis. However, many of these initiatives are still too costly to be implemented. In this context, open hardware principles have made the use of laboratory automation more accessible and more easily implemented for a variety of applications. We have demonstrated the use of a versatile automatic tool-changing platform (Jubilee) configured for automated ultrasound application, a liquid-handling robot (Opentrons OT2) and a well-plate spectrometer for the synthesis of CdSe nanocrystals. A total of 625 unique sample conditions were prepared and analyzed in triplicate with an individual sample volume of as little as 0.5 mL, which drastically reduced chemical waste and experimental time. Furthermore, we coupled the high-throughput workflow to a data-driven approach for the interpretation of the results provided a holistic view of the design space investigated. While successful, the previous study relied on three different instruments to conduct the workflow. Further improvements have allowed for integrating all the synthesis, processing, and characterization tools onto the same Jubilee platform for a closed-loop experimental campaign. This new ecosystem uses a simple Python API and allows for new tools to be easily integrated and interfaced, for simpler experimental orchestration. Thanks to the high-throughput capabilities of this low-cost and open-hardware platform, the ease in scalability of the system, and the modularity of the protocol, the overall workflow was adapted to study a variety of nanocrystal design spaces.

4:15 PM MT03.07.08
Understanding Design Rules of Colloidal Self-Assembly Using Autonomous Phase Mapping Kiran Vaddi, Huat Thart Chiang, Sage Scheiwiller, Karen Li and Lilo D. Pozzo; University of Washington, United States

Automation in many experimental pipelines at laboratory and central facilities has shifted the bottleneck to autonomously driven data analysis and decision-making. Exponential growth in tools available for data-driven modeling resulted in the advent of self-driven laboratories (SDL) that aim to automate and accelerate the entire workflow starting from synthesis to characterization and device integration for emerging technologies and energy needs. Platforms based on solution-processible materials (polymers, colloids, and nanoparticles) are amenable to automation both at the synthesis and characterization levels. Techniques such as scattering and spectroscopy provide faster high-throughput alternatives to capture a signal of the underlying structure allowing us to construct composition-structure phase maps. However, one of the common goals in ‘phase mapping’ a system is to accurately identify phase boundaries that can have materials with interesting structures and properties. In the realm of SDL, the problem of mapping phase boundaries is tackled using a combination of Bayesian active learning and data clustering. These techniques however cannot predict the phase map by ‘filling’ in the unexplored space that can provide information about the type of phase transition a boundary represents. We address this problem by reformulating the closed-loop phase mapping as a Bayesian active learning of a surrogate model that predicts measurement curves (spectroscopy, diffraction, or scattering). We apply the proposed approach to several classes of nano-scale colloidal and polymeric materials to learn phase maps that can be effectively used in understanding design rules to engineer colloidal self-assembly.
SESSION NM01.01: Synthesis and Characterization I
Session Chairs: Stefano Ippolito and Michael Naguib
Tuesday Morning, April 23, 2024
Room 330, Level 3, Summit

10:30 AM NM01.01.01
High-Yield and High-Throughput Delamination of Multilayer MXene via High-Pressure Homogenization

Alex Inman1, Kateryna Shevchuk2, Joseph Capobianco3 and Yury Gogotsi1
1Drexel University, United States; 2USDa ARS, United States

Two-dimensional (2D) MXenes are a large family of materials with unique properties and numerous potential applications. They are typically produced by selective chemical etching of MAX phase precursors, which is a top-down approach allowing for scalable manufacturing. Multilayer MXenes are then further processed by chemical intercalation and delamination to produce a stable dispersion of 2D flakes in water. The current process of delamination requires multiple time-, energy-, and waste-intensive steps and still fails to delaminate some MXenes. Herein, we demonstrate a method of high-energy delamination called high-pressure homogenization (HPH) that combines high shear, cavitation forces, and impact forces to delaminate MXene without any post-process refinement steps or chemical intercalants. HPH-delaminated MXene can be made at scale with high throughput and yield with virtually no waste. We demonstrate the viability of this process by fabricating free-standing films with the material for use as electrodes for energy storage and as an effective antimicrobial coating where any residual lithium is undesirable. HPH-MXene electrodes demonstrated comparable capacitance to that of lithium-delaminated films with better rate capability. HPH-MXene coatings proved effective as antimicrobial coatings with over a two-log reduction in pathogenic microbes without the concern of chemical leaching by the coating. We anticipate that this method will decrease the cost of MXene manufacturing and be applicable to a variety of MXenes, including those that cannot be currently delaminated via intercalation.

10:45 AM NM01.01.02
A-Modified MXenes: Interlayer Incorporation of A-Elements into MXenes via Selective Etching of A’ from Mn+1A’1-A’XnTzc MAX Phases

Alexander Sinitskii
University of Nebraska-Lincoln, United States

MXenes are a large family of two-dimensional materials with a general formula M
d+1XnTzc, where M is a transition metal, X = C and/or N, and Tzc represents surface functional groups. MXenes are synthesized by etching A elements from layered MAX phases with a composition of M
d+1AXn. As over 20 different chemical elements were shown to form A layers in various MAX phases, we propose that they can provide an abundant source of new MXene-based materials [1]. The general strategy for A-modified MXenes relies on the synthesis of a Mn+1A’1-A’XnTzc phase, in which the higher reactivity of the A’ element compared to A enables its selective etching, resulting in A’-modified Mn+1A’XnTzc. In general, the A’ element could modify the interlayer spaces of MnXene flakes in a form of metallic species or oxides, depending on its chemical identity and synthetic conditions. We demonstrate this strategy by synthesizing Sn-modified Ti3C2Tmxene from Ti3Al75Sn25C2 MAX phase, which was used as a model system. Although the incorporation of Sn in the A layer of Ti3AlC2 decreases the MAX phase reactivity, we developed an etching procedure to completely remove Al and produce Sn-modified Ti3C2Tmxene. The resulting MXene sheets were of high quality and exhibited improved environmental stability, which we attribute to the effect of uniform Sn modification. We demonstrate a peculiar electrostatic expansion of Sn-modified Ti3C2Tmxene, which may find applications in MXene-based nanoelectromechanical systems. Overall, these results demonstrate that in addition to different combinations of M and X elements in MAX phases, an A layer also provides exciting opportunities for the synthesis of new MXene-based materials. Synthetic approaches to MXenes modified with A-elements other than Sn, as well as applications of such materials, will also be discussed.


11:00 AM NM01.01.03
Synthesis and Electronic Transport of Ultrathin Single Crystal WC and W2C

Alexander J. Sredensheck, David Sanchez, Jiayang Wang, Da Zhou, Le Yi, Morteza Kayyalha, Susan B. Sinnott and Mauricio Terrones; The Pennsylvania State University, United States

The transition metal carbide (TMC) family has historically been studied and applied for its high hardness, chemical stability, and electrocatalytic activity. Initially studied in bulk, non-layered morphologies, TMCs have received renewed interest with the development of novel top-down and bottom-up approaches to isolate layered TMCs (MXenes)1 and ultrathin, non-layered TMCs (UThTMCs)2, respectively. The MXene family is large, but challenges persist in phase control and isolation of tungsten carbide owing to the lack of appropriate precursor material.3 Following recent works in bottom-up synthesis of UThTMCs4,5, we show the isolation of tungsten carbide phases using a liquid-metal-assisted chemical vapor deposition (LMCVD). Moreover, in the tungsten carbide system, little attention has been given to the influence of diffusion barrier and reactive gas ratios on the thickness, morphology, and phase of the crystalline products. In this work, we report the synthesis of WC (P-6m2) with copper/tungsten foil stacks, and W2C (Pheen) from gallium/tungsten substrates. We identify the phase of these compounds using a combination of X-ray diffraction and planar/cross-sectional selected area electron diffraction. The chemical compositions of WC and W2C are investigated by planar energy dispersive X-ray spectroscopy (EDX) in the scanning transmission electron microscope. Moreover, we probe the dependence of crystal morphology with changes in growth temperature as well as methane/hydrogen (CH4/H2) ratios. Another aspect of the synthesis that we have investigated are byproducts in the synthesis of WC/Cu/W and W2C/Ga/W by combination of scanning electron spectroscopy (EDX) in the scanning transmission electron microscope. Herein, we compare in-plane and out-of-plane magnetic field measurements to assess the dimensionality of this superconducting state.
In 2011, the synthesis of 2D materials through selective etching of specific layers in laminated 3D precursors was demonstrated, leading to the discovery of MXenes. Since then, the quest for 2D materials via etching has relied primarily on experimental methods, given the lack of accurate and efficient computational protocols. We here present the first steps towards a general theoretical approach for predicting 2D materials formed by selective etching under acidic conditions. Among ~60,000 3D materials, we identify ~100 potentially exfoliable candidates, including several material families. We corroborate the existence of well-established materials such as both TMD and MXene. Furthermore, and as a proof-of-principle, we selectively etch Y from a Ru-based compound, resulting in freestanding 2D sheets of Ru-based material. Our discoveries hold promising implications for experimental realizations and further advancements in theoretical investigations.

SESSION NM01.02: Synthesis and Characterization II
Session Chairs: Stefano Ippolito and Michael Naguib
Tuesday Afternoon, April 23, 2024
Room 330, Level 3, Summit

1:30 PM *NM01.02.01
Synthesis Science between MAX phases and MXenes Christina S. Birkel1,2 and Rose Snyder1; 1Arizona State University, United States; 2Technische Universität Darmstadt, Germany
The synthesis of MAX phases and their two-dimensional siblings MXenes, especially when pushing beyond Ti-based compounds, is far from trivial. Our group uses diverse preparation techniques across new versions of these intriguing types of materials. Recent examples include Cr2GaC in the shape of carbonaceous microfibers,1 hollow and full microspheres2 as well as hitherto unknown carbonitride phases, such as Cr2GaC1-xNy and V2GaC1-xNy.3 We specialize in non-conventional methods, such as sol-gel chemistry4–6 and microwave heating7 to synthesize the MAX phases.

In this talk, I will highlight two of our recent projects: (i) Our work on a unique “514” MAX phase (Mo0.75V0.225)AlC4, its structural investigation and transition to the respective MXene including its electrocatalytic properties. (ii) The transition from a MAX-like “221” compound Mo0.6Ga0.4C to the fully exfoliated MXene Mo0.6C1.4 as well as Mn-doped variants. All materials are structurally characterized by diffraction and microscopy techniques and a deeper understanding of their chemical composition, formation mechanism and stability is obtained through spectroscopy and thermogravimetric methods.

2:00 PM NM01.02.02
Synthesis of High-Quality Monolayers of Cr2TiC2T3 MXene, Their Mechanical Properties, p-type Electrical Transport and Positive Photoresponse Saman Bagheri1, Michael J. Loe1, Alexey Lipatov1,2, Haidong Lu1, Alexei L. Gruverman1 and Alexander Sinitskii1; 1University of Nebraska-Lincoln, United States; 2South Dakota School of Mines and Technology, United States
In the rapidly growing family of MXenes, Cr2TiC2T3 is one of the most intriguing materials as an ordered double-transition-metal MXene with peculiar magnetic properties. In this work, we developed a synthetic procedure for high-quality Cr2TiC2T3 and produced monolayer sheets with lateral sizes exceeding 15 μm for single-flake measurements. The results of such measurements on Cr2TiC2T3 further establish it as a unique material among the MXenes experimentally tested so far. Field-effect electrical measurements on monolayer Cr2TiC2T3 flakes reveal an average conductivity of 66.18 S cm^-1. While solid solutions on the M (metal) site have been studied, the partial replacement of carbon with nitrogen (carbonitrides) has received little attention. By applying this concept, herein we report the synthesis of three families of titanium carbonitride TiN xC 2T x flakes that can find numerous applications due to their attractive mechanical characteristics and transport properties that are complementary to other established MXene materials.

2:15 PM NM01.02.03
Evidence of Metallic Conductivity in Ti3C2Tn by Temperature-Dependent Resistivity Measurements. Alexey Lipatov1, Saman Bagheri2 and Alexander Sinitskii2; 1South Dakota School of Mines & Technology, United States; 2University of Nebraska - Lincoln, United States
Ti3C2Tn, the most popular MXene to date, is widely regarded as a metallic material based on numerous theoretical predictions and the results of experimental studies. Yet, despite this general consensus on the metallic nature of Ti3C2Tx, there have not been reports on its temperature-dependent resistivity (ρ) measurements that would demonstrate the expected increase of resistivity with temperature. In this work, we fabricated electronic devices based on individual high-quality Ti3C2Tn flakes and measured their temperature-dependent resistivity. The resistivity of flakes was found to increase with temperature in the entire 10-300 K range, and the resulting ρ(T) dependences can be accurately fitted by the Bloch-Grüneisen formula for the temperature dependence of resistivity of metals, confirming the metallic nature of Ti3C2Tn. We also demonstrate that oxidation of a Ti3C2Tn monolayer transforms a monotonically increasing ρ(T) curve into a dependence with a minimum that looks similar to the previously reported results for percolating MXene films. We also demonstrate that multilayer Ti3C2Tn flakes retain their purely metallic behaviour even after annealing in air, suggesting that the outer layers of multilayer flakes effectively protect the core layers from oxidation. This novel behavior can find applications for instance in multilayer films of graphene-based materials.

2:30 PM BREAK

3:00 PM NM01.02.05
Synthesis of Three Families of Titanium Carbonitride MXenes Teng Zhang, Christopher E. Shuck, Kateryna Shevchuk, Mark Anayee and Yury Gogotsi; Drexel University, United States
Layered MAX phases and 2D MXenes derived from them are among the most studied materials due to their attractive properties and numerous potential applications. The tunability of their structure and composition allows every property to be modulated over a wide range. Particularly, elemental replacement and forming a solid solution without changing the structure allows fine-tuning of material properties. While solid solutions on the M (metal) site have been studied, the partial replacement of carbon with nitrogen (carbonitrides) has received little attention. By applying this concept, herein we report the synthesis of three families of titanium carbonitride Ti1-yAl1+y(C1-xNy)2 MAX phases and Ti1-yC1+y(N1-y)yCn MXenes with one, two and three C/N layers. This greatly expands the variety of known MAX phases and MXenes to encompass 16 titanium carbonitrides with tunable X-site chemistries and different 2D layer thicknesses, including MXenes in the Ti(C1-xNy)2 system, which have not been previously reported. We further investigated the relationship between the composition, structure, stability, and synthesis conditions of the MXenes and their respective Al-based MAX phases. This range of materials will enable fundamental studies of the N:C ratio effect on optoelectronic, electromagnetic and mechanical properties of MXenes, as well as tuning those properties for specific applications.

3:15 PM *NM01.02.06
Organic and Inorganic Surface Chemistry of MXenes Dmitri V. Talapin1,2, Young-Hwan Kim1, Chenkun Zhou1 and Di Wang1; 1University of Chicago, United States; 2Argonne National Laboratory, United States
Two-dimensional (2D) transition-metal carbides and nitrides (MXenes) show impressive performance in supercapacitors, batteries, electromagnetic interference shielding, and electrocatalysts. These materials combine the electronic and mechanical properties of 2D inorganic crystals with chemically modifiable surfaces, and surface-engineered MXenes represent an ideal platform for fundamental and applied studies of interfaces in 2D functional materials. The comprehensive understanding of MXene surfaces is required for prescriptive engineering of their physical and chemical properties. We discuss general strategies to install and remove surface groups by performing topotactic substitution and reductive elimination reactions. Successful synthesis of MXenes with halido-, oxo-, imido-, thio-, seleno-, or telluro- terminations, as well as bare MXenes (no surface termination) can be synthesized both by traditionally (from MAX phases) and directly synthesized MXenes. We also successfully synthesized a series of hybrid organic-inorganic MXenes by covalently attaching dense carpets of organic surface groups. Since organic and inorganic materials are, in many aspects, complimentary to each other,
organic-inorganic MXenes open a pathway to merge the benefits of both worlds into a hybrid material that combines engineerability of molecules with the electronic, thermal, and mechanical properties of inorganic 2D materials. The description of MXene surface structure and reactivity requires a mix of concepts from the fields of coordination chemistry, self-assembled monolayers and surface science. MXene surface groups control biaxial lattice strain, phonon frequencies, electrochemical performance, the strength of electron-phonon coupling, making MXene surfaces not spectators but active contributors to conductivity, superconductivity, and catalytic activity.

SESSION NM01.03: Synthesis and Characterization III
Session Chairs: Stefano Ippolito and Ruoane Wang
Wednesday Morning, April 24, 2024
Room 330, Level 3, Summit

8:45 AM *NM01.03.02
Tuning The Microenvironment of Water Confined in Ti3C2T x MXene by Cation Intercalation Mailis Lounasvuori1, Teng Zhang2, Yury Gogotsi2 and Tristan Petit1; 1Helmholtz-Zentrum Berlin, Germany; 2Drexel University, United States

The local microenvironment, which is often tuned by adding alkali metal cations to the electrolyte, has been recently found to play a major role in the electrocatalytic activity of nanomaterials. (1) Modulating the microenvironment can be used to either suppress hydrogen or oxygen evolution, thereby extending the electrochemical window of energy storage systems, or to tune the selectivity of electrocatalysts. MXenes are a large family of two-dimensional transition metal carbides, nitrides and carbonitrides that have shown potential for use in electrochemical energy storage applications. Due to their negatively charged surfaces, MXenes can accommodate cations and water molecules in the interlayer space. Nevertheless, the nature of the aqueous microenvironment in the MXene interlayer remains poorly understood. Here, we apply Fourier transform infrared (FTIR) spectroscopy to probe the hydrogen bonding of intercalated water in Ti3C2T x as a function of different cation concentration and relative humidity. Being highly sensitive to hydrogen bonding of water confined within the MXene layers,(2,3) especially in the O-H stretching mode region, FTIR spectroscopy enables the direct characterization of the H-bonding network of water and gives information on the relative amounts of water present in the samples. Because anions do not intercalate into MXene,(4) we are able to probe the hydration shell around isolated cations in a 2D confined environment. Strong changes in the hydrogen-bonding of water molecules confined between the MXene layers is observed after ex situ measurements. Furthermore, the IR absorbance of the confined water correlates with resistivity estimated by 4-point probe measurements and interlayer distance calculated from XRD patterns. This work demonstrates that cation intercalation strongly modulates the confined microenvironment, which can possibly be used to tune the activity or selectivity of electrochemical reactions in the interlayer space of MXenes in the future.

References

9:00 AM *NM01.03.03
MXene Reactivity and Its Role in Development of Applications Vadym Mochalin; Missouri University of Science and Technology, United States

A large family of two-dimensional transition metal carbides and nitrides (MXenes) raises interest for many applications due to their high electrical conductivity, mechanical properties [1], potentially tunable electronic structure [2], nonlinear optical properties [3], and the ability to be manufactured in the thin film state [4]. However, their chemistry that is key to development of these applications, still remains poorly understood [5,6]. In this presentation, we will discuss recent progress in understanding fundamental MXene chemistry and harnessing it for suppressing unwanted reactions and stabilizing properties of these materials.

For example, suppressing oxidation and hydrolysis at high pH was demonstrated as an effective way to prolong shelf-life and stability of MXene aqueous colloids [7]. Use of polyphosphate also has been shown to improve chemical stability of MXene aqueous colloids [8]. Other selected examples illustrating connections between understanding MXene chemistry and development of their applications will also be considered.

References
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S. Huang, V. N. Mochalin, ACS Nano 14(8), 10251-10257 (2020)
S. Huang, V. N. Mochalin, Inorganic Chemistry, 61(26), 9877 (2022)

9:30 AM BREAK

10:00 AM NM01.03.05
Defect Engineering of MXenes at Elevated Temperatures Brian Wuyt1, Matthew G. Boebinger2, Paul Kent3, Zachary D. Hood2, Shiba Adhikari4, Kartik Nemani1, Murali Gopal Muraldeeharan1, Annabelle Bedford1, Wyatt Highland1, Raymond R. Uono12 and Babak Anasori1; 1Purdue University, United States; 2Center for Nanophase Materials Sciences, United States; 3Oak Ridge National Laboratory, United States; 4Argonne National Laboratory, United States

The chemically diverse family of 2D MXenes have been widely adopted in areas such as energy storage, conversion, and electronics. From the ceramic perspective, MXenes uniquely enable the atomic control of its structure at the ~1 nm scale. In this presentation, we demonstrate the defect engineering of Mo2TiC2T x, Ti3C2T x, Mo2TiC3T x, and Nb2CT x MXenes at elevated temperatures using alkali cations. We demonstrate the improved phase stability of MXenes and control of formed carbide phases using in situ x-ray diffraction and scanning transmission electron microscopy techniques. Further, we present evidence for the role of partial occupation of alkali cations in defective sites in MXenes using computational methods paired with in situ and ex situ methods. Overall, this cation-based engineering of defects in 2D MXenes demonstrates the potential for improving their stability and further develops the tools for researchers to apply MXenes as a diverse and tunable family of nanomaterials for high temperature applications.
Achieving Environmental Stability of MXenes in Air, Water and Electrolytes

Asaph S. Lee, Mark Anayee, Mikhail Shekhterov and Yury Gogotsi; Drexel University, United States

MXenes display extraordinary electrical, optical, chemical, and electrochemical properties. There is a perception though that MXenes are unstable and degrade quickly in ambient environment, limiting potential applications and requiring specific storage conditions for a long time. However, significant developments in MXenes’ synthesis, processing, and understanding of its chemistry led to dramatic increases in their environmental stability. Herein, we analyze delaminated Ti$_3$C$_2$Tx MXene flakes in solution and on a substrate, electrodes in acidic electrolyte as well as free-standing films aged up to a decade. Structural, chemical, and morphological characterization along with electronic conductivity measurements reveal the effect, or lack thereof, of prolonged storage under ambient conditions. Up to 90% conductivity was retained after 5 years of storage by the films dried after synthesis. Further, we show that decrease in electronic conductivity over time is largely caused by uptake of water by the hydrophilic surfaces of MXenes, and its effect can be, at least partially, reversed by vacuum drying at elevated temperature. MXene supercapacitor electrodes performed well over 500,000 cycles at 20 mV/s. The effects of Ti$_3$C$_2$Tx stoichiometry, surface chemistry, defects, intercalants, interlayer spacing and storage condition on hydrolysis are discussed. While no systematic data is available for other MXenes, we demonstrate that the same principles are applicable to V$_2$C, Nb$_2$C$_x$ and other 2D carbides.

Raman Spectroscopy Characterization of 2D Carbide and Carbonitride MXenes

Kateryna Shevelukh1, Asia Sarycheva1,2, Christopher E. Shuck1,3 and Yury Gogotsi1; Drexel University, United States; 2Lawrence Berkeley National Laboratory, United States; 3Rutgers, The State University of New Jersey, United States

The first step to wider adoption of two-dimensional (2D) materials is understanding their fundamental properties by employing characterization methods, among which Raman spectroscopy plays a unique role, being a fast and nondestructive tool. The number, frequencies, and intensities of the modes (or bands) in the Raman spectrum have been used to identify the 2D materials’ crystal lattice, bonding, and even the number of layers. MXenes, 2D transition metal carbides, nitrides, and carbonitrides, span diverse chemistries and structures, but only a few Raman spectra have been reported. This work is the first systematic experimental Raman study of the MXene family. We explore the vibrational spectra and provide peak assignments for ten MXenes with varying structures (from 2 to 4 atomic layers of transition metal) and compositions - Ti$_3$C$_2$T$_x$, Nb$_2$C$_x$, Mo$_2$CT, V$_2$CT, Ti$_3$C$_2$T$_x$, Mo$_2$TiC$_2$T$_x$, Ti$_3$CNT, Nb$_2$C$_x$T$_x$, V$_2$C$_x$T$_x$, and Mo$_2$Ti$_2$C$_2$T$_x$ (terminated with –F, –OH, and =O) based on the experimental results and previously reported computational studies. We discuss the effects of MXene layer thickness, surface terminations, and MXene’s metallic properties on Raman scattering. Additionally, we employ polarized Raman spectroscopy to identify out-of-plane vibrations and explain the higher frequency region of the spectra, and computational predictions to assign the peaks to the Raman-active modes. By creating the Raman spectra library of the most frequently used MXenes, we open the door for the use of Raman spectroscopy for fingerprinting of various MXenes.

Local Surface Chemistry of Ti$_3$C$_2$T$_x$ MXenes in Aqueous Electrolyte Monitored by In Situ Scanning Transmission X-Ray Microscopy

Peer Bärmann, Namrata Sharma, Faïdra Amargianou, Tianxiao Sun, Markus Weigand and Tristan Petit; Helmholtz Zentrum Berlin, Germany

The pseudocapacitive behavior of Ti$_3$C$_2$T$_x$ MXenes promises high power and energy densities thanks to redox reactions occurring during the (de-)protonation of the MXene surface in acidic electrolyte. Nevertheless, local electrochemical processes occurring at the MXene-electrolyte interface and the associated changes of the MXene surface chemistry are currently largely unexplored. To this aim, soft X-ray spectroscopies are particularly relevant as they enable the selective characterization of either the electrolyte or the material of interest thanks to their element specificity. Furthermore, the high spatial resolution (<30 nm) offered by X-ray Microscopy can provide precious information about local inhomogeneities at the nanoscale, enabling the characterization of single MXene flakes. In this talk, the chemical bonding of Ti atoms in single few-layered Ti$_3$C$_2$T$_x$ MXene flakes was monitored in different electrolytes using synchrotron-based in situ Scanning Transmission X-ray Microscopy (STXM) at the Ti L-edge. Significant changes of the Ti chemical environment are observed between acidic and neutral Li$^+$-containing aqueous electrolyte and sub-inhomogeneities in the MXene surface chemistry were evidenced. Finally, potential-induced changes of MXene local surface chemistry will be discussed. In situ STXM will open new perspectives on the characterization of electrochemical processes in MXenes that can be monitored down to the single flake level.

Mechanistic Study of MXene Current Collectors for Lithium-Metal-Based Batteries

Ruoum Wang1,2, Raymond R. Unocic3, Jaehoon Choi1, Yan Bures1,2, Mark Anayee1,2, Geetha Valurouthu1,2, Wan-Yu Tsai3 and Yury Gogotsi1,2; Drexel Nanomaterials Institute, United States; 1Drexel University, United States; 2Oak Ridge National Laboratory, United States; 3University of Picardie Jules Verne, France

Lithium metal is widely investigated as a high-energy-density anode replacement for graphite in lithium-ion batteries. It is important for next-generation lithium-metal-based battery technologies. However, lithium dendrites tend to grow during deposition and stripping, resulting in poor battery life or short circuits. Literature shows that using MXene instead of copper as the current collector can mitigate lithium dendrite growth. Two mainstream hypotheses for dendrite suppression include forming a hexagonal close-packed structured lithium layer and a homogeneous growth of solid-electrolyte interphase (SEI) on the surface of MXene. However, there is a lack of experimental evidence to support those hypotheses. Here we used a suite of characterization techniques, including cryo-transmission electron microscopy (cryo-TEM), X-ray photoelectron spectroscopy (XPS), in situ Raman spectroscopy, scanning electron microscopy (SEM), and operando optical microscopy to investigate the crystal structure, SEI, and morphology of lithium nucleated on Ti$_3$C$_2$T$_x$ MXene at different rates and capacity.

Photocatalytic MBenes: the next generation of MXene-like 2D structures

Agnieszka M. Jastrzębska; Warsaw University of Technology, Poland

MBenes family is a novel member in the flatland and a recent derivative of ternary MAB phases. However, MBenes differ from MXenes in many ways. Compared to MXenes, MBenes’ structure is more complex due to multiple lattice arrangements. At the same time, boron opens the door to the rich structural chemistry of MBene, excellent reactivity, and energy harvesting abilities, to mention a few. In this talk, I will present a new synthetic approach to Mo$_2$B$_x$ MBene from its parental MoAlB phase, supported by theoretical calculations. In addition, I will demonstrate the tremendous photocatalytic potential of MBene compared to MXene. While research interest is rapidly accelerating, practical applications require better control over MBene's surface terminations and oxidation. MBene’s vast compositional space and versatility provide almost limitless potential for designing structural variants with tailored optical and electronic properties. However, further research is needed to fully understand these novel materials and unlock their exotic light-driven phenomena. In summary, I expect MBenes to boost the fundamental research toward exploring their catalytic features in the next decade and development of MBene-based technologies that can manipulate light like never before.
Two-dimensional (2D) transition metal carbides and nitrides (MXenes) are a large family of earth-abundant materials with more than forty compositions synthesized since 2011, such as Ti₃C₂Tx, NbₓCₓTx, TiₓCₓTx, and MoₓTiₓCₓTx. MXenes have emerged as promising candidates for catalytic energy storage and conversion due to their electrochemically active surfaces combined with hydrophilicity, high electrical conductivity, and affinity to bond to molecules and nanomaterials to form hybrid structures. The ease of production of MXenes and their earth-abundant elements can overcome one of the major obstacles to the large-scale implementation of durable and efficient catalysts. In this talk, we will discuss the control of MXene transition metals and their surfaces to tune their electrocatalytic behavior. Specifically, we present a systematic study of 20 different MXenes, including novel compositions such as W₂TiC₂Tx and Mo₂NbCₓTx, and high-entropy MXenes, and discuss how we achieve low overpotential for hydron evolution reaction (as low as ~160 mV).

References:
6. Sixbert P. Muhoza1, Shiba Adhikari1, Anupma Thakur2, Babak Anasori2 and Zachary D. Hood1; 1Argonne National Laboratory, United States; 2Purdue University, United States
8. Anupma Thakur and Babak Anasori
9. 8:45 AM NM01.05.01
Ti₃C₂Tx MXene-Based Electrochemical Sensors for Phosphate Detection Thiba Nagaraja, Shiseido Robinson, Rajavel Krishnamoorthy and Suprem R. Das; Kansas State University, United States
The recent surge of the Internet of Things (IoT) has left an indelible mark on the global sensor market, spurring further research in a similar direction. At the heart of any sensor lies the sensing material and its intrinsic characteristics that define the key sensor metrics such as selectivity, sensitivity, limit of detection and dynamic range. Electrochemical sensors, known best for their dominance in rapid detection, cost efficiency and accuracy, are no exception to this paradigm. To date, many nanomaterials, including two-dimensional (2D) graphene, have been discovered and used as electrochemical sensing platforms for various biomedical and environmental applications. 2D transition metal carbides/nitrides (also known as MXenes), with their unique structure and presence of transition metals, have demonstrated large surface to volume ratio, high electrical conductivity, ease of functionalization and solution processibility. However, their electrochemistry and electrochemical stability have received limited exploration. Recently, there has been a growing focus on delving deeper into these aspects. Phosphate ions are intriguing molecules with significant relevance in environmental and biomedical applications. Understanding its detection in a solution environment using MXene as a sensing electrode will unveil MXene’s outstanding properties for unique applications as a phosphate sensor. Herein, we studied the performance of Ti₃C₂Tx MXene on a standard glassy carbon electrode in detecting phosphate ions in an electrochemical setup in the presence of molybdenum in an acidic media. The quality of Ti₃C₂Tx MXene was extensively characterized prior to serving as the sensing material in the electrochemical system. The proposed method demonstrated high selectivity in the presence of common interfering ions. The Ti₃C₂Tx MXene sensor also exhibited low detection limit and high sensitivity towards phosphate ions along with a large linear detection range with reliable performance. This research lays the groundwork for the advancement of Ti₃C₂Tx MXene-based phosphate sensors, promising future applications in environmental monitoring and sensing.

Acknowledgements
This material is based upon work supported by Laboratory Directed Research and Development (LDRD) funding from Argonne National Laboratory, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-06CH11357. This research used resources of the Center for Nanoscale Materials, U.S. Department of Energy (DOE) Office of Science user facilities operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. This research used resources of the Center for Nanoscale Materials, U.S. Department of Energy (DOE) Office of Science user facilities operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

References:
1. 9:00 AM NM01.05.02
A Wide Look at MXene-Based CO₂ Reduction Electrocatalysts: Pioneering Pathways for Green Formaldehyde Production Sixbert P. Muhoza1, Shiba Adhikari1, Anupma Thakur2, Babak Anasori2 and Zachary D. Hood1; 1Argonne National Laboratory, United States; 2Purdue University, United States
Transition metal carbides, oxy-carbides, nitrides, and carbonitriles (MXenes) constitute an ever-growing class of two-dimensional materials with unique properties, including high conductivity and surface area as well as versatile and tunable surface chemistry.1–3 Such a wide-ranging array of properties primes MXenes for various applications and, hence, provides them with the potential to tackle some of the most pressing challenges faced by our planet. Climate change is one such challenge, and the electrochemical CO₂ reduction reaction (CO₂RR) provides a potent pathway to alleviate the effects of CO₂ emission on the environment.4 The maturation of electrochemical CO₂RR, however, will require the development of electrocatalysts that maximize the value gained from converting the CO₂ feedstock. For this reason, we have developed a novel class of MXene-based electrocatalysts that leverage the unique properties of MXenes to convert CO₂ to formaldehyde. Formaldehyde is a key ingredient in manufacturing many value-added products, including resins, coatings, and vehicle components.5 However, formaldehyde is not typically generated with traditional electrocatalysts, indicating that the herein introduced MXene catalysts drive CO₂RR through new reaction pathways. This work highlights the behavior of a wide array of MXenes: ranging from single-layered traditional MXenes (Ti₃C₂Tx, MoₓTiₓCₓTx, and WₓTiₓCₓTx) to multi-layered MXene/metal heterostructures (Ti₃C₂Tx/CuM, M = Ag, Sn, Zn, Ru, Ni, Fe). The Ti₃C₂Tx/CuM heterostructures were developed through a novel electroless deposition of the bimetal onto the surface of MXenes by oxidizing the Ti moieties of the Ti₃C₂Tx MXene. The reduction potential of the adsorbed metals dictated this process, with the strongly oxidizing metals reaching their lowest oxidation states while the weakly oxidizing metals were only partially reduced. In all cases, formaldehyde was generated and the highest efficiencies were achieved at low, industrially relevant, cell potentials (between -1.4 V to -2.2 V). These results, as they pertain to pioneering green formaldehyde production and favorability for industry adoption, warrant further exploration of the MXene-based CO₂RR electrocatalysts.

Seawater desalination presents a tremendous opportunity to utilize abundant water resources as approximately 70% of the Earth’s surface is covered by the ocean. A recent advancement in the field involves an innovative approach that integrates reverse osmosis (RO) with feed heating through membrane distillation (MD), creating a hybrid thermal–membrane process to vaporize hot saline water and transport it through the pores of the hydrophobic membrane. However, this hybrid process still faces practical limitations, primarily due to the necessity of introducing an external heater, resulting in increased energy loss and thermal resistance. In this talk, I introduce a novel strategy to overcome these limitations by incorporating surface heating MD systems with MXene-based membranes. Specifically, MXene, known for their excellent electroconductivity, makes it an efficient material for Joule-heating. Additionally, surface-modified MXene exhibited remarkable oxidation stability and corrosion resistance. Ultimately, our MXene-based membrane demonstrated superior desalinating performance, achieving a high permeate flux and an outstanding heat utilization efficiency, all while maintaining excellent material stability.

9:45 AM NM01.05.03
MXene-based membranes for water-treatments Tae Hee Han; Hanyang University, Korea (the Republic of)

10:15 AM NM01.05.04

Advancing wearable MXene bioelectronics to human translation. Elivia Vitala; University of Pennsylvania, United States

Wearable bioelectronics are widely adopted in clinical, research, and consumer electronics for health and fitness tracking. MXenes, and Ti$_3$C$_2$T$_x$ in particular, have emerged as ideal materials for soft, conformal, and multimodal wearable interfaces for sensing and modulating different body functions. In this talk, I will discuss our most recent works on designing, fabricating, and translating wearable MXene bioelectronics for use in humans. First, I will review how ad hoc manufacturing schemes allow leveraging the remarkable electronic, electrochemical, and magnetic properties of Ti$_3$C$_2$T$_x$ MXene at the molecular scale, while enabling full customization of the device functionality, geometry, and area coverage. Then, I will present examples of application of MXene wearables for non-invasive brain monitoring in outpatient clinical settings and neuromuscular diagnosis and rehabilitation in Achilles tendinopathy patients.

10:45 AM *NM01.05.06 Multispectral Electromagnetic Shielding Capacities of 2D MXenes Chong Min Koo; Sungkyunkwan University, Korea (the Republic of)

The increasing prevalence of advanced electronics, mobiles, telecommunication, and medical devices operating across a wide range of EM waves (from ultralow kHz-level to high THz-scale frequencies) necessitates the development of EM shielding materials operating in multispectral EM bands. MXenes, a class of two-dimensional materials comprising transition metal carbides, nitrides, and carbonitrides, have emerged as cutting-edge functional EM shielding materials since their initial report in 2016. This is attributed to their exceptional metallic conductivity, expansive surface area, numerous surface terminations, and excellent solution processability. Here, this presentation aims to demonstrate that MXenes can deliver outstanding multispectral EM shielding capacities against radio-frequency (RF) waves, GHz-range microwaves, and THz/infra-red (IR)-frequency waves, all achieved with minimal thickness and in various structural forms. Pristine MXene films with nanometer-scale thickness effectively interact with EM waves across the RF, GHZ, and THz frequency ranges, while simultaneously demonstrating remarkably low IR emissivity. This low IR emissivity is a critical characteristic for applications such as selective thermal management, IR camouflage, stealth, and anti-counterfeiting measures. Through this exploration, I aim to highlight the versatility and efficacy of MXenes in addressing the evolving demands of EM shielding across a wide range of electromagnetic frequencies and applications.

11:15 AM *NM01.05.07 Integration of MXene (Ti3C2Tx)-PVA-PAAPComposite into Hanji: A Multifunctional Smart Fabric for Energy Harvesting, Thermoregulation, and EM Shielding Yong Choe; Jeheon Kim and Byangseok Seo; Korea University, Korea (the Republic of)

Multifunctional smart fabrics have attracted a lot of attention due to the rapid downsizing of numerous electronic components and the emergence of wearable devices. One of the most advanced functions of these fabrics is their energy harvesting in operating environments, while multiple other performances in terms of thermoregulation and electromagnetic interference (EMI) shielding would be desirable. Currently, heat, pressure, and triboelectricity are major energy sources that can be used with typical multifunctional materials. Herein, we report a novel smart fabric integrating energy harvesting using human perspiration and ambient moisture, as well as zonal heating for body temperature regulation and EMI shielding performances. In the smart fabric design, a blend of MXene(Ti3C2Tx)-PVA-PAA is integrated into the environmentally friendly, traditional Korean paper, Hanji. This composite exhibits high flexibility, oxidation resistance, hydrophilicity, and electrical conductivity. A precipitate of the mixture is obtained through ultrasonic treatment at room temperature, and then the asymmetric coating is applied to both sides of the Hanji using a vacuum filtration process. When the working fluid contacts the opposite side of the coated fabric, it rapidly penetrates through the coated interface of Hanji and generates electricity through negatively charged nanofluidic channels. The introduction of hydrophilic polymer modulates the spacing of MXene layers and prevents oxidation due to fluid exposure. The synergy between conductive MXene and resistive hydrophilic polymer leads to achieving outstanding EMI shielding performance. Remarkably, even at low voltages, this composite shows efficient electricity-to-heat conversion and serves as a zonal heating element. The hydrophilic functional groups in the coating also provide humidity-sensing capabilities. The developed multipurpose smart fabric in this work will contribute to rationally designing multifunctional yet efficient energy harvesters using multiple sources.

13:30 AM *NM01.08.10 Vacancy and Growth Modulation of Cobalt Hexacyanoferrate by Porous MXene for Zinc Ion Batteries Aiping Yu and Maiwen Zhang; University of Waterloo, Canada

Prussian blue analogues (PBAs) featuring with three-dimensional open framework are recognized as promising cathode candidates for Zinc-ion batteries, but unsatisfactory active site utilization, low conductivity and abundant structural vacancies have impeded fulfillment of their potential. In this work, a highly conductive in-plane porous MXene is for the first time adopted as a multifunctional host material to enhance cobalt hexacyanoferrate (CoHCF) growth and crystallinity. Particularly, the uniform MXene surface charges are identified to induce anisotropic vacancy and growth modulation of CoHCF and improve its electrochemical performance. A precipitate of the mixture is obtained through ultrasonic treatment at room temperature, and then the asymmetric coating is applied to both sides of the porous MXene host. A porosity of 70% is obtained. The CoHCF nanotube on porous MXene composite realizes high surface area and low defectiveness, achieving a high capacity of 197 mA h g$^{-1}$ at 0.1 A g$^{-1}$ and robust capacity retention of 94.4% even over 3000 cycles of operation at 2.0 A g$^{-1}$. This composition strategy, utilizing MXene as a multifunctional template, enhances PBAs' surface area, conductivity, and crystallinity, optimizing cathode capacity and stability for ZIBs, and showcasing the potential for large-scale energy storage.

Keywords: Zinc-ion battery, Porous MXene, Prussian blue analogues, induce growth, low vacancy

SESSION NM01.06: Applications II
Session Chairs: Stefano Ippolito and Xuehang Wang
Thursday, Afternoon, April 25, 2024
Room 330, Level 3, Summit

1:30 PM *NM01.06.01 Tailoring MXene Synthesis and Assembly for Enhanced Performance in Diverse Applications Yeonjin Baek1, Kiandokht Pakravan1 and Majid Beidaghli2, 1Auburn University, United States; 2The University of Arizona, United States

Two-dimensional (2D) MXenes have garnered significant attention in recent years due to their exceptional properties and wide-ranging potential applications. This presentation showcases our group's recent research dedicated to optimizing the synthesis process and assembly techniques to enhance MXenes' electrochemical, mechanical, and membrane performance. The synthesis of MXenes plays a pivotal role in shaping their properties, including electrical conductivity and mechanical strength. Our studies reveal that the details of the synthesis process have a profound impact on MXene morphology, defect concentrations, and surface chemistry, ultimately influencing their electrical, electrochemical, and mechanical properties. Given the substantial impact of synthesis on MXene properties, the development of standardized synthesis protocols is imperative, as is the establishment of consistent performance reporting protocols across various fields of application. Furthermore, the performance of MXene-based devices is greatly influenced by the synthesis process. The presentation highlights our most recent works on designing, fabricating, and tailoring the surface functional groups of the MXenes obtained from electron microscopic and spectroscopic techniques have been correlated with their catalytic activity during dry reforming at 3000 cycles of operation at 2.0 A g$^{-1}$. This composition strategy, utilizing MXene as a multifunctional template, enhances PBAs' surface area, conductivity, and crystallinity, optimizing cathode capacity and stability for ZIBs, and showcasing the potential for large-scale energy storage.

Keywords: Zinc-ion battery, Porous MXene, Prussian blue analogues, induce growth, low vacancy

2:00 PM *NM01.06.02 Exploiting Properties of MXenes to Improve Performance of Dry Reforming Catalysts Placidus B. Amama, Joshua Ighalo, Ahmed Al Mayahi and Haider Almhlefe; Kansas State University, United States

The development of efficient catalysts for dry reforming of methane (DRM) is critical for the sustainable production of syngas, an essential precursor for many industrial processes. DRM is known to have a high energy penalty due to the intrinsic chemical stability of the CO$_2$ molecule. The mechanism suggests that CO$_2$ is activated at the metal-support interface whereas methanol is activated on the surface of the active metals. Therefore, the reaction can be significantly improved by designing new catalysts that maximize the metal-support interactions (MSI) and consequently facilitate CO$_2$ activation. In this work, MXene (Ti$_3$C$_2$T$_x$) is used as support for Ni catalysts to address their low deactivation resistance during DRM. Wet impregnation was used to synthesize MXene-supported Ni catalysts (Ni/Ti$_3$C$_2$T$_x$) and a reference catalyst (γ-Al$_2$O$_3$-supported Ni) with 10 wt% loadings. The morphology and composition of the catalysts and the tailored surface functional groups of the MXenes obtained from electron microscopic and spectroscopic techniques have been correlated with their catalytic activity during dry reforming at atmospheric pressure. Simulations using Aspen Plus have been used to compare the experimental conversion with the thermodynamic benchmark by the Gibbs free energy minimization method.

2:15 PM *NM01.06.04 Ti$_3$C$_2$T$_x$ Co-Catalyst on CuO: Size Effects on Enhanced Photocatalytic Activity Lu Chen1,2; Taotao Qiang1, Matyas Daboczi2, Yasmine Baghdadi2 and Salvador Eslava2; 1, Shaanxi
Co-catalysts play a crucial role in photocatalytic reactions, and titanium carbide (Ti$_3$C$_2$Tx) is a promising alternative to expensive noble metal co-catalysts. However, size effects and charge transfer mechanisms of Ti$_3$C$_2$Tx co-catalysts on semiconductors for photocatalytic water splitting remain under-researched. Herein, we coupled copper (II) oxide (CuO) semiconductor with either Ti$_3$C$_2$Tx nanosheets (T2D) or Ti$_3$C$_2$Tx quantum dots (T0D) to create composite photocatalysts: T2D/CuO and T0D/CuO. The effects of size, morphology, and energetics of Ti$_3$C$_2$Tx were investigated and hydrogen production rates were tested. The results show that T0D are better co-catalysts for photocatalytic hydrogen production in comparison to T2D. The optimal T0D/CuO sample achieved a hydrogen production rate of 2174 μmol g$^{-1}$ h$^{-1}$, which is 19 times that of the optimal T2D/CuO samples, and more than 100 times that of pure CuO. The size of T2D in the composites is 200 nm, whereas the size of T0D is only 7 nm. This difference serves to decrease light obstruction and parasitic light absorption. Simultaneously, the surface area increases from 29 cm$^2$/g for T2D/CuO to 43 cm$^2$/g for T0D/CuO, indicating a higher abundance of active sites. This study highlights the impact of the size effects of Ti$_3$C$_2$Tx co-catalysts on photocatalytic performance and lays the foundation for the research of other quantum dot sized co-catalysts.

2:30 PM BREAK

3:00 PM NM01.06.05
MXene Iontronics for Neuronal Computer and Actuators Max M. Hamedi; KTH, Sweden

2D materials and in particular MXenes can not only form passive metallic or supercapacitive structures but can also become active structures in which their optoelectronic or structural properties change as a function of doping. We term these materials 2D mixed ionic electronic materials (MIEC) or iontronics. Here we highlight two specific MXene MIECs devices that we have developed:

1) A component for in memory computers called MXene electrochemical random-access memories (ECRAMs). The MXene ECRAM components has a channel like a conventional transistor, where the channel comprises a multi-layered MXene film formed using a highly accurate layer-by-layer self-assembly method developed by us.[1] In the ECRAM, however, an electrolyte between the channel and gate is used instead of the dielectric used in a solid-state field-effect transistors (FET). As a result, we can electrochemically switch the redox state of the MXene MIEC material using a gate electrode. Conducting polymer ECRAMs were until now the only shown ECRAMs but can not be integrated into silicon chips because organic materials burn at the high temperatures used in CMOS fabrication. The multilayers of titanium carbide MXene[1] can form ECRAMs with promising metrics for in-memory computation (also termed neuromorphic computers)[2] and can withstand high temperatures for integration. In recent studies we analyze these components and describe their characteristics using equation derived for organic electrochemical transistors.[3]

We think our work paves the way for ECRAM based computers and MXene electrochemical transistors.

2) We recently developed an MXene based actuators that we call Electrochemical Osmotic (ECO) actuators.[4] These actuators are formed from bulk composite electroactive hydrogels, fabricated from cellulose nanofibrils from trees, and 2D MXenes.[5] These nanoparticles self-assemble into an anisotropic composite network with an open mesoporous structure that can hold lots of water and be highly permeable to substances in their surroundings, while being mechanically very strong. The anisotropy of the network allows high expansion in one direction while maintaining very high strength and high electric conductivity in the other. The electrochemical charge/discharge of the MXene in the hydrogels controls the internal salt concentration and consequently their osmotic swelling. This allows direct electrochemically controlled actuation where around 700 water molecules expand/contract the structure for each ion/electron pair inserted/deinserted at only ±1 volt, resulting in 300% electroosmotic expansion, with very high pressures reaching 1 MPa. This mode of electronic actuation has not been shown before, and has emergent properties not present in any previously known soft material. ECOs allow for monolithic integration of sensors and other functions into one composite, rendering a new form of smart soft material not achievable with other materials system.

References
Stability of Pseudocapacitive Energy Storage in Ti$_3$C$_2$T$_x$ based devices to power fully programmable microcontrollers capable of motion tracking and environmental sensing for extended times. High energy storage capacity that can be integrated into textiles, making them an ideal candidate for textile-based energy storage. We demonstrate the use of MXenes in two different textile-reported in the literature don't store enough energy to power the electronics necessary to realize this vision. MXenes are conductive 2D materials with an electrochemically active surface and high energy storage capacity that can be integrated into textiles, making them an ideal candidate for textile-based energy storage. We demonstrate the use of MXenes in two different textile-based devices to power fully programmable microcontrollers capable of motion tracking and environmental sensing for extended times.

Stability of Pseudocapacitive Energy Storage in Ti$_3$C$_2$T$_x$, MXene in a Wide Temperature Range [1] Russoon Wang, 2,3, Man Anayee 1,2, Mohammad Nihal Naseer3, Teng Zhang1,2, Yuan Zhang1,2, Mikhail Shekhirev1,2, Kateryna Shevchuk1,2, Yong-Jie Hu2 and Yury Gogotsi1,2; 1A.J. Drexel Nanomaterials Institute, United States; 2Drexel University, United States; 3University of Picardie Jules Verne, France

Pseudocapacitors have the potential to achieve high energy and high power density simultaneously, a holy grail for electrochemical energy storage. However, one obstacle facing pseudocapacitors is their shorter lifetime than commercial supercapacitors using the double-layer charge storage mechanism. In MXene-based pseudocapacitors, this concern is pronounced particularly at high temperatures due to the limited stability of the active material in aqueous solutions. This work shows that Ti$_3$C$_2$Tx MXene thin-film electrodes in 5 M H$_2$SO$_4$ possess excellent rate capabilities from -50 °C to 70 °C but also a sufficient lifetime at 70 °C using a float test holding at -0.9 V vs. Hg/Hg$_2$SO$_4$. Post-mortem characterization using X-ray photoelectron spectroscopy and Raman spectroscopy showed negligible signs of oxidation in the bulk of the film. This work suggests sufficient stability of Ti$_3$C$_2$Tx MXene as a negative electrode in protic aqueous electrolytes across a wide temperature range rooted in thermodynamics, making it promising for pseudocapacitor energy storage.

Colorful MXene inks for multifunctional textiles [1] Inovy Bi, Danzhen Zhang, Ksenia Vorotilo, Richard Vallett, Genevieve Dlou and Yury Gogotsi; Drexel University, United States

Textiles are the ultimate wearables, providing 24/7 next-to-skin coverage of large areas of our body. They present large surface areas to host sensing devices. Great effort has been made to impart electronic properties - movement tracking, biological signal monitoring and actuation functions for haptic interactions—by incorporating conductive materials into traditional textiles. However, metal and carbon-based conductive materials not only limit the hues to silver, black and grey but also require a large amount to be deposited for sufficient electrical conductivity—an approach that makes these textiles dull and harsh, deviate from the vibrant and comfortable textiles we love and experience every day. MXenes could pose a solution. MXenes are a family of two-dimensional transition metal carbides and nitrides with the highest electrical conductivity among solution processable nanomaterials. MXenes exhibit distinct colors from green, blue to purple, gold of different shades depending on the transitional metal(s) present (e.g., Ti, V, Nb, Mo, and Cr) and on their structuring. Moreover, the functional groups on the surfaces of MXenes allow them to establish strong interactions with the substrates, making them ideal conductive additives for durability and scale. Here, screen printing—a widely adopted technique in the textile industry—was demonstrated as an economical method for not only faithfully replicating MXene colors and achieving high conductivities on fabrics but also for carefully placing and combining MXenes for many electronic functions.

Annaling Ti3C2Tx MXenes to control surface chemistry and friction [1] Kailash Arole, Hong Liang, Miladin Radovic, Jodie Lucutenhaus and Micah Green; Texas A&M University, United States

Although surface terminations (such as -O, -Cl, -F, -OH) on MXene nanosheets strongly influence their functional properties, synthesis of MXenes with desired types and distribution of those terminations is still challenging. Here, it is demonstrated that thermal annealing help to remove much of the terminal groups of molten salt-etched multi-layered (ML) Ti3C2Tx. In this study, the chloride terminations of molten salt etched ML-Ti3C2Tx were removed via thermal annealing at elevated temperatures under an inert (argon) atmosphere. This thermal annealing created some bare sites available for further functionalization of Ti3C2Tx. XRD, EDS, and XPS measurements confirm the removal of much of the terminal groups of ML-Ti3C2Tx. Here, the annealed ML-Ti3C2Tx were re-functionalized by -OH groups and 3-aminopropyl triethoxysilane (APTES), which was confirmed by FTIR. The -OH and APTES surface-modified ML-Ti3C2Tx are evaluated as a solid lubricant, exhibiting ~70.1% and 66.7% reduction in friction compared to steel substrate, respectively. This enhanced performance is attributed to the improved interaction or adhesion of functionalized ML-Ti3C2Tx with the substrate material. This approach allows for effective surface modification of MXenes and control of their functional properties.

Efficient Delamination and Dispersion of 2D MXenes in Organic Solvents for Fabrication of Polymer Nanocomposites [1] James FitzPatrick and Yury Gogotsi; Drexel University, United States

MXenes, a family of two-dimensional (2D) transition metal carbides and nitrides, have attracted significant attention in recent years for their unique optical, electronic, and chemical properties, to name a few. These materials represent a variety of surface terminations. MXenes can be tailored for an incredibly broad range of applications, but are still often hindered by manufacturing, stability, and mechanical challenges. Many of these challenges can be overcome by integrating the 2D material into polymer matrices, leading to composites with distinct properties that can serve specific or multiple functions. To date, only a small portion of MXene research has been focused on polymer composites. Several hurdles exist for crafting high performance composites, including uniform distribution of flakes and interfacial compatibility with certain polymers, specifically hydrophobic ones. Current methods for compositing nanoparticles with polymers typically involve blending the two materials in an organic solvent, but dispersing the MXene in this medium either involves complex processing or lengthy sonication that can greatly reduce the average flake size and deteriorate properties. Herein, a more efficient approach to delaminating multilayer Ti$_3$C$_2$T$_x$ MXene in an organic solvent is proposed, forming stable colloidal solutions that can be used to process composites with highly uniform flake distribution. This delamination method requires little more work than typical methods for obtaining single-layer MXene flakes and does not require any sonication or surface functionalization to improve interfacial compatibility and dispersion in a hydrophobic polymer matrix. Certain organic solvents such as propylene carbonate are highly effective in forming stable MXene solutions as well as enhancing formation of electroactive crystalline phases in polymers like PVDF. The properties of MXene-PVDF composites made through this process are examined.
through several characterization techniques, and potential applications of similar composite structures are explored.

5:00 PM NM01.07.14
MXene as Electrochemical Sensing Chip for On-site Heroin Detection – New Era in Forensic Illicit Drug Monitoring Vimala Ravghan, Arghya Chakravorty, Sudip Das and Aarucha A.M.; Vellore Institute of Technology, India

In developing nations as well as across the globe, the abuses of narcotics are increasing drastically. In 2019, 1.3 million Europeans were heroin-addicted, while heroin production worldwide was 509-739 tons in 2022. Thus, a need arises to develop sensors that will lead to the detection of drugs even at lower concentrations. In this research study, we have fabricated titanium carbide MXene/Pt/Au nanocomposite on carbon paste screen printed electrode for developing a user-friendly, cost-effective sensing chip to detect illicit drug heroin. Scanning electron microscopy (SEM), X-ray powder diffraction (XRD), BET surface area analysis, and energy dispersive X-ray spectroscopy (EDX) are used for the characterization of composition and morphology of MXene/Pt/Au nanocomposite, demonstrating its high specific surface area of the synthesized material. The synthesized MXene possesses wall thicknesses of about 15 nm, nanoparticles’ size was less than 70 nm on average. The mentioned properties provided rapid electron transfer and large electrochemically active surface area and assisted in the discrimination of analytes that reduce or oxidize under the same potentials. The enhanced electrode demonstrated appropriate sensing ability to heroin after performing fixation of MXene/Pt/Au nanocomposite. Kinetic factors charge transfer coefficient, standard heterogeneous electron transfer rate constant, and other different electrochemical factors are predicted using voltammetry methods. At a glance, the developed electrochemical chip ensures a unique LOD for device making and a wide linear range during detecting heroin. In addition, the mentioned suggested a suitable potential for profiling of heroin with appropriate long-term stability, repeatability, and reproducibility. The excellent efficiency for the measurement of real samples demonstrated the most significant future perspectives of this sensor.

5:00 PM NM01.07.15
MXene-Derived Sodium Titanate Nanoribbon/Lanthanum Composite as High-Performance Electrochemical Point-of-Care Sensor – A Step towards Achieving One Health Arghya Chakravorty, Aarucha A.M.; Sudip Das and Vimala Ravghan; Vellore Institute of Technology, India

One Health is an approach to designing and implementing programs, policies, legislation, and research in which multiple sectors communicate and work together to achieve better public health outcomes. The One Health approach is critical to addressing health threats in the animal-human-environment interface. Among global health problems, antimicrobial resistance (AMR) is the one that best illustrates the One Health approach. In this context, the antibiotic enrofloxacin plays an important role in terms of therapeutic drug monitoring in humans, and administration in poultry, animals, and aquaculture, which includes the threat to food as well as environmental safety. Thus, a need arises to develop sensors that will lead to the detection of enrofloxacin even at lower concentrations of target particles in a liquid. In this research study, we have developed MXene-Derived Sodium Titanate Nanoribbon/Lanthanum nanocomposite on carbon paste screen printed electrode for developing a user-friendly, cost-effective sensing chip to detect illicit drug heroin. Scanning electron microscopy (SEM), X-ray powder diffraction (XRD), BET surface area analysis, and energy dispersive X-ray spectroscopy (EDX) are used for the characterization of the composition and morphology of MXene-Derived Sodium Titanate Nanoribbon/Lanthanum nanocomposite, demonstrating its high specific surface area of the synthesized material. The synthesized nanoribbon possesses wall thicknesses of about 15 nm, nanoparticles’ size was less than 70 nm on average. The mentioned properties provided rapid electron transfer and large electrochemically active surface area and assisted in the discrimination of analytes that reduce or oxidize under the same potentials. The enhanced electrode demonstrated appropriate sensing ability to heroin after performing fixation of the nanocomposite. Kinetic factors charge transfer coefficient, standard heterogeneous electron transfer rate constant, and other different electrochemical factors are predicted using voltammetry methods. At a glance, the developed electrochemical chip ensures a unique LOD for device making and a wide linear range during detecting enrofloxacin in different real matrices, viz. milk and food samples; human blood, serum, and urine; waste water, and pharmaceutical industry effluents. In addition, the mentioned suggested a suitable potential for profiling of enrofloxacin with appropriate long-term stability, repeatability, and reproducibility. The excellent efficiency for the measurement of real samples demonstrated the most significant future perspectives of this sensor.

5:00 PM NM01.07.16
First-principles investigation of surface functionalization and CO2 adsorption in MXenes Michelle Bescera and Cormac Toher; The University of Texas at Dallas, United States

Ever-increasing amounts of carbon dioxide (CO2) are being expelled into the atmosphere, and without some type of countermeasure the environmental consequences will be dire. Motivated by the fact that CO2 sensors are a fixed part of our technological society which may be reduced, but not fully removed; research efforts have been directed towards utilizing these high concentrations of atmospheric CO2 as a sustainable resource. Carbon capture, specifically post-combustion, captures CO2 from a single source, removing it from the air and allowing further operations to be performed later. 2D early transition metal carbides and nitrides known as MXenes are investigated as an effective sorbent material thanks to their diverse composition, chemical active surface stemming from surface functionalizations and overall versatile and tunable nature. The computational characterization of MXene surface functionalizations, both the native surface inherited from synthesis and non-native surface groups introduced afterwards, are being systematically explored through calculated adsorption energies from density functional theory (DFT) as well as material optimization via machine learning (ML) methods. Molecules and surfaces being modeled are: pristine surfaces (Ti2C, Mo2C), attaching molecules (CO2, H2O, O2, N2, SO2), native functional surface groups (F, O2, O, OH, Cl and H), non-native surface functional group (NH2) and the interactions between them. The characterizations so far have shown that when adsorbing to a pristine Ti2C surface, single ions of F, O, OH, Cl and attaching molecules CO2, H2O and O2 all preferred binding to hollow sites, while ions of H and NH2 favored the bridge site before relaxing into a hollow site. Single fluorine ions bound to the surface were more thermodynamically stable when H2O adsorbed, when compared to CO2 and O2, but saturation of the surface with fluorine resulted in CO2 and H2O having similar adsorption energies. The unknowns revolving around MXenes and their surface functionalizations is a knowledge gap that is preventing MXenes from being fully utilized in the field of sustainable chemistry. The characterizations and MXene designs generated by this research will not only fill in the divide between MXenes and carbon capture, but also unite industries and our environment through more accessible carbon capture methods.

5:00 PM NM01.07.18
Enhanced SERS Sensing via 3D Microstructures Hybridized with 2D MXenes Shehua C. Thor1, Zhiao Lin1, Sodom Choi2, Chiwon Ahn2 and Jeong-Hyun Cho1; 1University of Minnesota, United States; 2Korea Advanced Institute of Science & Technology (KAIST), Korea (the Republic of)

Surface-Enhanced Raman Spectroscopy (SERS) is a targeted analytical technique that can be used to detect target particles on a plasmonically enhanced surface. This has applications in fields such as medicine and environmental pollution. The advantage of SERS detection is that it can be used to detect very small amounts of a sample and it is noninvasive. However, traditional SERS requires that the target particles be in contact with the plasmonic materials on the sensing surface. For the detection of very low concentration target particles in a liquid, traditional SERS techniques are limited by the diffusion limit. More specifically, it can take hours for nanoscale target particles in a liquid at very low concentrations to diffuse to the sensing surface for detection. In this study, we address the diffusion limitation by merging MXenes, a 2D material, with a 3D microstructure, establishing a micro-scale surface optimized for detecting minute concentrations of target particles in a liquid. The self-assembly of MXene/TiO2 nanotubes creates a nanopore at the center curvature of the tubular structure. When fluid is flown through this tubular structure, an enhanced Raman signal can instantaneously be obtained. As fluid is flown from one end of the twin tubular structure to the other end, some fluid will flow between the center curvature (a nanogap). At this center curvature, some of the analytes will be caught in between the nanogap of the center curvature. Furthermore, both sides of this nanogap is flown through this tubular structure, an enhanced Raman signal can instantly be obtained. As fluid is flown from one end of the twin tubular structure to the other end, some fluid will flow between the center curvature (a nanogap). At this center curvature, some of the analytes will be caught in between the nanogap of the center curvature. Furthermore, both sides of this nanogap

5:00 PM NM01.07.20
Delamination of uniformly terminated MXene produced using the molten salt etching Teng Zhang, Kateryna Shevchuk and Yury Gogotsi; Drexel University, United States

MXenes produced by molten salt of MAX phases have attracted attention of the community due to their controllable surface chemistry. However, their delamination is challenging due to the hydrophobicity of multilayer MXene and strong interactions between halogen-terminated MX sheets. The current delamination method involves dangerous chemicals such as N-Butyllithium or NaH, making scale-up difficult and limiting practical application. In this work, we present a low-cost, sustainable, and eco-friendly methodology for the delamination of molten salt synthesized MXenes while maintaining their surface chemistry. We demonstrate successful delamination. MXene films produced from the delaminated MXene had a conductivity of 8,000 S/cm and it didn’t change after exposure to 95% humidity conditions for a week. This validation of successful delamination, preservation of inherent surface properties, and stability under high-humidity conditions broadens the range of potential applications of MXenes. This research marks a significant leap towards the sustainable and economical production of two-dimensional materials.
Two-dimensional (2D) materials, exemplified by graphene and MXenes, hold immense potential for various flexible display applications. Nevertheless, the practical use of these materials has been hampered by the high charge injection barrier at the interface between stretchable electrodes and organic layers. In this study, we innovatively introduced a 2D graphene layer onto silver nanowire percolation networks, creating a comprehensive two-dimensional contact stretchable electrode (TCSE). This graphene layer effectively tailored the work function, facilitated charge distribution, and acted as a barrier against the ingress of oxygen and moisture. Our breakthrough enabled the development of intrinsically stretchable organic light-emitting diodes (ISOLEDs) boasting a remarkable efficiency of 20.3 cd/A. To further enhance electrode solution processability, we designed an environmentally stable MXene conductive electrode characterized by outstanding conductivity and a work function (WF) of 5.84 eV. Implementing the MXene electrode in ISOLEDs resulted in a substantial boost in current efficiency over 25 cd/A. These pivotal advancements not only establish a robust foundation but also offer a comprehensive blueprint for the creation of highly-efficient stretchable displays.

**Reference**


**9:00 AM NM01.08.04**

**MXenes as Hydrogen Storage Materials**

Yi Zhi Chu1,2 and Kah Chun Lai1,2; 1California State University Northridge, United States; 2Michigan Technological University, United States

The ever-increasing need for electricity will require foremost increased efficiency in the use of electric energy, more secure and sustainable energy resources and storages. To be better tailored to these challenges, novel materials for electrochemical and chemical energy storages that can efficiently store and deliver electric energy is highly important. In this case, hydrogen fuel stands out as a promising energy solution, and able offering a clean alternative to conventional energy sources while exhibiting the highest specific energy among many alternatives. Due to their high aspect ratio and tunable surface, slit-shape ion/mass transport channels, MXenes is a promising candidate in hydrogen storage materials. To address this issue, I will share with you our recent efforts based on theoretical studies with experimental supports from our collaborators. Based on our findings, some key avenues for future research that may help overcome the challenges and enable MXenes materials attain its full potential in this problem will be discussed.

Acknowledgement: This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering.

**9:15 AM BREAK**

**9:45 AM NM01.08.05**

**Engineering 2D Mo-Based MXenes and Application in Ammonia Synthesis**

Amanda Sfeir1, Christopher E. Shuck2, Maya Marinova3, Jean-philippe Daquin1, Yury Gogotsi1,2, Saïd Laageist1 and Sébastien Royer1; 1Université de Lille, CNRS, ENSCL, Centrale Lille, University Artois, UCCS-Unité de Catalyse et de Chimie du Solide, France; 2Drexel University, United States; 3Université de Lille, CNRS, INRA, Centrale Lille, Université Artois, IMEC – Institut Michel-Eugène Chevreul, France; 4Chemical & Biochemical Sciences, Green Process Engineering (CBS), Mohammed VI Polytechnic University, Morocco

Ammonia, which is one of the most important chemicals for synthesis of dyes, pharmaceuticals, and fertilizers, is conventionally produced by the reaction of molecular hydrogen with nitrogen, over an iron-based catalyst at 400-500 °C under pressure of over 200 bar, the Haber-Bosch process. While the H-B process is credited for providing a simple and cost-effective route for nitrogen-based fertilizer production, it is highly energy-intensive, accounting for ~2 % of the world’s energy production, and as it relies on fossil-based resources, resulting in a staggering emission of 2.5% of global CO2 annually. Decreasing the temperature and pressure of this century old, highly energy intensive process, would greatly decrease the energy consumption in the world and reduce carbon emissions. Fundamentally, producing ammonia at lower pressures is not thermodynamically prohibited, providing that the reaction takes place at temperatures below 300 °C. However, due to the high energy barrier for the activation/dissociation of the strong triple covalent NN bond (945 kJ mol⁻¹), most developed catalysts, including the industrial H-B catalyst, operate at temperatures over 400 °C. Consequently, high-pressure operation is required to increase ammonia yields to acceptable industrial production (15% conversion per cycle). In this work, for the first time in the literature, we engineered Co decorated Mo₂CTₓ MXene multilayers as catalysts for ammonia synthesis under mild conditions. The MXene functionalized by Co showed catalytic activity for ammonia synthesis from H₂ and N₂ at temperatures as low as 250 °C, without any pre-treatment. The developed catalyst was highly active for ammonia synthesis, demonstrating a high rate up to 9500 µmol g⁻¹ active phase h⁻¹ at 400 °C under ambient pressure in steady state conditions, and did not suffer from any deactivation after 15 days of reaction. The apparent activation energy (Eₐ) was found to be in the range of 68 to 74 kJ mol⁻¹ which aligns with the value reported for highly active catalysts such as Li-MT, Mn₄N-BaH₂, Ru/C₂A7:e⁻, and BaTiO₂.₅H₀.₅. This improved catalyst may decrease the energy consumption in synthesis of ammonia and its derivatives, as well as facilitate the use of ammonia as a hydrogen carrier for renewable energy storage. Numerous characterization techniques were used to analyze the catalysts including, XRD, SEM, TEM, H₂-TPR, XPS, EPR and ICP to understand their unique properties. Post-reaction analysis revealed partial substitution of lattice carbon with nitrogen, as well as partial reduction of Co⁺ during ammonia synthesis. The catalytic activity profiles, supported by post-reaction catalyst characterization, suggest that active sites generated upon reaction might be cobalt decorated carbonitrides Co-Mo₂CTₓ-NₓTᵧ. Upon reaching the steady state, the activity becomes stable upon cycling between low- and high-temperature conditions with no induction time. The results reported in this work demonstrate the appropriate modification of Mo₂CTₓ resulted in a high-performance ammonia synthesis catalyst capable of operating under mild reaction conditions in the intermittent regime.

**10:00 AM NM01.08.06**

**MXene Nanosheet-Derived N, S-Codoped Quantum Dots for Ultrasensitive Detection of 3-Nitro-L-Tyrosine in Biological Fluids**

Nguyen Thi Ngoc Anh, Van Thanh Nguyen and Ruey-An Deong; National Tsing Hua University, Taiwan

3-Nitro-L-tyrosine (3NT) is an oxidative stress metabolite of neurodegenerative diseases, and the rapid and effective detection of 3NT in human fluids for early diagnosis is important. Herein, for the first time, the nitrogen, sulfur co-doped graphene quantum dots derived from nitrogen-doped Ti₃C₂Tₓ MXene nanosheets via the hydrothermal method in the presence of mercaptosuccinic acid was synthesized as an optical sensing probe to detect 3NT in human serum. Tetramethyl ammonium hydroxide, the nitrogen source and delamination agent, was used to prepare nitrogen-doped MXene nanosheets via one step at room temperature. The as-prepared NS-MXene QDs (NSMQDs) are uniform with an average size of 1.2 ± 0.6 nm, and can be stable in aqueous solution for at least 90 d to serve as the fluorescence probe. The N atoms in N-MXene reduce the restacking and aggregation of MXene nanosheets, while the sulfur dopant in NSMQDs increases the quantum yield from 6.2 to 12.1% as well as enhances the selectivity of 3NT over the other 12 interferences via coordination interaction with nitro group in 3NT. A linear range of 0.02 – 150 µM in PBS and 0.05 – 200 µM in human serum with a recovery of 97 – 108% for 3NT detection is observed. Moreover, the limit of detection can be lowered to 4.2 and 7.7 nM in PBS and 1 µM diluted human serum, respectively. Results obtained clearly indicate the potential application of the Ti₃C₂Tₓ-derived NSMQD for effective detection of 3NT, which can open a window for treatment of diseases such as Alzheimer's disease and Parkinson's disease.

**10:15 AM NM01.08.01**

**Enhanced Gas Sensing Performance of MₓC₂Tₜ/MO (M = Ti, V, Nb, Mo) Nanocomposites**

M S Bhargava Reddy and Shampa Aich; Indian Institute of Technology Kharagpur, India

Gas sensors are in high demand across various fields, from disease diagnosis through breath analysis to ensuring environmental safety and enhancing food and agriculture processes. The continuous discovery of new materials drives advances in gas sensor technology. Notably, 2D materials have gained significant attention for gas sensing due to their remarkable electrical, optical, and mechanical properties. Among them, 2D MXenes have emerged as compelling candidates due to their high specific area and rich surface functionalities with tunable electronic structure which make them compelling for sensing applications. MXenes are generally represented by MₓTₜ where M represents an emerging transition metal, X denotes either carbon or nitrogen...
or carbonitriles or oxy-carbides. $T_x$ signifies surface terminations ($T_x = -OH, -O, -F, -Cl$), and $n$ can be 1-4. M$_2$CT, MXenes, in particular, show promise for VOC/gas detection based on theoretical calculations. However, research has predominantly focused on Ti$_3$C$_2$T$_x$ MXenes due to their established status, leaving limited exploration of other MXene variants as gas sensors. By altering the transition metal in MXenes, selectivity for specific gases can be achieved. Our research involves synthesizing MXenes from parent precursors (MAX and non-MAX phases) and conducting thorough property characterizations. We employ optimized synthesis methods to obtain single-/few-layered MXenes via selective etching and delamination. However, when comes to practical applications, pristine MXene layers have low sensitivity, significant baseline drift, susceptibility to cross-interference, and a narrow band gap, which limits gas reaction and responsiveness. The self-stacking of MXene layers also impedes the diffusion of gas molecules and hinders surface-active sites, restricting the gas sensor response and limiting the detection of low-concentration gases [1]. To enhance gas sensing capabilities (response and stability), we fabricate M$_2$CT$_x$/MO (M = Ti, V, Mo, Nb) nanocomposites, introducing multiple in-situ Schottky barriers through surface oxidation to enhance VOC sensing capabilities. The MXene/MO nanocomposites were prepared by using the concept of in-situ conversion using MXene surfaces as reactants. MXene layers expose metallic atomic layers on their outer basal planes, which are highly oxophilic and prone to surface reactions like oxidation (e.g., Ti to TiO$_2$ in Ti$_3$C$_2$T$_x$). The MXene surface is transformed partially, to form MO material in these processes. This approach lays the foundation for understanding the surface-sensitive behavior of MXenes in gas sensing by investigating the impact of surface chemistry. It represents a critical step towards expanding the scope of MXene-based gas sensors beyond Ti$_3$C$_2$T$_x$ and advancing the field of gas sensing technology.

**Keywords:** Ti$_3$C$_2$T$_x$; M$_2$X MXenes; surface chemistry; gas sensing; in-situ Schottky barriers.

**References:**

We recently depicted the “Nano-immunity-by-design” where the characterization of 2D materials is not solely based on their physical-chemical parameters but also on their immunoprofile. [1] The immune-profiling can be revealed on its complexity by unique, informative ways: high dimensional approaches. [2,3] We exploited high-dimensional approaches, such as single-cell mass cytometry and imaging mass cytometry on graphene and other novel two dimensional materials, such as transition metal carbides/carbonitrides (MXenes). [4-6] We revealed that the amino-functionalization of graphene oxide increased its immunocompatibility. [4] Moreover, we combined graphene with AgInS2 nanocrystals, enabling its detection by single-cell mass cytometry on a large variety of primary immune cells. [5] Together with our published works, I will present unpublished results on a wider variety of novel 2D materials, MXenes, MoS2, WS2, and bismuthene. The Chromium Carbide MXene opens up new avenues for energy storage owing to its electrical conductivity, mechanical properties, and high surface area. Chromium MXene was synthesized by using FeC$_3$, well known etchant to etch Al layer for Cr$_2$AlC and Ascorbic acid was used for the removal of by-products. Delamination of the layers was done by sonication the sample for energy storage using its electrical conductivity, mechanical properties, and high surface area. We recently depicted the “Nano-immunity-by-design” where the characterization of 2D materials is not solely based on their physical-chemical parameters but also on their immunoprofile. [1] The immune-profiling can be revealed on its complexity by unique, informative ways: high dimensional approaches. [2,3] We exploited high-dimensional approaches, such as single-cell mass cytometry and imaging mass cytometry on graphene and other novel two dimensional materials, such as transition metal carbides/ carbonitrides (MXenes). [4-6] We revealed that the amino-functionalization of graphene oxide increased its immunocompatibility. [4] Moreover, we combined graphene with AgInS2 nanocrystals, enabling its detection by single-cell mass cytometry on a large variety of primary immune cells. [5] Together with our published works, I will present unpublished results on a wider variety of novel 2D materials, MXenes, MoS2, WS2, and bismuthene. Our results conceptualize that chemical and immunological designs of 2D materials offer new strategies for their safe exploitation in biomedicine.


**8:05 AM • NM01/NM03.05**

**High-Dimensional Approaches for Immune Profiling of 2D Materials**

**Lucia G. Delogu**

**University of Padua, Italy**

We recently depicted the “Nano-immunity-by-design” where the characterization of 2D materials is not solely based on their physical-chemical parameters but also on their immunoprofile. [1] The immune-profiling can be revealed on its complexity by unique, informative ways: high dimensional approaches. [2,3] We exploited high-dimensional approaches, such as single-cell mass cytometry and imaging mass cytometry on graphene and other novel two dimensional materials, such as transition metal carbides/ carbonitrides (MXenes). [4-6] We revealed that the amino-functionalization of graphene oxide increased its immunocompatibility. [4] Moreover, we combined graphene with AgInS2 nanocrystals, enabling its detection by single-cell mass cytometry on a large variety of primary immune cells. [5] Together with our published works, I will present unpublished results on a wider variety of novel 2D materials, MXenes, MoS2, WS2, and bismuthene. Our results conceptualize that chemical and immunological designs of 2D materials offer new strategies for their safe exploitation in biomedicine.


**8:35 AM • NM01/NM03.06**

**Multilayer Carbon Nanotubes and CuO Nanoparticles Composite based H2S Sensors**

**Sumit Kumar** and Mahesh Kumar; Indian Institute of Technology Jodhpur, India

H$_2$S is an extremely hazardous air pollutant that harms the human respiratory system and world ecosystems. The main sources of H$_2$S emissions are sewage, petroleum industries, and natural gas. The demand for some sensing mechanism to monitor its emissions is paramount. Herein, we demonstrate CuO nanoparticles and multilayer carbon nanotubes (MWCNTs)-based H$_2$S sensors. The conventional chemical vapor deposition technique (CVD) is used for growing MWCNTs. The optimal amount of MWCNTs and CuO nanoparticles in the composite enhanced the H$_2$S sensor response. The experimental data confirmed that the bare CuO sensor response (ΔR/R%) for 1 ppm H$_2$S was 31%; further MWCNTs/CuO heterojunction sensor responses reached 53%. The enhanced sensing characteristics are a result of the formation of nano-heterojunctions between MWCNTs and CuO nanoparticles, which enhance the chemical and electronic sensitivity properties. In addition, the heterojunction sensor demonstrated excellent H$_2$S selectivity over other oxidizing and reducing gases.

**8:40 AM • NM01/NM03.07**

**New Mechanisms in Cell-Nanomaterial Interactions: Boron Nitride Nanosheets Inducing Water Channels Across Lipid Bilayers**

**Xinping Fan1, Matteo Andrea Lucherelli2, Wenpeng Zhu2, Paolo Samorì1, Huaqian Gao1, Alberto Bianco3 and Annette von dem Bussche1**

Understanding the interaction between two-dimensional (2D) materials and cell membranes is pivotal for nanomedicine and safe nanotechnology applications. In this study, we investigate how hexagonal boron nitride (hBN) interacts with the cell membrane by combining molecular dynamics (MD) simulations and in vitro experiments. Our MD simulations reveal that sharp hBN wedges can penetrate lipid bilayers, forming cross-membrane water channels along their exposed polar edges, a behavior not exhibited by round hBN sheets. We hypothesize that such water channels can facilitate cross-membrane transport, potentially leading to lysosomal membrane permeabilization. To test this hypothesis, we prepared two types of hBN nanosheets, the former with a cornered morphology and the latter with a round morphology, and exposed human lung epithelial cells to both hBN nanosheets. The cornered hBN with exposed polar edges resulted in a dose dependent cytotoxic effect, whereas round hBN did not cause significant toxicity, thus confirming our hypothesis. These results highlight the significance of 2D materials in facilitating nanoscale water and molecular transport across lipid membranes and have substantial implications for the design of hBN-based drug delivery systems and safe design of future advanced hBN containing composites and devices.
SYMPOSIUM NM02

Advances in Nanodiamonds
April 23 - April 24, 2024

Symposium Organizers
Jean-Charles Arnault, CEA Saclay
Huan-Cheng Chang, Academia Sinica
Shery Chang, University of New South Wales
Peter Pauzauskie, University of Washington

* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION NM02.01: Quantum Sensing with Nanodiamonds
Session Chairs: Silvia Orlanducci and Peter Pauzauskie
Tuesday Morning, April 23, 2024
Room 338, Level 3, Summit

10:30 AM *NM02.01.01
Optical Hyperpolarization of Nuclear Spins in Nanodiamonds
Fedor Jelezko; Ulm University, Germany

Dynamic nuclear spin polarization allows to enhance signals in NMR and MRI by orders in magnitude. We show that electron spin of NV centers in diamond can be used as efficient source of nuclear spin polarization allowing to orient nuclear spins associated with $^{13}$C in nanodiamonds. We show that coherent control tools allow to realize efficient polarization transfer in randomly oriented nanodiamonds including isotopically engineered diamond nanoparticles. Efficient hyperpolarization together with long spin lattice relaxation time of diamond nuclear spins has the potential for applications in magnetic resonance imaging. Furthermore, hyperpolarized nanodiamonds can be employed as spin batteries for polarization transfer to external nuclear spins.

11:00 AM *NM02.01.02
Engineering Nanodiamonds for Quantum-Enhanced Bio-Sensing
Philip Hemmer; Texas A&M University, United States

Diamond color centers like the nitrogen-vacancy (NV) have shown much promise for nanoscale sensing of magnetic and electric fields and temperature. So far however the quantum properties of the NV have not been used to full advantage, for example quantum entanglement of NV qubits has rarely been used for sensing. In this talk I will review recent advances in the fabrication of NVs, and other magnetic color centers in diamond, and in the growth of high quality nanodiamonds. Combining these advances, I will discuss the future prospects of engineering quantum-enhanced sensors in nanodiamonds.

11:30 AM *NM02.01.03
Long Spin Coherence and Relaxation Times of Nitrogen-Vacancy Centres in Nanodiamonds
Gavin W. Morley; University of Warwick, United Kingdom

The negatively charged nitrogen-vacancy center (NVC) in diamond has been utilized in a wide variety of sensing applications. The long spin coherence and relaxation times ($T_2^*$, $T_2$, and $T_1$) of the center at room temperature are crucial to this, as they often limit sensitivity. Using NVCs in nanodiamonds allows for operations in environments inaccessible to bulk diamond, such as intracellular sensing. We report long spin coherence and relaxation times at room temperature for single NVCs in isotopically purified polycrystalline ball-milled nanodiamonds. Using a spin-locking pulse sequence, we observe spin coherence times, $T_2$, up to 786 $\pm$ 200 $\mu$s. We also measure $T_2^*$ times up to 2.06 $\pm$ 0.24 $\mu$s and $T_1$ times up to 4.32 $\pm$ 0.60 ms.

We also magnetically levitate micron-sized diamonds in vacuum towards putting them into a superposition of being in two places at once. This provides a platform for testing fundamental physics which could include, in time, a test of the quantum nature of gravity.

SESSION NM02.02: Biological Applications of Nanodiamond Sensors
Session Chairs: Yuen Hui and Alexander Shames
Tuesday Afternoon, April 23, 2024
Room 338, Level 3, Summit

1:30 PM *NM02.02.01
Diamond Quantum Sensing Microscopy of Spin Crossover and Cytochrome C Molecules
Abdelghani Larouiti1, Suvechhya Lamichhane1, Rupak Timalsina1, Kayleigh McElveen1, Cody Schultz1, Adam Erickson1, Ilya Fescenko2, Kapildeb Ambal3, Shuo Sun1, Yinsheng Guo1, Sy-Hwang Liou1 and Rebecca Lai1; 1University of Nebraska-Lincoln, United States; 2University of Latvia, Lao People's Democratic Republic; 3Wichita State University, United States

Diamond Quantum sensing (DQS) microscopy based on nitrogen vacancy (NV) centers has become a unique tool to probe weak static and fluctuating magnetic fields with an excellent combination of spatial resolution and magnetic sensitivity, opening new routes to study solid-state [1] and biological materials [2]. In this work, we present two examples of using DQS in wide-field geometry to probe nanoscale magnetic phenomena in molecules.

First, we discuss DQS wide-field microscopy measurements on individual Fe(Htrz)2(trz)[BF4](Fe triazole) spin-crossover (SCO) nano-rods of size varying from 20 to 1000 nm. Fe triazole SCO molecules show thermal switching between low spin (LS) and high spin (HS) states which are applicable in thermal sensors and molecular switches. While the bulk magnetic properties of these molecules are widely studied by bulk magnetometry techniques, their properties at the individual level are not yet explored. Scanning electron microscopy (SEM) and Raman spectroscopy are performed to determine the size of the nano-rods and to confirm the spin state (LS vs HS) of the Fe triazole molecule respectively [3]. The stray magnetic fields produced by...
individual nano-rods are imaged by DQSY microscopy as a function of temperature (up to 150 °C) and applied magnetic field (up to 350 mT) and correlated with SEM and Raman. We found that in most of the nanorods the LS state is slightly paramagnetic, probably originating from the surface oxidation and/or the greater Fe 3+ presence along the nanorods' edges. NV measurements on the Fe-triazole doped magnetic and paramagnetic behaviors [3]. Then, we show DQSY wide-field microscopy measurements on cytochrome C (Cyto-C) nanoclustered molecules. Cyto-C is an iron-containing biomolecule that plays an important role in the electron transport chain of mitochondria [4]. Under ambient conditions, the heme group remains in the Fe 3+ paramagnetic state [5]. Initially, we performed NV T 2 relaxation measurements on a carboxylated diamond chip doped with 8-nm thick NV-layer without any Cyto-C, which revealed a relaxation time T 2 of ~1.2 ms. Subsequently, we varied the concentration of Cyto-C from 6 mM to 54 mM and show a reduction of the NV relaxation time T 2 from ~800 μs to 150 μs respectively, explained by the spin noise generated from the intracellualr iron spins in the Cyto-C molecules [6]. Additionally, we performed magnetic relaxation imaging of Cyto-C proteins on a nanostructured diamond substrate by which we estimate the density of adsorbed iron from 1.4 × 10 9 to 1.7 × 10 10 per μm 2 [6]. [1] A. Larouei, K. Ambal, Appl. Phys. Lett. 121, 060502 (2022). [2] I. Fesenko, A. Larouei, et al., Phys. Rev. Appi. 11(3), 034029 (2019). [3] S. Lamichanhe, A. Larouei, et al., ACS Nano 17 (9), 6949-8704 (2023). [4] I. Bertini, et al., Chem. Rev., 106 (1), 90–115 (2006). [5] J. Liu, et al., Chem. Rev. 114 (8), 4366–446 (2014). [6] S. Lamichanhe, A. Larouei, et al., under review, arXiv:2310.08065 (2023).

Acknowledgment: This material is based upon work supported by the NSF/EPSCoR RII Track-1: Emerging Quantum Materials and Technologies (EUQATE) Award OIA-2044049, and NSF Award 2328822. I.F. acknowledges support from Latvian Science Foundation project Izp-2021-1-0379. K.A. would like to acknowledge the support of the National Science Foundation/EPSCoR RII Track-4 Award OIA-2033210 and NSF Award 2328822. The research was performed in part in the Nebraska Nanoscale Facility: National Nanotechnology Coordinated Infrastructure and the Nebraska Center for Materials and Nanoscience (and/or NERCF), which are supported by NSF under Award ECCS: 2025298, and the Nebraska Research Initiative.

2:00 PM *NM02.02.02

On The Optimal Chemical Interface of Diamond for Quantum Biosensing Petr Cigler;

Institute of Organic Chemistry and Biochemistry of The CAS, Czechia

Non-perturbing techniques solving high-sensitivity results are of growing importance. These techniques are currently of central interest in the biosciences. Nanodiamond (ND) is a highly biocompatible nanomaterial for construction of nanosensors, which can accommodate nitrogen-vacancy (NV) centers. The NV spin properties can be read optically, which enables design of various probes based on quantum mechanical interactions. NDs can be distributed to biological environment and report sensitivity on the spin-related processes occurring in a close vicinity of the particle employing for example the NV spin relaxation measurements. NV relaxation however reaches its limitations in terms of poor colloidal stability in physiological environment and non-specificity to detect only the magnetic field originated from the spins of interest.

To ensure colloidal stability in biologically-relevant environment we stabilize ND probes using thin polymer coatings that can be further modified to allow specific sensing of physical or targeted molecules. To that end, we design molecular transducers for transposing the presence of particular analytes to a selective and unambiguous readout. Different types and surface of architectures including those for selecting sensitive measurements of pH, temperature, redox potential, and ascorbate concentration under physiological conditions will be discussed. Additionally, our recent developments of ND probes for detection of biomolecules using relaxometry together with a proof-of-principle results will be presented.

3:00 PM NM02.02.03

Detection of Alzheimer’s Disease Through Fluorescent Nanodiamonds-Based Spin-Enhanced Latera Flow Immunossays Stefaqna Angad1, Wesly Wei-Wen Hsiao1, Gianna Fadhilah1, Trong-Nghia Le2, Huan-Cheng Chang2 and Wei-Hung Chiang1; 1National Taiwan University of Science and Technology, Taiwan; 2Academia Sinica, Taiwan

Fluorescent nanodiamond (FND) has recently been regarded as a feasible alternative reporter for lateral flow immunassays (LFIA). The negatively charged nitrogen-vacancy (NV–) center in FND is a point defect with unique magneto-optical properties, giving outstanding characteristics to detect biomarkers of diseases. Alzheimer’s disease (AD) is the most common form of dementia, characterized by decreased memory, thinking, cognition, behavior, personality, and ability to conduct everyday duties, which might result in complete brain failure and, eventually, death. The two most commonly used detection techniques to detect changes in the brain caused by AD are brain imaging (CT, MRI, PET) and lumbar puncture. However, while brain imaging is expensive and timely consuming, lumbar puncture is controversial since 30% of patients get severe headaches followed by nausea and vomiting lasting more than a week. To this end, we have developed a Spin-Enhanced Latera Flow Immuno-Assay (SELFIA) for non-invasive AD diagnostics utilizing the spin properties of the NV– centers in FND to achieve background-free ultrasensitive detection. In addition, to enhance sensitivity and specificity, we employed a sandwich assay of SELFIA to further noncovalently conjugate FND to anti-pTau antibodies toward detecting pTau protein (a critical AD biomarker involved in AD pathology), while the capture antibody immobilized on the membrane. Note that we have a comparable result with Enzyme-Linked Immunosorbent Assay (ELISA), as our FND-based SELFIA only requires approximately 30 minutes to reach a detection limit of 7 pg/mL for pTau (the sensitivity/specificity threshold is 15 pg/mL in plasma). Hopefully, this study will contribute to developing a safe, simple, and accurate AD detection platform that can identify this illness in its earliest stages and might also be applied to other diseases in precision health.

3:15 PM *NM02.02.04

Intracellular Thermometry with Fluorescent Polymer Sensors and Nanodiamonds Yoshi Harada; Osaka University, Japan

Intracellular temperature fluctuations are thought to be closely related to higher order cellular phenomena. We have developed a method for imaging the temperature distribution in single living cells using a fluorescent polymer thermometer and fluorescence lifetime imaging microscopy to study the effects of intracellular temperature on cellular physiological activity. Previous experiments using the developed method have shown that during the G1 phase, the temperature of the nucleus is approximately 1°C higher than the temperature of the cytoplasm, as well as some mitochondria in the centrosomes. The mechanisms that maintain this intracellular temperature heterogeneity and its physiological significance are not well understood. Recently, however, the mechanisms of physiological phenomena caused by fluctuations in intracellular temperature have been elucidated. We hypothesized that intracellularly generated heat is not only a product of reactions, but also drives cellular responses. To test this hypothesis, we focused on cell differentiation, in which cells dramatically change their protein expression patterns. Using the neuronal model cell PC12, we investigated the relationship between neuronal differentiation and intracellular temperature. The results showed that intracellular temperature is involved in neuronal differentiation and associated neurite outgrowth. In addition to the aforementioned fluorescent polymer temperature sensor and fluorescence lifetime imaging microscopy, we also measured temperature using fluorescent nanodiamond particles containing negatively charged nitrogen vacancy centers as temperature sensors. We have previously shown that fluorescent nanodiamonds are able to measure temperature independent of external environmental influences such as pH, salt, and viscosity. To measure intracellular thermal conductivity, we also fabricated nanoparticles coated with polydimethylsiloxane, which generates heat when exposed to light, around fluorescent nanodiamonds. Although the intracellular thermal conductivity has been assumed to be the same as the thermal conductivity of water, whether this is true or not was verified by actually measuring the intracellular thermal conductivity using the fabricated hybrid particles of polydimethylsiloxane and fluorescent nanodiamonds. The results showed that, although the data were very uneven, on average the thermal conductivity inside the cell was several times smaller than the conductivity of water. In the present study, it is clear from microscopic observations that the hybrid particles are present inside the cell, but it is not known where in the cell they are localized. The variability of the data suggests variations in thermal conductivity depending on the location within the cell. Future work will use techniques to chemically modify the surface of the polydimethylsiloxane-fluorescent nanodiamond hybrid particles, such as localizing the particles in mitochondria and nuclei, to measure thermal conductivity at different local positions in the cell to clarify what exactly produces such low thermal conductivity.

3:45 PM NM02.02.05

Diamond-Based Quantum Sensing of Free Radicals in Migrating Human Breast Cancer Cells Claudia R. Reyes San Martin1, Arturo Elias-Llumb1,2, Marcia Manterola2, Aldona Mayk3 and Romana Schirhagl1; 1University Medical Center Groningen, Netherlands; 2University of Chile, Chile; 3Technical University of Denmark, Denmark

Diamond migration is a crucial parameter for disease progression in cancer. It is known that ROS levels are involved in the regulation of migration process, however, the exact role of free radical generation and where it occurs is unknown. Here we use a diamond-based quantum sensing technique to detect free radical generation during cancer cell migration in real time with subcellular resolution. We investigated highly metastatic MDA-MB-231 human breast cancer cells and observed free radical formation after 16 hours of starvation and 24 h of migration under low-serum conditions. Intracellular radical dynamics was monitored at different migration points (0, 12, and 24 h), and cell morphology was evaluated. Additionally, the number of focal adhesions was analyzed as an indicator of the migratory potential of the cells. All the parameters were addressed using a homemade script on the FIJI platform. We further measured free radical generation under NO2 inhibition by apocynin. We found that free radical levels decreased after 24 h treatment with 36 μg/mL apocynin while the levels of ROS increased and also the migratory capacity of the cells. Our results evidence the complexity of the regredation in migrating cancer cells and offer a novel approach to specifically and locally interrogate pivotal players of the oxidative network behind metastatic success.

4:00 PM NM02.02.06

Synergic Effects of Nanoparticle Geometric Shape and Post Curing on Nanodiamond-Reinforced Epoxy Nanocomposites: Characterization, Microstructure and Mechanical
Nanodiamond, a significant member of carbon-based nanoparticles, is characterized by a spherical geometric shape and typically classified as a 0-D material due to its extremely small diameter of individual nanoparticles. The unique characteristics of nanodiamonds distinguish them from other carbon-based nanoparticles and have gained considerable interest in the fields of medicine, electronics, sensors, and particularly as nanofililers in polymeric nanocomposites. One of the primary challenges associated with nanocarbon-reinforced nanocomposites is achieving a homogeneous and consistent dispersion of the nanoparticles within the polymer matrix. Compared to other commonly used carbon-based nanoparticles such as cylindrical carbon nanotubes and planar graphene, the enormous differences in shape and dimension may inevitably lead to notable variations in dispersion, which further greatly influences the overall properties of reinforced nanocomposites. This study explores the dispersion characteristics of nanodiamond in epoxy nanocomposites and examines the resulting effects on viscosity, microstructure, and mechanical properties of the epoxy nanocomposites. Systematic comparisons are made between nanodiamond along with carbon nanotube and graphene, while also considering the synergistic effects with post curing of epoxy. Experimental results indicate that the nanodiamond-reinforced epoxy nanocomposite exhibit a more homogeneous nanoparticle dispersion, lower viscosity, reduced porosity, and stronger pull-off adhesion, while the graphene-reinforced epoxy nanocomposites achieve a higher lap shear strength. Although post curing is effective in reducing porosity and improving adhesion properties of the nanocomposites, its impact became less pronounced with the addition of nanoparticles.

Acknowledgement:
CDots open up new opportunities for the development of highly potent carbon-based non-traditional photodynamic antimicrobial agents. Mechanistically, upon photoexcitation on CDots, there are rapid charge transfers and separation to form electrons and holes redox pairs, followed by the radiative recombinations of the electrons and holes. The interactions between H2TPP and OHND in water result in a bathochromic shift of the porphyrin Soret band and a quenching of both the porphyrin singlet and triplet state. The results are discussed in the context of what is known regarding the energetics of ND in solution and a model of porphyrin quenching by OHND is proposed.

SESSION NM02.04: Synthesis and Characterization of Nanodiamonds
Session Chairs: Peter Pauzauskie and Olga Shenderova
Wednesday Morning, April 24, 2024
Room 338, Level 3, Summit
8:45 AM NM02.04.03
Carbon Dots: Visible Light Activated Antimicrobial Functions and Their Property–Function Correlations Liu Wang1, Yongan Tang2 and Ya-Ping Sun2,1; North Carolina Central University, United States; 2Clemson University, United States
Carbon dots (CDots), generally defined as small carbon nanoparticles (CNPs) with various surface passivation schemes, represent the nanoscale carbon allotrope at zero-dimension. Attributed to the π-plasmon-associated electronic transitions, CDots have remarkable broad optical absorptions in the entire visible spectrum, extending into both near-UV and near-IR, making them excellent visible-light-excitable agents.
In recent years, a large number of studies have provided strong evidence to support the establishment of CDots as a new class of effective and efficient visible/natural light-activated antimicrobial agents. Experimentally, our teams have demonstrated the highly effective photoactive antimicrobial abilities of CDots against various bacteria and viruses, ranging from laboratory model bacteria (E. coli, Bacillus subtilis), pathogenic foodborne pathogens (Listeria, Salmonella), to multi-drug resistant (MDR) nosocomial pathogens (Enterococcus), and biofilms, as well as various viruses (model MS2 virus, vesicular stomatitis virus (VSV), marine norovirus (MVN), and norovirus-like particles (VLPs)). Mechanistically, upon photoexcitation on CDots, there are rapid charge transfers and separation to form electrons and holes redox pairs, followed by the radiative recombinations of the separated redox pairs resulting in emission excited states, which are responsible for the brightness of CDots in addition to the photodynamic production of classical reactive oxygen species (ROS). It is the combined action of the initially separated redox pairs and the generated classical ROS that are responsible for the observed uniquely effective photoactivated antimicrobial function of CDots. Associated oxidative damages in CDots-treated bacterial cells have been confirmed, including increased levels of lipid peroxidation, increased membrane permeability, and cytoplasmic structural disruptions. Degradation in viral proteins and genomic RNAs have also been confirmed. The presentation will also include the insights on property-function correlations in CDots for their photoactivated antimicrobial activities. Extensive experimental results have revealed that the optical properties, the surface functional groups and charges, the passivation layers of CDots, as well as the synthesis processes, are highly correlated with their photoinduced antimicrobial functions. Such correlations make CDots to be excellent tunable and expandable material platforms for further improvement in their desirable functions. Along with their non-toxic nature, CDots open up new opportunities for the development of highly potent carbon-based non-traditional photodynamic antimicrobial agents.
Acknowledgement: The research was supported by NSF grants #2102021, #2102056, & #1855905, and USDA grants #2019-67018-29689 & #2023-67018-40681.
5:00 PM NM02.03.01
Photophysical Characterization of Non-Covalently Bound Porphyrin-Nanodiamond Assemblies in Water William A. Maza, Daniel Ratchford, Adam D. Dunkelberger and Jeffrey C. Owrustsky; US Naval Research Laboratory, United States
Photoinduced charge transfer dynamics between nanodiamond, ND, particles and adsorbed dyes can potentially provide the necessary driving force to induce chemical reactions. We present steady-state and time-resolved fluorescence and UV/visible absorption data of self-assembled aggregates of the free-base porphyrin meso-(tetra-carboxyphenyl)porphyrin, H2TCP; and surface modified ND. Surface modification of H-terminated nanodiamond was carried out by the laser ablation method in water which has been reported to result in a OH-rich surface of ND, OHND. Interactions between H2TCP and OHND in water result in a bathochromic shift of the porphyrin Soret band and a quenching of both the porphyrin singlet and triplet state. The results are discussed in the context of what is known regarding the energetics of ND in solution and a model of porphyrin quenching by OHND is proposed.

SESSION NM02.03: Poster Session
Session Chairs: Arsène Chemin and Peter Pauzauskie
Tuesday Afternoon, April 23, 2024
Flex Hall C, Level 2, Summit
8:30 AM NM02.04.01
Improving The Creation of SiV Centers in Diamond via Sub- Pulsed Annealing Treatment Yan-Kai Tseng; SLAC National Accelerator Laboratory, United States
Silicon-vacancy (SiV) centers in diamond are emerging as promising quantum emitters in applications such as quantum communication and quantum information processing. Here, we demonstrate a sub-pulsed annealing treatment that dramatically increases the photoluminescence of SiV centers in diamond. Using a silane-functionalized adamantane precursor and a laser-heated diamond anvil cell, the temperature and energy conditions required to form SiV centers in diamond were mapped out via an optical thermometry system with an accuracy of ± 50 K and a 1 temporal resolution. Annealing scheme studies reveal that pulsed annealing can obviously minimize the migration of SiV centers out of the diamond lattice, and a 2.5-fold increase in the number of emitting centers was achieved using a series of 200-ns pulses at 50 kHz repetition rate via acousto-optic modulation. Our study provides a novel pulsed annealing treatment approach to improve the efficiency of the creation of SiV centers in diamond.

9:00 AM NM02.04.05
Imaging and Sensing Extreme Ultraviolet Radiation with Nanodiamonds containing Nitrogen-Vacancy Centers Yuen Y. Hui1, Teng-I Yang2 and Huan-Cheng Chang1,1; Academia Sinica, Taiwan; 2National Applied Research Laboratories, Taiwan
Extreme ultraviolet (EUV) radiation with wavelengths ranging from 121 nm to 10 nm has been applied for photolithography to fabricate nanoelectronic devices. This study demonstrates that Fluorescent Nanodiamonds (FNDs) containing Nitrogen-Vacancy (NV) centers as scintillators to image and characterize EUV radiations. The FNDs employed are 100 nm in size; they form a uniform and stable thin film (~1 μm in thickness) on an indium–tin–oxide-coated slide by electrospray deposition. The film is non-hygrosopic and photostable and can emit bright red fluorescence from the neutral NV centers when excited by EUV light. An FND-based imaging device has been developed for beam diagnostics of 50 nm and 13.5 nm synchrotron radiation respectively, achieving a spatial resolution of 30 μm. The noise equivalent power density is 29 μW/(cm² Hz1/2) for the 13.5 nm radiation. Our method can be extended to the imaging of Vacuum Ultraviolet radiation and soft X-ray.
9:15 AM NM02.04.07

Control of Synthesis and Structural Analysis of Poly(glycerol) Functionalized Nanodiamonds  

Masahiro Nishikawa1,2, Ming Liu1, Taro Yoshikawa1, Hidekazu Takeuchi1, Naoyoshi Matsuno3 and Naoki Komatsub1, Daicel Corporation, Japan; 2Kyoto University, Japan

Poly(glycerol) (PG) functionalization is one of the most common surface functionalization methods for a variety of nanoparticles (NPs). The hyperbranched hydrophilic polymer on NP surface gives advantageous features; dispersibility in aqueous media with high ionic concentration and extensibility for further functionalization through abundant -OH group. In addition, PG layer suppresses the adsorption of serum proteins in physiological environment to evade immune response or other non-specific interactions.

For PG functionalized nanodiamonds (ND-PG), to enable material and process design more quantitatively, we conducted the analyses of PG functionalization reaction, in which ring opening polymerization of glycidol (GID) on ND surface is done in ethylene glycol (EG) as a solvent, and structure of ND-PGs. As a result, we found that the amount of PG can be precisely controlled by the reaction conditions, use amount of GD and EG, and properties of ND core, oxygen content and particle size. In the structural analysis, the abundance ratios of substructures of glycerol unit in PG chain and the thicknesses of PG layer in dispersion for ND-PGs of different PG amounts and ND cores were elucidated by NMR, TGA and DLS.

M. Nishikawa et al., Carbon 2023, 205, 463–474.

9:30 AM NM02.04.08 Paramagnetic Defects in e-Beam Irradiated and Annealed Flake Polycrystalline Nanodiamonds Produced by External Shock-Wave Detonation Synthesis

Alexander I. Shames1, Frederick T. So2,3, Takuya F. Segawa1, Shinobou Onoda1, Hideaki Takashima4,5, Takeshi Ohshima4,5, Shigeki Takeuchi6, Masahiro Shirakawa7 and Norikazu Mizuochi2,8, Ben-Gurion University of the Negev, Israel; 9Kyoto University, Japan; 5National Institutes for Quantum Science and Technology, Japan; 2ETH Zurich, Switzerland; 3Chitose Institute of Science and Technology, Japan; 4Tohoku University, Japan

Polycrystalline NanoDiamonds (PCNDs), manufactured by an external shock-wave detonation (the DuPont method), are among directly synthesized diamond nanoparticles which attract growing interest to their use in biomedical and quantum sensing application. In contrast to detonation nanodiamonds (DNs), origin and evolution of paramagnetic defects in PCNDs induced by various treatments such as thorough purification, irradiation, annealing were beyond the scope of diamond community. We report on results of room temperature electron paramagnetic resonance (EPR) experiments done on a series of PCND samples undergone purification and e-beam irradiation at increasing fluences up to $1 \times 10^{19}$ e/corr followed by standard annealing at 600 °C. The paramagnetic defects’ pool in all samples consists of high abundant primary defects (mostly of $S = 1/2$) and low abundant triplet ($S = 1$) defects [1]. The total content of primary defects in the pristine PCND sample reaches 1200 ppm whereas the content of triplet NV$^{-}$ centers does not exceed 35 ppm. Boiling acid treatment of the non-irradiated and non-annealed sample PCND-BA causes significant reduction of primary defects (down to ~780 ppm) but does not really affect triplet centers. Annealing of that sample retains the content of all defects untouched, however causes prolongation of spin-lattice relaxation times of primary defects. Deconvolution of the intense singlet quasi-Lorentzian line of primary defects into broad and narrow components allowed attributing these components to dangling bonds (broad) and exchange coupled P1 centers (narrow) [2]. The content of dangling bonds in the annealed PCND-BA sample was estimated to ~620 ppm and that of P1 of ~160 ppm. E-beam irradiation (fluences $1 \times 10^{18}$, $3 \times 10^{18}$, $5 \times 10^{18}$ and $1 \times 10^{19}$ e/corr) increases the total content of primary defects at that contribution of the broad component practically does not change, the increase occurs due to the narrow one (up to ~400 – 500 ppm). At the same time content of the triplet centers in e-beam irradiated PCND-BA samples remains at the same low level. The PCND-BA sample irradiated with $1 \times 10^{19}$ e/corr fluence was further undergone the annealing treatment. It was found that annealing reduces total amount of primary defects (to ~400 ppm) due to reduction of both broad (~310 ppm) and narrow (~90 ppm) components. Some insignificant growth of NV$^{-}$ content (up to 50 ppm) was observed as well. The observed findings allow attributing the increase of the content of defects contributed to the narrow component in e-beam irradiated samples to appearance of radiation-induced paramagnetic $V^+$ centers. Annealing of these samples causes diffusion and recombination of $V^+$ centers accompanying by formation of a certain amount of radiation induced NV$^{-}$ centers. Surprisingly, the effect of NV$^{-}$ centers formation in PCND samples by e-beam irradiation and annealing was found to be at least on the order of magnitude weaker than that in both DNs obtained by nanozonization of HPHT diamonds and DNDs. In strong contrast, DNDs show an NV$^{-}$ concentration of ~100 ppm in pristine sample, which increases up to ~500 ppm under identical electron irradiation and annealing condition [3]. This specificity of PCND samples is discussed within the framework of models recently proposed in the Ref. [3].


10:15 AM NM02.04.09

Excitation and Charge Transfers in Functionalized Nanodiamonds in Water

Arsène Chemin1, Ronny Golnaks1, Jie Xia2, Andreas Weisser2, Benjamin Kiendl2, Anke Krueger2 and Tristan Petit1,2,3

1Helmholtz-Zentrum Berlin, Germany; 2Institut für Organische Chemie, Germany

Generating solvated electrons from sunlight using diamond material has been proposed as a promising strategy to achieve CO2 or N2 reduction in liquid phase [Zhu, D. et al. Nat. Mater (2013), Zhang, L. et al. Angew. Chem. (2014)]. The high conduction band energy and negative electron affinity of diamond surfaces facilitate easy electron transfer to water. Despite the diamond’s large band gap (5.47 eV), reports have demonstrated CO2 photo(electro)chemical reduction using visible light [Knittel, P. et al. J. Phys. Chem. Lett. (2017)], as well as the emission of solvated electrons from nanodiamonds [Buchner, F. et al. Nanoscale (2020)]. Our recent investigation of the sub-bandgap excitation on diamond materials has demonstrated the implication of the surface states in the photon absorption and the charge transfers in air [Chemin, A. et al. Small Methods (2023)] by combining surface sensitive X-ray absorption spectroscopy (XAS) to surface photovoltaics. However, ex-situ measurements have shown limitation in explaining charge transfers in liquid.

In this work, we investigate in-situ the nanodiamond-water interface to unravel the charge transfers and excitation process of detonation nanodiamonds functionalized with Ru complex, which showed promising photoelectrocatalytic properties [Kiendl, et al. Preprint (2022)]. While XAS characterisation is easily performed into vacuum, measurement in water is much more challenging due to the short penetration depth of soft X-ray in liquid. A recently introduced detection mode for XAS in liquid [Schön, D. et al. J. Phys. Chem. Lett. (2017)], performed at BESSY II synchrotron in Berlin, is used to characterize the unoccupied states at the nanodiamond surface as well as the structure of the water molecules at the interface with nanodiamonds. By comparing this measurement to XAS in vacuum, we determined that the interaction with the liquid lead to strong modification of the surface states. By coupling this information with UV-Vis absorption spectroscopy and photocurrent spectroscopy, we discuss further the impact of the water interface in the possible excitation path and charge transfer of the functionalized nanodiamonds.

This project has received funding from the European Commission under the Horizon 2023 grant agreement 665085 (DIACAT) and Volkswagen Foundation under the Freigeist Fellowship No. 89592.

10:00 AM BREAK

10:30 AM NM02.04.10

Phonon Green’s Function Method for Multiscale Modeling of Color Centers in Nanodiamonds

Vinoth K. Thapar1 and Edward J. Garboczi; National Institute of Standards and Technology, United States

Nanodiamonds are materials of strong topical interest because of their unusual properties and diverse potential applications in biomedical, communications, and sensing devices. Their dimensions range from a few to several hundred nanometers. There is special interest in color centers in nanodiamonds, which give them unique photonic and spin characteristics. These characteristics are useful for their applications in optical and quantum devices.

Color centers are lattice defects such as vacancies. A lattice defect causes a break in the translation symmetry of the lattice. Consequently, it causes a distortion or strain in the lattice, which also distorts the electronic wave functions and perturbs the associated energy levels. This effect is likely to be a serious material issue, which can affect the reliability and the performance of the finished device based on the use of nanodiamonds. It is, therefore, of paramount importance to develop modeling and measurement techniques of the lattice distortion/strain field due to a color center in nanodiamond, which is the objective of this work.

A unified theory for lattice defects in nanodiamonds is a challenging problem because the nanodiamonds can be too small or too big for a conventional theoretical treatment. A 5 nm color center in nanodiamond, which is the objective of this work.

control parameter defined in terms of the derivatives of the continuous displacement field. The inherent assumption in a continuum model is that the discrete lattice distortion is smeared out into a

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
continuum, which is valid only at distances much larger than the interatomic separations. For the final results to be physically realistic, the near field and far field formulation must be seamlessly linked. We describe a Green’s function (GF) method for modeling a color center in a nanodiamond of arbitrary size. The model is computationally efficient and can simulate even several hundred million atoms on an ordinary computer. It links the different length scales smoothly and seamlessly so can be used to estimate the nanodiamond size effect. We calculate the lattice GF by using a simple Born-von Karman model, in which each atom interacts with up to its second neighbor atoms. We also assume the harmonic approximation and the adiabatic approximation.

In this model, the main parameters are the interatomic force constants. These are given by the derivatives of the total potential energy, evaluated at the positions of equilibrium for each atom. In practice, the force constants are treated as adjustable parameters, which are determined phenomenologically by fitting them to elastic constants and phonon dispersion. Hence, an explicit knowledge of the interatomic potential is not needed. Our selected set of force constants correctly reproduces the measured elastic constants of bulk diamond and gives a reasonable agreement with the observed phonon spectrum over the first Brillouin zone.

Nanodiamonds (NDs) hold promise for a vast range of various distinct applications including drug delivery, cellular labeling and imaging, quantum sensing (such as thermometry and magnetic field/spin sensing), selective biomolecule binding or energy harvesting, and (photocatalysis - to name a few. Although researchers employ nanodiamonds in all these applications, due to the great variety of this nanomaterial, the actual nanoparticles used can differ substantially. Sometimes to the extent that they could be defined as a different material. In this contribution, we will focus on the two most common ND types, detonation NDs (DNDs) and high-pressure high-temperature (HPHT) NDs which will be highlighted. We will review recent experimental advances in the preparation of sub-5 nm NDs of both detonation and HPHT origin, including the HPHT NDs synthesized from molecular precursors (E. Ekmov et al., Nanomaterials 2022, 12, 351). The presentation aims to critically compare these two ND types from the Raman spectroscopy point of view as this technique is broadly used to assess not only the ND phase composition (C-sp² and C-sp³ content) but also the ND size. We show that the Raman spectra of DND and HPHT NDs on the 3-5 nm scale are size-insensitive yet significantly different from each other which limits the application of the current phonon confinement models for the ND size distribution analysis (S. Stehlik et al., J. Phys. Chem. C 2021, 125, 5647−5669). The diamond structural quality, and temperature (instability) caused by laser irradiation during the measurement are the key features reflected in the ND’s Raman spectrum. The first time observed low-frequency (20−200 cm⁻¹) Raman scattering signals may correspond to “breathing-like” modes of NDs as these signals exhibit clear size dependence. The low-frequency Raman scattering may thus provide another way for size distribution analysis of nanodiamonds (A. Vlk et al., J. Phys. Chem. C 2022, 126, 6318−6324).

SESSION NM02.05: Characterization and Processing of Nanodiamond Materials

Session Chairs: Petr Cigler and Yuen Hui
Wednesday Afternoon, April 24, 2024
Room 338, Level 3, Summit

1:30 PM *NM02.05.01
New Techniques of Depositing Detonation Nanodiamonds onto Substrates and Their Applications
Taro Yoshikawa1,2, Akira Kaga1 and Tomoaki Mahiko1; 1Daicel Corporation, Japan; 2Kanazawa University, Japan

Detonation nanodiamonds (DNDs) are considered exciting candidates for various applications, such as lubricant additives, semiconductor quantum dots, magnetic mapping sensors, protein mimics, and initial seeds for chemical vapor deposition (CVD) of diamond thin films on heterogeneous substrates. Essentially, these potential applications can be categorized into two groups: solution-based applications that use DND colloidal suspensions, and solid-state applications based on systems of DNDs supported by substrates, tips/probes, etc. The former applications have shown tremendous progress toward practical realization over the past decades. This progress is the result of thorough investigations and technological development in material preparation, including disassembling tightly bound aggregates, isolated/segmented dispersion through graphitization or oxidation of surfaces, annealing in a hydrogen atmosphere, insertion of appropriate surfactants, surface functionalization with organic molecules, and stirred-media milling with ceramic or zirconia microbeads. Meanwhile, development of the latter applications has been primarily hindered by the technical challenge of depositing/coating DNDs on the surfaces of solid-state materials with the desired layer thickness, particle density, and surface roughness. Recently, we have established two new techniques for depositing DNDs onto substrates. One technique involves the nanometer-scale ordered arrangement of DNDs onto substrates. The signs of surface charges, i.e., zeta potentials, of substrate surfaces are locally inverted through a combination of electron beam lithography and surface functionalization with 3-aminopropyltriethoxysilane. As a result, selective electrostatic deposition of DNDs onto the substrates is performed with line-and-space and dot array patterns at a length scale of ≥20 nm. Another technique involves the electrostatic layer-by-layer deposition of DNDs onto substrate surfaces using DND colloidal suspensions with different zeta potentials. By treating substrate surfaces in DND colloidal suspensions with positive and negative zeta potentials alternately, DNDs are deposited homogeneously on the substrate surfaces layer-by-layer. During the presentation, these techniques are introduced in detail, along with specific applications we have recently demonstrated. The nanometer-scale ordered arrangement technique is tested for patterning of sub-5 nm diameter dots on substrates. This could contribute to the manufacture of smaller diamond-based micro/nano electromechanical systems devices through a bottom-up process, rather than the conventional top-down method that requires costly polishing and etching of the diamond films. Meanwhile, the electrostatic layer-by-layer deposition technique is applied to fabricate diamond photocatalytic electrodes, enabling CO₂ reduction with visible light irradiation. The results indicate that the DND layer thickness of the electrode strongly affects the photosensitivity of the CO₂ reduction reaction.

2:00 PM *NM02.05.02
Fluorescent Diamond Particles for Bioimaging and Quantum Sensing
Olga A. Shenderova1, Marco Torelli2, Nicholas Nun3, Alex I. Smirnov2 and Ashok Ajoy3; 1Adamas Nanotechnologies, United States; 2North Carolina State University, United States; 3University of California, Berkeley, United States

Diamond nanoparticles containing fluorescent color centers exhibit a favorable combination of optical properties including photosensitivity that outlasts quantum dots and molecular probes, a broad emission color palette, and excellent biocompatibility. Fluorescent nanodiamonds containing nitrogen-vacancy (NV) color centers enable unique quantum sensing capabilities by reporting on nearby analytes, such as free radicals and other paramagnetic species, by decoding fluctuating magnetic fields induced by these external spins. This information can be conveniently imaged optically by adapting conventional microscopes or via hyperpolarized magnetic resonance methods. For the latter, quantum sensing is based on hyperpolarizing ¹³C nuclei in nanodiamond particles by optical pumping of NV centers and then imaging chemical information by ¹³C NMR scanners at high resolution. In this presentation, material developments for quantum sensing applications will be highlighted. The progress of several projects on quantum sensing with a biological scope under development by our team will be presented, with a more detailed focus on a near-term application such as using nanodiamond particles as sensors of paramagnetic species in biological media.

2:30 PM BREAK

3:30 PM NM02.05.03
High Pressure High Temperature Synthesized Diamond Particles with Controlled Nitrogen Content
Nicholas Nun1,2, Sergey Milikisiyants1, Marco Torelli2, Alexander Healey3, Roy Styles4, Brett Johnson5, Philipp Reineck3, Christopher Long6, Timothy Dunn7, Adam Dalis4, Takeshi Ohshima8, Emmanuel Druga9, Ashok Ajoy3, Alexander I. Shames7, Alex I. Smirnov3 and Olga Shenderova2; 1North Carolina State University, United States; 2Adamas Nanotechnologies, Inc., United States; 3RMIT University, Australia; 4Hyperion Materials & Technologies, United States; 5National Institutes for Quantum Radiological Sciences and Technology, Japan; 6University of California, Berkeley, United States; 7Ben-Gurion University of the Negev, Israel

Diamond particles hosting nitrogen vacancy centers is a platform for material potential for use in emerging nano and microscale sensing technologies. These envisioned quantum sensors are based on optical manipulation and readout of NV centers under the influence of external environmental stimuli (e.g., temperature, electromagnetic fields, mechanical strain). The important prerequisites for such measurement protocols are NV centers with suitable spin properties such as long coherence and relaxation times. While such properties are observed in bulk diamond crystals of suitable quality, the properties of diamond particles are often severely degraded by the presence of paramagnetic defects such as electronic spins associated with surface defects and other paramagnetic centers (primarily nitrogen P1 centers). Here we demonstrate HPHT grown microparticulate diamond with good crystal quality and a controlled nitrogen content in the range of ca. 5-50 atomic ppm. A resultant improvement in NV electronic spin coherence times by approximately 3-fold is directly observed by pulsed electron paramagnetic resonance (EPR) across the range of
Riccardo Salvio, Laura Micheli, Rocco Cancelliere, Giorgia Magnante, Emanuele Rea and Silvia Orlanducci

The unique surface properties of detonation nanodiamonds, such as their stability, high surface area, and the ability to be easily functionalyzed, make them a versatile and promising material for various catalytic applications. The large surface area and diverse surface functional groups on detonation nanodiamonds can promote heterogeneous catalysis and they can be used in a variety of reactions, including hydrogenation, reduction, oxidation, and other industrial processes. Here are some ways, developed in our laboratory, to modulate catalytic activities of ND by surface functionalization or by decorating ND with gold nanoparticles (AuNP). Gold nanoparticles and nanodiamonds are indeed remarkable nanomaterials with unique properties and a wide range of potential applications. The teamwork between AuNP and ND is related to the ability to control the shape and size of gold nanoparticles on the surface of nanodiamonds, modulate the colloidal properties, and the interactions with their surroundings. The hybrid system can exhibit unique catalytic and sensor activities, as both components contribute to these properties. In this communication, we will explore the use of AuNP-ND system as a platform for immobilizing enzymes and antibodies on electrode surfaces and test them in electroanalytical applications. Finally modified ND will be investigated as a catalyst in the reductive degradation of pollutants (nitrophenols class) and as enzyme mimics in the transesterification reaction. In summary, the combination of gold nanoparticles and nanodiamonds offers a powerful platform for a wide range of applications in various fields. Their unique properties, surface chemistry, and biocompatibility make them highly versatile, and the synergy between these two components can lead to innovative solutions in the areas of imaging, drug delivery, biosensing, and beyond. Research continues to explore and develop these hybrid systems to unlock their full potential for practical applications.

Group-IV Split Vacancy Nanodiamonds Synthesized via High-Pressure High-Temperature Techniques for Enhanced Quantum Sensing

Developments in quantum sensing which surpass the capabilities of classical measurements will improve the understanding of complex events in molecular disease biology and enable new modalities for drug and biomarker discovery. The negatively charged nitrogen-vacancy (NV) center in fluorescent nanodiamond can sense local electromagnetic fields, free radicals, temperature, and pH with nanoscale resolution. However, charge transfer and electromagnetic noise from the particle’s surface destabilize negatively charged NV⁰ emitters and convert them to non-sensing, neutral NV⁰ centers. This effect is important because sensing has a strong dependence on distance, and thus the quality of shallow NVs relates to sensing characteristics.

Additionally, at small particle sizes the fraction of destabilized NV centers near the surface becomes significant. Here we report results for conversion and stabilization of NV⁰ by plasma surface modification with fluorine and nitrogen groups to provide enrichment and stabilization of NV⁰. The treatment is shown to be suitable for particles of differing sizes and initial surface chemistries, allowing for scalable production of nanodiamond particles adapted for quantum sensing applications.

Catalytic, Photocatalytic and Electrochemical Properties of Surface-Treated Nanodiamond and of Multifunctional Gold Decorated Nanodiamond Systems

NM02.05.04

Catalytic, Photocatalytic and Electrochemical Properties of Surface-Treated Nanodiamond and of Multifunctional Gold Decorated Nanodiamond Systems

Emanuela Tamburri, Riccardo Salvio, Laura Micheli, Rocco Cancelliere, Giorgia Magnante, Emanuele Rea and Silvia Orlanducci

SYMPOSIUM NM03

Nanoscale Mass Transport Through 2D and 1D Nanomaterials

April 24 - April 25, 2024

Symposium Organizers

Michael Boutiller, Western University
Ngoc Bui, The University of Oklahoma
Piran Ravichandran Kidambi, Vanderbilt University
Sui Zhang, National University of Singapore
9:00 AM *NM03.01.03

**Nanofluidics under Extreme Confinement in 1D and 2D Channels**

Alekandr Noy 1,2; 1Lawrence Livermore National Laboratory, United States; 2University of California Merced, United States

Extreme spatial confinement in narrow fluidic channels strongly influences their transport properties and enables unconventional selectivity mechanisms that can often mimic some of the selectivity and transport characteristics of biological membrane channels. Modern nanomaterials have enabled experimental platforms that can recreate such extreme confinement in a range of 1D and 2D channels with defined geometry and controllable electronic properties. I will discuss several of these nanomaterials-based channel systems and show how confinement phenomena, coupled with the different electronic effects and dynamic charge equilibria in these channels can shape their transport properties and ion selectivity characteristics. Overall, these observations can pave the way for developing a new generation of precision separation platforms for biomedical and industrial use.

9:30 AM NM03.01.04

**Mechanistic Study of Electroosmotic Pumping through Atomicsmooth Carbon Nanotube Membranes with Application in Programmed Drug Delivery**

Bruce Hinds; University of Washington, United States

Mechanistic study of electroosmotic pumping through atomically smooth carbon nanotube membranes with application in programmed drug delivery

An important challenge for the membrane community is to mimic natural protein channels that outperform, by orders of magnitude, man-made systems based on pore size and coarse chemical selectivity. To mimic protein channel on a robust engineering nanomaterial platform, applied bias can be used to charge gatekeepers and induce ion pumping. Carbon nanotubes have three key attributes that make them of great interest for novel membrane applications: 1) atomically flat graphite surface allows for ideal fluid slip boundary conditions and extremely fast flow rates, 2) the cutting process to open CNTs inherently places functional chemistry at CNT core entrance for chemical selectivity and 3) CNTs are electrically conductive allowing for electrochemical reactions and reaction of electric fields gradients at CNT tips. The CNT membrane, with tips functionalized with charged molecules, is a nearly ideal platform to induce electro-osmotic flow with high charge density at pore entrance and a nearly frictionless surface for the propagation of plug flow. The use of the electro-osmotic phenomenon for control of ionic/neutral species ratio, the relative contribution of electroosmosis and electrophoresis within atomically smooth CNT conduits was quantified. More recent work with the direct measurement electroosmotic flow in a capillary flow cell shows the enhancement is due to atomic smoothness of CNTs, as seen the reversible stopping of flow by benzyl alcohol adsorption but no effect by H-bond chain disrupter NaSCN. Increased cation size had minimal improvement in EO pumping through DWCNT conduits.

6 “Electrically controlled nicotine delivery through Carbon nanotube membranes via electrochemical oxidation and nanofluiddically enhanced electroosmotic flow” Gulati G.K., Hinds B.J. Biomedical Microdevices 2021 DOI: 10.1007/s10054-021-00590-1
Due to their high transport rates, a great deal of attention has been recently given to 2D materials and slippery 1-D nanochannels as promising building blocks for next generation membranes. While in 2-D materials high flux is expected because of the classical inverse scaling of the flow rate with the pore thickness, in smooth channels such as carbon nanotubes (CNT), orders of magnitude rate enhancements are expected due to changed theories which are attributed to a vanishing friction at the pore wall. Irrespective of the high flux origin, in both atomically thin and thicker but slippery nanopores, the flow rates are largely dictated by the entrance/exit hydrodynamic resistance.

For CNT channels, experimental quantification of the magnitude of end and inner resistances is still lacking despite its importance for both practical applications and fundamental understanding. This has led to inaccuracy and disagreement in the calculation of slip lengths and flow rate enhancements from experimentally measured permeation rates, since often entrance/exit resistances are neglected altogether, or an arbitrary magnitude is assumed. Here, we quantified these resistances for both gases and liquids in CNT channels by fabricating membranes with controlled CNT length and known number of open pores. We found that the end resistance dominates the total resistance. For liquid water, measured viscous energy dissipation at the nanotube ends is quantitatively described by Sampson equation. For 2.4 nm wide single-walled CNTs, measured slip lengths approach several microns. A prevailing contribution of the end resistance was also found in pressure-driven gas transport, and recorded flow rate enhancements with respect to Knudsen theory appear to be independent of the gas type. These findings further advance the community understanding of the peculiar and often unusual CNT fluidic properties and may help reconciling “conflicting” literature reports on the subject.

Efficient and selective membranes are essential for advancing sustainable membrane processes, with the potential to address the separation of problematic contaminants and reduce environmental waste. The present landscape of conventional membrane fabrication techniques falls short in achieving the required solute-solute selectivity at the molecular level. Traditional approaches, such as interfacial polymerization for thin-film composite (TFC) membranes, were developed to enhance water-solute selectivity but lack precise control over local pore structures and chemical properties.

Herein we demonstrate by using triangular macrocyclic hosts as biomimetic channels, offering a remarkable degree of tunability. By merely substituting the bridging groups, we can directly influence local pore size and structure, resulting in enhanced selectivity and efficiency. This innovation offers the possibility of a bottom-up approach to membrane fabrication that can be customized for specific separation needs, providing an array of advantages. These include precise control over sub-nanometer pore structures, size, and chemical environments through subcomponent modifications, excellent processability, and simplified assembly of subcomponents, thus offering a promising solution for advanced membrane fabrication.

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Pushing The Limits of Size-Selectivity in Nanoscale Solute Separations

NM03.02.01

Pore dimension, resulting in significant retention of undesirable middle molecules (occurs via size exclusion as well as differences in diffusivity of the permeating species. However, transport in such polymeric pores is increasingly hindered as the molecule size approaches the pore dimension, resulting in significant retention of undesirable middle molecules (≥15–60 kDa) and uremic toxins. Enhanced removal of middle molecules is usually accompanied by high albumin loss (≥66 kDa) causing hypoalbuminemia. Here, the scalable bottom-up fabrication of wafer-scale carbon nanotube (CNT) membranes with highly aligned, low-friction, straight-length-capillaries and narrow pore-diameter distributions (0.5–4.5 nm) is demonstrated, to overcome persistent challenges in hemofiltration/hemodialysis. Using fluorescein isothiocyanate (FITC)-Ficoll 70 and albumin in phosphate buffered saline (PBS) as well as in bovine blood plasma, it is shown that CNT membranes can allow for significantly higher hydraulic permeability (more than an order of magnitude when normalized to pore area) than commercial high-flux hemofiltration/hemodialysis membranes (HF 400), as well as greatly enhance removal of middle molecules while maintaining comparable albumin retention. These findings are rationalized via an N-port membrane model that highlights the critical role of molecular flexibility and deformation during size-selective transport within nanoscale confinements of the CNTs. The unique transport characteristics of CNTs coupled with size-exclusion and wafer-scale fabrication offer transformative advances for hemofiltration, and the obtained insight into molecular transport can aid advancements in several other bio-systems/applications beyond hemofiltration/hemodialysis.


1:30 PM NM03.02.01
Pushing The Limits of Size-Selectivity in Nanoscale Solute Separations

Feng Gao1, Wen Chen1,2, Jamila Fatman1,2, Paul Nealey1,2 and Seth Darling1,2; 1Argonne National Laboratory, United States; 2The University of Chicago, United States

Transport of a spherical solute through a cylindrical pore has been modeled for decades using well-established hindered transport theory, predicting solutes with a size smaller than the pore to be rejected nonetheless because of convective and diffusive hindrance; this rejection mechanism prevents extremely sharp solute separations by a membrane. While the model has been historically verified, solute transport through near-perfect isoporous membranes may finally overcome this limitation. We achieve encouraging solute rejections using nanofabricated, defect-free, thin silicon nitride isoporous membranes. The membrane is challenged by a recirculated feed of dextran molecules to increase the opportunity for interactions between solutes and the pore array. Results show the membrane completely rejects solutes with greater size than the pore size while effectively allowing smaller solutes to permeate through. A steep size-selective rejection curve takes shape in distinct contrast to the conventional S-shape rejection curve predicted by hindered transport theory. With this traditional hurdle overcome, there is new promise for unprecedented membrane separations through judicious process design and extremely tight pore-size distributions.

1:45 PM NM03.02.02
Soft Artificial Materials based on Droplet Interface Bilayers and Their Application as Membranes for Electrically Driven Separations

Aida E. Fica Conceição1, Harekrushna Behera1, Mckayla Torbet2, A. Derya Bakiler1, Elisabeth Lloyd1, Robert Hickey1, Berkin Dortdivanlioglu1, Stephen A. Saries2 and Manish Kumar1; 1University of Texas at Austin, United States; 2The University of Tennessee, Knoxville, United States.

Soft tissue-like materials mimicking biological tissues' functionality, responsiveness, and reconfigurability hold immense potential for revolutionizing robotics, sensing, computing, biomanufacturing, and separations. Key features involve replicating cell structure by compartmentalizing aqueous environments with lipid membranes and incorporating membrane proteins for ion and solute transport. Droplet interface bilayers (DIBs) emerge as a promising platform, forming cell-like compartments enclosed by lipid membranes, serving as building blocks for 2D and 3D soft, responsive tissues. Conductive pathways are established by associating membrane proteins with lipid bilayers, providing tunable transport properties. A rapid, scalable protocol combining emulsification and centrifugation has been devised for creating artificial tissues based on DIBs. This process successfully produces tissues from lipids, and polymers, and integrates ion channels like self-inserting peptides, integral membrane proteins, and artificial channels. Additionally, a platform has been designed to employ these tissues as membranes for electrically driven separations. The process hinges on three main components: an aqueous solution, hydrophobic media, and a bilayer-forming amphiphile as the emulsifier. Emulsification leads to aqueous droplet formation enclosed by a monolayer. Centrifugation creates a tightly packed system and displaces the excess oil. The contact of monolayer-enclosed droplets creates a bilayer, forming a network of communicating water compartments. This process enables the formation of tissues from microliter to liter scale, with resulting material exhibiting exceptional properties including high electrical resistance, viscoelasticity, and self-healing behavior.

Modifications to the process can significantly alter tissue's electrical properties. By incorporating ion channels during emulsification, the tissue can become electrically conductive. This enables the creation of biomimetic membranes that replicate and amplify channel properties, such as selectivity and pore size exclusion. The system allows for the incorporation of various natural or artificial channels, as they self-arrange in the monolayer/bilayer due to the hydrophobic effect. Channels like gramicidin (self-inserting peptide), Outer Membrane Protein (OmpF), Ammonium Transporter Protein (AmtB), and artificial channels like LAP510, a highly selective lithium channel, have been successfully incorporated through this method.

The use of DIB-based artificial tissues as membranes for water treatment has been proposed and demonstrated at the laboratory scale. To fabricate the membrane, the tissue is placed in a glass or plastic container, separated by two hydrogel layers on each side, which are in contact with an aqueous media. The assembly order is aqueous solution/hydrogel/tissue/hydrogel/aqueous solution. Applying voltage between the two aqueous solutions drives the transport of charged molecules or ions across the membrane through ion channels. The membrane's selectivity is controlled by the tissue's width and the selectivity of the channels used, as each layer of droplets acts like a membrane. For example, two layers of droplets containing a channel with 90% selectivity for a specific molecule will behave like two 90%-selectivity membranes in series, yielding an overall 99% selectivity provided all droplets contain the selective channel. This feature allows fine-tuning of membrane selectivity even when using low-selectivity channels. Overall, this innovative platform for fabricating soft membranes holds tremendous promise for advancing water treatment separations.

2:00 PM *NM03.02.03
Nanofluidic Interfaces with Electrified Materials

Narayana R. Aluru; The University of Texas at Austin, United States

The coupling between liquids and solids at atomic limit is currently of great interest. In particular, understanding properties of simple and complex liquids interfacing with electronically active materials is an active area of research. In this talk, we will discuss how properties of liquids are affected by mechanically tuning the electrical properties of solids. In the second part of the talk, we will discuss the quantum coupling between the electronically active solid material and the interfacing liquid.

2:30 PM NM03.02.04
Computationally Guided Study of Cross-Linked Covalent Organic Frameworks for Membrane Applications

Alathe E. Davies, Michael J. Wenzel, Cailin L. Brugger, Jordan Johnson,

In this presentation I will discuss how HA-ADF STEM tomograms can be collected, calculated, and combined with electron energy loss spectroscopy data to produce three-dimensional images of chemistry and sample density to inform water transport simulations [6] and membrane synthesis. Particular emphasis will be given to the experimental and geometrical limitations on quantitativeness, such as the limited range of angles from which a membrane can be viewed in TEM, and how optimization and machine-learning techniques can be employed improve quantitativeness beyond the current state-of-the-art. Last, prospects for a ‘closed-loop’ unifying synthesis, characterization, and computational design will be discussed.

For decades, thin film composite membranes, in particular those employing an aromatic polyamide active layer, have become the dominant technology for the purification of water by nanofiltration and reverse-osmosis [1]. The extreme physical and chemical requirements demanded of these membranes (selectivity, permeability, fouling resistance, mechanical strength) combined with unique difficulties in studying their structure-property relationships on the nanoscale, have largely frustrated efforts to develop viable membranes based off new technologies. After more than 40 years, synthetic polymer membranes, many of which were discovered serendipitously, remain state-of-the-art. As the world confronts a changing climate, growing demand for water, and a transition away from fossil fuel it is increasingly important that new effective, energy-efficient separation technologies be developed [2]. This will require advances in computational modeling and synthesis, informed by new and improved methods of material characterization.

TEM has long been a powerful tool for the nanoscale characterization of membranes; however, all TEM methods fundamentally produce some sort of two-dimensional projection of the sample. Although there can be great value in 2D top-down and cross-sectional imaging of membranes [3], the structure of a membrane must be studied in more than two dimensions to fully describe its function. Unlike conventional TEM-tomography methods, which have been successfully employed to study 3D morphological properties of separation membranes [4] high angle darkfield scanning transmission microscopy (HA-ADF STEM) scans a focused probe over the sample and is capable of producing images at the highest achievable resolutions whose contrast is proportional to sample density and thickness. Further, each scan line can be acquired with a different defocus, allowing large areas of the sample to be kept in-focus even at high tilt angles [5].

Taken together, these qualities allow for three-dimensional images that accurately reflect the sample’s scattering density to be computed from the HA-ADF tilt series data.

In this presentation I will discuss how HA-ADF STEM tomograms can be collected, calculated, and combined with electron energy loss spectroscopy data to produce three-dimensional images of chemistry and sample density to inform water transport simulations [6] and membrane synthesis. Particular emphasis will be given to the experimental and geometrical limitations on quantitativeness, such as the limited range of angles from which a membrane can be viewed in TEM, and how optimization and machine-learning techniques can be employed improve quantitativeness beyond the current state-of-the-art. Last, prospects for a ‘closed-loop’ unifying synthesis, characterization, and computational design will be discussed.


5:00 PM NM03.02.08
Defect-Healed Carbon Nanomembranes for Enhanced Salt Separation: Scalable Synthesis and Performance
Zhen Yao
Zhejiang University, China

Carbon Nanomembranes (CNMs) are promising materials for separating salt mixtures due to their high selectivity and permeability. However, defects in CNMs can significantly affect their performance. We present a scalable method for defect healing that allows for the synthesis of large-scale, fully functional CNM-based composite membranes. These membranes exhibit high permeance and reasonable selectivity for H2/CO2 separation, making them promising for practical applications.

4:15 PM NM03.02.09
Interlayer-Shifting and Functionalization of 2D COF Membranes for Controlled Transport
Sui Zhang
National University of Singapore, Singapore

2D COF membrane is a versatile platform for controlling iontophoretic transport with its microporosity, interlayer spacing and rich space of chemistry. In the first part of our work, we attempted to regulate the interlayer alignment of 2D COF membranes by using the different types of catalyst. In contrast to traditional acid, the Lewis acid is able to accelerate the polymerization of imine-based COF and drives the interlayer shifting between adjacent layers, thereby resulting in pore redistribution and reduced pore size. The membrane exhibits high permselectance and reasonable selectivity for H2/CO2 separation. In the second part of our work, we functionalized the COF with sulfonate groups and observed interesting coordination-facilitated ion transport in the mixed ion environment. While single ion tests do not show much selectivity towards divalent and monovalent ions, the ion transport is much accelerated in the mixed ion solution, enabling high Mg2+/Li+ selectivity.

SESSION NM03.03: Poster Session
Session Chairs: Ngoc Bui and Piran Ravichandran Kidambi
Wednesday Afternoon, April 24, 2024
Flex Hall C, Level 2, Summit

5:00 PM NM03.03.01
Novel Copper-Nickel Pe-Por-Based Electrocatalysts for Highly Selective CO2 Reduction and Multi-Carbon Compound Synthesis
Abebe B. Workie
National Taiwan University of Science and Technology, Taiwan

Efforts are focused on developing an efficient strategy to combat global warming while also advancing the electrochemical conversion of carbon dioxide (CO2) into multi-carbon compounds and improving C-C coupling processes. For accelerating the transformation of CO2 into high-value chemicals, Metalloacarboxylic compounds have shown great potential among the many materials under investigation. However, they have thus far run across issues including low current density, limited catalytic activity, poor product selectivity, and stability worries. In this work, we present a novel achievement in the form of stable and conductive ultrathin dimeric Copper-Nickel Pe-Por-based electrocatalysts, synthesized through a solvent-assisted strategy. The manipulation of electron polarization between metal atoms is made feasible by adjusting the functionality and size of ligands, which enhances catalytic activity. This, in turn, leads to heightened atom utilization efficiency, customized catalytic behaviors, and exceptional selectivity, surpassing the benchmarks in C-C coupling and multi-carbon product formation. Our electrocatalyst exhibits remarkable selectivity for acetylene production, as demonstrated in an H-type cell. When operating in a 0.5 M KHC03 solution, it achieves outstanding Faradaic efficiencies (FEs) for CO2 reduction at 0.61 V (vs. RHE), yielding over 94% acetylene with a current density exceeding 85 mA cm2. These results surpass the performance of the majority of previously reported CO2 electrocatalysts. This study introduces a practical approach for designing future generations of cost-effective, efficient, and selective electrocatalytic reduction of carbon dioxide, offering potential solutions to mitigate global warming.

5:00 PM NM03.03.02
Separation of High-Purity C2H2 from Binary C2H2/CO2 with Robust Al-Based MOFs Constructed with Nitrogen(N)-Containing HeterocyclicDicarboxylate Se Min Jeong
1,2, Donghyun Kim1, Ji woong Yoon1, Su-Kyung Lee1, Jong Suk Lee1, Donghui Jo1, Kyung-Ho Cho1 and U-hwang Lee1; 1Korea Research Institute of Chemical Technology, Korea (the Republic of); 2Sogang University, Korea (the Republic of); 3Yonsei University, Korea (the Republic of)

The separation of acetylene (C2H2) from carbon dioxide (CO2) holds considerable industrial importance, primarily in acetylene purification. Indeed, the conventional distillation process poses
Single-step purification of the ternary C₂ hydrocarbon mixture to produce ethylene (C₂H₄) directly using adsorption-based technologies is desirable for reducing large energy consumption. However, it is challenging to develop an appropriate adsorbent, having preferential adsorption characteristics toward ethane (C₂H₆) and acetylene (C₂H₂) rather than C₂H₄ coupled with high adsorption capacity owing to their similar physicochemical properties. Herein, we present a highly stable, cheap, and scalable CAU-23 adsorbent, which enables single-step production of high-purity C₂H₂ (99.9%) from the ternary C₂ hydrocarbon mixture. CAU-23 exhibited higher uptake capacity of C₂H₂ (4.0 mmol g⁻¹) and C₂H₄ (4.7 mmol g⁻¹) compared to that of C₂H₆ (3.8 mmol g⁻¹). Further, it showed the reasonable selectivity for both C₂H₂/C₂H₄ (1.54) and C₂H₂/C₂H₆ (1.5) with an equimolar binary mixture, indicating that the separation performance of CAU-23 is comparable to the benchmark porous materials for separating C₂ ternary gas mixture. The breakthrough experiments demonstrated its capability to produce high-purity C₂H₄ (>99.9%) with various C₂H₆/C₂H₂/C₂H₄ compositions at 298 K and 1 bar with high recyclability. The origin of the separation performance was further explored by using computational simulations of the grand canonical Monte Carlo (GCMC) and density functional theory (DFT).

**References**

1. Kim, Dongheon et al. (2024). Single-step purification of the ternary C₂ hydrocarbon mixture to produce ethylene (C₂H₄) directly using adsorption-based technologies is desirable for reducing large energy consumption. *Journal of Chemical Technology and Metallurgy*. 39(2), 261-270.

Covalently Linked Fullerene Membranes for Gas and Water Transport De-en Jiang; Vanderbilt University, United States

It is extremely challenging to create long-range-ordered sub-nanometer pores in carbon materials. Recent breakthroughs in synthesis of covalently linked fullerene networks in gram scales provide a great opportunity to realize 2D and 3D ordered sub-nanometer pores at the interstices among linked C60 units. Here we show from both first principles and molecular dynamics simulations that the square-latticed monolayer fullerene membranes based on the experimental quasi-tetragonal phase of the fullerene 2D network possess the pore size, shape, and geometry promising for gas separations and water transport. Our simulation results suggest that there is a great potential in using covalently-linked fullerene membranes for separations.

Mechanistic understanding of oxidation of graphitic lattice for gaining control over the incorporation of Å-scale pores in graphene Kumar Varoon Agrawal; EPFL, Switzerland

Porous two-dimensional (2D) selective layer hosting zero-dimensional pores is attractive for molecular differentiation because one can tune molecular selectivity (by tuning pore size) and molecular flux (by tuning pore density). Porous graphene is an attractive candidate for this given that single-layer graphene can be conveniently synthesized in single-layer polycrystalline film morphology by chemical vapor deposition. Several promising results towards molecular separation have been demonstrated by incorporating pores in graphene by a variety of methods including physical etching (bombarding lattice with energetic beams) and oxidative etching.

In this presentation, I will highlight the important role of oxidative etching of graphene in highly scalable and easy-to-implement porosity incorporation in graphene with excellent control in the incorporation of Å-scale pores. I will discuss our recent efforts in understanding the mechanism of incorporation of these pores in the graphene lattice, starting with a single oxidation event, followed by cooperative assembly of the chemisorbed oxygen (epoxy) into clusters which then regulate the final pore size. I will discuss how clusters have ordered superlattice of O (against expectations of amorphous structure), which then leads to a series of sequences resulting in the incorporation of pores. I will discuss further examples of oxidation reactions that allow one to tune the size of pores in a highly controllable manner. Finally, I will discuss recent activities in scaling up graphene membranes, thanks to a highly scalable graphene oxidation chemistry.

Nanoporous Graphene Based Nanofluidics, From Mechanisms to Applications Luda Wang; Peking University, China

Nanofluidics has not only drawn significant research interest due to its abnormal behavior compared to bulk fluids, but also has numerous applications such as separation, sensing, and energy conversion. Graphene provides an ideal two-dimensional platform to investigate the transport behaviors of nanofluids owing to its ordered structure, chemical stability, and easy modification. Nanopores in graphene membranes provide 0D confined spaces to study transport mechanisms. Controlling the pore size in graphene membranes is a prerequisite, as even a small variation in pore size can result in a significant difference in transport properties. By decoupling defect site nucleation and defect growth with two successive plasma treatments, we achieved a narrow pore size distribution from gas-selective sub-nanometer pores to a few nanometers in size for small molecule separation. Moreover, we used a new strategy and achieved high solvent flux via organic solvent forward osmosis. After the precise introduction of the confined space, we then focus on designing functional groups, which provide a new degree of freedom. Through controlled nitrogen plasma, a highly proton-selective membrane was fabricated. By controlling the grain boundary density, proton permeance can be tuned within a range of 2 orders of magnitude with high selectivity and high proton conductivity. Through the synergistic regulation of the pore size and chemical properties of in-situ covalent modification, asymmetric ion transport behaviors and efficient sieving of monovalent metal ions (K+/Li+ selectivity ~ 48.6) can be achieved. Meanwhile, it also allows preferential transport for cations. The resulting membranes exhibit a K+/Cl− selectivity of 76 and an H+/Cl− selectivity of 59.3. The synergistic effects of steric hindrance and electrostatic interactions impose a higher energy barrier for Cl− or Li+ to cross nanopores, leading to ultra-selective H+ or K+ transport.

Besides the proof-of-concept experiments, we tried to bridge the gap between theory and reality to utilize graphene membranes in specific applications. For large-scale production, decimeter-scale (15 x 10 cm2) large-area nanoporous single-layer graphene membranes and stability-enhanced double-layer graphene membranes were fabricated. An application paradigm of graphene in a membrane-based precision instrument with higher precision and better stability was achieved. One step further, regarding realizing the module of graphene membrane, the poor resistance to deformation under tension and bending of composite membrane is the limit. We designed a large-area nanoporous graphene separation membrane supported by a fiber-reinforced structure, whose rates can decrease with temperature if, for example, adsorbed intermediates are involved. In this study, we perform temperature-variable permeation experiments in the range from -50 to +50 °C and observe anti-Arrhenius behaviour of water and ammonia permeating in two-dimensional freestanding carbon nanomembranes (CNMs). The permeation rate of water vapour is found to drop manifold with warming, while the passage of ammonia molecules strongly increases when the membrane is cooled down to the dew point. Liquefaction of isobutylene shows no enhancement for its transmembrane flux which is consistent with the material’s pore architecture.

Selective proton permeation through atomically thin graphene while maintaining impermeability to even small gas atoms i.e. He or hydrated ions, presents potential for advancing proton exchange membranes (PEMs) across a range of energy conversion and storage applications. The incorporation of graphene into state-of-the-art proton conducting polymers e.g. Nafion can enable improvements in PEM selectivity as well as mitigate reactant crossover. The development of facile integration approaches are hence imperative. Here, we systematically study the parameters influencing the integration of monolayer graphene synthesized via scalable chemical vapor deposition (CVD) on polycrystalline Cu foils with a model proton conducting polymer (Nafion) via a facile hot-press process. The hot-press time (t), temperature (T) and pressure (P) are found to not only influence the quality of graphene transfer but can also introduce additional defects in the CVD graphene. Graphene transfers to Nafion performed below the optimum temperature (Topt ~ 115 °C) remain patchy with ruptures, while transfers above Topt showed defect features, and transfers near Topt showed minimal ruptures and defect features. We demonstrate Nafion|graphene|Nafion sandwich membranes with the optimal temperature conditions that allow for 50% reduction in hydrogen crossover (0.17 mA cm−2) in comparison to Nafion control membranes (0.33 mA cm−2) while maintaining comparable proton area specific resistance < 0.25 Ω cm2 (area conductance 4–5 S cm−2), that are adequate to enable practical PEM applications such as fuel cells, redox flow batteries, and beyond.

The bottom-up synthesis is a powerful approach for fabricating graphene-based nanomaterials (GNMs) with atomic precision. This approach relies on well-defined chemical reactions between specially designed molecular precursors that dictate the structure of the resulting GNMs. Therefore, preparing a new GNM generally requires the design and synthesis of a new molecular precursor, which is often very challenging and laborious. In this work, we demonstrate a family of molecular precursors based on 7,10-dibromo-triphenylenes that can selectively produce...
different varieties of atomically precise GNMs, porous nanographenes (pNGs), and porous graphene nanoribbons (pGNRs), using different synthetic environments. More specifically, we show that upon Yamamoto polymerization of these molecules in a solution environment, the free rotations of the triphenylene units around the C-C bonds result in forming cyclotrimeres at high yields. In contrast, in the case of on-surface polymerization of the same molecules on Au(111), these rotations are impeded, and the coupling proceeds toward forming long polymer chains. These chains can then be converted into pGNRs by annealing. Correspondingly, the solution-synthesized cyclotrimeres can also be deposited onto Au(111) and converted into pNGs via a thermal treatment. Thus, both processes start with the same molecular precursor and end with an atomically precise GNM on Au(111), but the product type, pNG or pGNR, depends on the specific coupling approach. We also produced extended nanoporous graphenes (NPGs) through the lateral inter-ribbon cyclodehydrogenation of highly aligned pGNRs at high coverage. All synthesized products were atomically precise, including the NPGs, which were shown to be deterministic in terms of the nanopore shape and size and contain only [18]annulene nanoropes if occasional defects are not considered. We demonstrate the generality of this approach by synthesizing two varieties of 7,10-dibromo-triphenylenes that produced six GNMs products with different dimensionalities. By constructing different GNMs from the same building blocks, it is possible to tune the band gap in a wide range. The basic 7,10-dibromo-triphenylene is amenable to structural modifications, potentially providing access to many new GNMs. The fact that the synthesized GNMs possess atomically precise nanopores suggests using these materials for fundamental studies of the nanopore effect on the electrical and mechanical properties of graphene and their potential use for electronic, optoelectronic, and molecular sieving applications.

This work was supported by the Office of Naval Research (N00014-19-1-2596)
dynamics initiated by a secondary pump pulse preceding the HHG driving field. This time-resolved HHGS (tr-HHGS) approach has the capability to probe phase transition and phonon dynamics with unprecedented spatial and temporal resolution.

In our work, we applied HHGS and tr-HHGS for the characterization of two semiconductor materials, germanium, and tellurium. We performed HHGS measurements in bulk germanium (001) driven by a linearly polarized MIR field centered at 3.2 μm. By focusing an intense linearly polarized MIR field, and collecting the harmonics generated in reflection, we observed harmonics up to the 15th order and we fully characterized the harmonic yield as a function of the crystal axis direction. All the harmonics reflect the cubic symmetry of the material but show very different behavior as a function of the driving field intensity and polarization direction. This is a signature of the non-linear dynamics taking place during the process. Moreover, we fully characterized the polarization state of the emitted harmonics up to the 7th order as a function of the crystal axis direction, showing that it can significantly diverge from the driving field polarization and demonstrating the emission of light at specific wavelengths having strong ellipticity. This could be attributed to the interference of different harmonic emission pathways, which can allow us to extract information about the complex sub-cycle ultrafast electron dynamics in germanium when it undergoes strong field interactions.

Furthermore, we used tr-HHGS for probing phase transitions in tellurium, an elemental semiconductor with chiral crystal structure. Preliminary results show how the extreme sensitivity of HHGS can be used for tracking the lattice and electron dynamics induced by the pump.

References:


11:15 AM *QTO1.01.03
New Routes for Label-Free Super-Resolution Microscopy and Attosecond Science via Transient High-Harmonic Generation Peter Kraus1,2, Advanced Research Center for Nanolithography, Netherlands; 2Vrije Universiteit Amsterdam, Netherlands

While the upconversion of infrared driving lasers into soft-X-ray pulses by high-harmonic generation (HHG) in gases has become an established technique for attosecond science and nanoscale imaging [1-3], HHG in solids is less explored. Gas-phase HHG is highly sensitive and thus controllable with regards to the microscopic generation mechanism, and the macroscopic buildup of the harmonics is governed by the properties of the material in contact with the laser field via phase matching [4,5]. Parallels between solid and gas-phase HHG suggest that solid-state HHG may be controlled in similar manners, which would enable a generally applicable all-optical light switch with wide application potential.

In this talk I will introduce femtosecond resolved solid-state HHG and highlight the applications of solid-state HHG for metrology, spectroscopy and imaging with recent examples from our group. On the nanoscale, we controlled HHG via engineering the surface topography of solids, which in turn demonstrates how solid HHG can be used for metrology on surfaces and tailored as a light source [6]. On the femtosecond time scale, we used the sensitivity of HHG to electronic band structure to follow ultrafast phase transitions in strongly correlated materials [7], and phasor dynamics in perovskites [8]. While the first set of measurements mentioned above showed nanoscale sensitivity, the second set of experiments demonstrated that photoexcitation can be used to control light emission via solid-state HHG.

Combining both efforts, I will outline and show first results how ultrafast control of solid HHG enables harmonic deactivation microscopy (HADEM) - a label-free super-resolution microscopy below the diffraction limit of light [9].

Thinking ahead, the development of these techniques may enable resolution on the nanometer and femtometer- to attosecond scale fitted into a regular microscope setting, with application potential ranging from strongly correlated materials to semiconductor metrology, photosynthetic processes, and medical imaging.

References:

9. K. Murzyn et al., P.M. Kraus, in preparation.

11:45 AM QT01.01.04
Advances in Hands-Off Femtosecond Parametric Amplifiers for Solid-State Materials Investigation Stefan Piontek, Valdas Maslinskas, Jonas Berzins and Marco Arrigoni; Light Conversion, Lithuania

Time-resolved and static nonlinear optics (NLO) experiments at surface and bulk of advanced solid-state materials require agile femtosecond and picosecond tunable sources with high peak power and excellent stability. Repetition rate agility, ease of use and a compact footprint enhance experimental productivity and eliminate the need for an "expert" laser user. Typical experimental set-ups for study of interfaces and bulk material properties on meso- and nanoscale include two-dimensional infrared (2D-IR)1, sum-frequency generation (SFG) 2, 3, as well as transient absorption (TA4 spectroscopy). Until recently, these experiments required titanium-sapphire amplifiers with repetition rates of 1-5 kHz, or mode-locked lasers at 80 MHz with limited power and excellent stability. Repetition rate agility, ease of use and a compact footprint enhance experimental productivity and eliminate the need for an “expert” laser user. Typical experimental set-ups for study of interfaces and bulk material properties on meso- and nanoscale include two-dimensional infrared (2D-IR)1, sum-frequency generation (SFG) 2, 3, as well as transient absorption (TA4 spectroscopy). Until recently, these experiments required titanium-sapphire amplifiers with repetition rates of 1-5 kHz, or mode-locked lasers at 80 MHz with limited energy and tuning ranges.

With technological advancements provided by flexible Yb-based regenerative amplifiers, experiments can now be realized at 100 kHz-1 MHz repetition rates with significant improvements including sealed, hands-off configurations, enhanced efficiency and short pulse generation.

References:

SESSION QT01.02: Ultrafast Dynamics in 2D Materials I
Session Chairs: Veronica Policht and Ursula Wurstbauer
Tuesday Afternoon, April 23, 2024
Room 420, Level 4, Summit

1:30 PM *QT01.02.01 Manipulation and Non-Linear Propagation of Excitonic Complexes in 2D Materials
Alexey Chernikov; Technische Universität Dresden, Germany

Two-dimensional transition metal dichalcogenides offer an excellent platform to study non-linear dynamics of tightly-bound exciton quasiparticles. The properties of the excitons and their optical response change drastically in the presence of free charges, leading to emergence of many-body states described as trions or Fermi polaron. The physics of such Bose-Fermi quasiparticle mixtures have attracted a lot of interest in the scientific community and motivated the development of methods to control them on ultrafast time-scales. In addition, excitonic complexes are known to be mobile both in monolayers and heterostructures, with the transport of optical excitations playing a central role from both fundamental and technological perspectives.

The first part of the talk will be focused on the use of intense THz pulses to transiently modify light-emission of exciton-electron ensembles in a monolayer semiconductor. We demonstrate a near complete, THz-induced trion-to-exciton conversion by monitoring time resolved photoluminescence after optical excitation. It offers new pathways to manipulate exciton-electron mixtures in monolayer semiconductors, triggering a non-linear optical response by low-energy photons on picosecond timescales. In the second part, I will discuss linear and non-linear propagation of interlayer excitons in atomically reconstructed heterobilayers for an extended density range up to the Mott transition. Key takehome message in absence of disorder- and Moiré-induced localization, role of the exciton-exciton interactions, and effectively negative diffusivity in the regime of dissociated excitons and dense electron-hole plasma.

2:00 PM QT01.02.02 Disentangling Many-Body Effects in The Coherent Optical Response of a 2D Semiconductor
Chiara Trovatello1,2, Florian Katsch3, Qiuyang Li1,4, Xiaoyang Zhu1, Andreas Knorr3, Giulio Nicola Felice Cerullo2 and Stefano Dal Conte2; 1Columbia University, United States; 2Politecnico di Milano, Italy; 3Technische Universität Berlin, Germany; 4University of Michigan–Ann Arbor, United States

Monolayer transition metal dichalcogenides (1L-TMDs) have received increasing attention because of their enhanced light-matter interaction, strongly bound excitons, exciton Rydberg states and many-body effects[1]. Transient absorption spectroscopy has been extensively used to study exciton dynamics on an ultrafast timescale. While it has been shown that on a test- to hundred-ps timescale, the exciton decay dynamics is dominated by thermal effects[2], the physical origin of exciton dynamics on a ps and sub-ps timescale is still under debate. In this temporal window, many-body effects lead to a renormalization of the bands, inducing a transient energy shift of the excitonic resonance. Simultaneously, the increase of the electronic temperature after photo-excitation, due to multiple electronic scattering events, broadens the excitonic linewidth.

Broadening and shift of the excitonic peak overlap in time with an abrupt absorption reduction due to phase-space filling effect[3]. All these processes are difficult to disentangle, and their dynamical interplay determines the complex shape of the transient absorption spectra of TMDs across the bandgap at early pump-probe delays. Transient exciton energy shifts have been roughly estimated from pump-probe measurements with contrasting results, e.g., blue vs red shift, and values from meV to tens of meV. In this work, we measure the transient optical response of 1L-WS2 on SiO2 across the A and B excitonic resonances. The sample is photoexcited on- and off-resonance with the A exciton, and at variable pump fluences below the exciton-Mott transition. In order to capture the origin of the different transient signal shapes for both excitations, we disentangle absorption reduction, energy shift and broadening of the excitonic peak from the transient optical response, using Kramers-Kronig constrained variational analysis. From the measured transient reflectivity (AR/R) of 1L-WS2 we retrieve the absorption spectrum as a function of pump-probe delay. When the sample is photo-excited the pump induces a dramatic change of the A exciton, resulting from several concomitant effects: a quenching of the exciton oscillator strength, a blue energy shift and an asymmetric lineshape broadening. All the spectra are well reproduced by a fitting function made by the sum of two Lorentz oscillators on top of a polynomial background. The transient energy shift persists over a timescale much longer than the temporal overlap of pump and probe pulses, excluding the possibility that it originates from optical Stark effect.

Microscopic calculations based on excitonic Heisenberg equations of motion quantitatively reproduce the non-linear absorption spectra of the material. All the lorentzian parameters show a linear dependence with rising excitation power for both the pump photon energies, and many-body effects are strongly enhanced for resonant excitation, resulting in a transient blue shift of the A exciton. The shift progressively decreases as the pump is detuned from the pump and turns into a small red shift when the energy of the pump is close to the B excitonic resonance. The energy shift originates from Coulomb-induced bandgap renormalization while the asymmetric broadening is related to excitation induced dephasing mechanism[4]. In conclusion, we provide a complete picture of the transient optical response of 1L-WS2 which can finally explain the strong differences observed in the pump-probe spectra following on- and off-resonant excitation[4]. Our combined experimental and theoretical studies give important insights into the complex interplay between many-body correlations and excitonic interactions determining the non-equilibrium response of 1L-TMDs.

References:

2:15 PM QT01.02.03 Ultrafast Charge Transfer Dynamics in Van der Waals Heterostructures
Ermin Malic; Philips University Marburg, Germany

Van der Waals heterostructures built by vertically stacked transition metal dichalcogenides (TMDs) exhibit a rich exciton energy landscape including spatially separated interlayer states, momentum-dark intervalley states, and hybrid exciton states. Recent experiments have demonstrated an ultrafast charge transfer in TMD heterostructures. However, the nature of the charge transfer process has remained elusive. Based on a microscopic and material-realistic exciton theory combined with time-resolved ARPES measurements, we reveal that phonon-mediated scattering via strongly hybridized dark intervalley excitons governs the charge transfer process [1,2]. We track the time-, momentum-, and energy-resolved relaxation dynamics of optically excited excitons and determine the temperature- and stacking-dependent charge transfer times for different TMD bilayers.

Furthermore, we demonstrate how the Coulomb interaction between the correlated electron- and hole-components of intra- and interlayer excitons facilitates the study of the ultrafast hole transfer mechanism in a twisted WS2/MoS2 heterostructure. Intriguingly, we find an increase of the photoelectron energy in the ARPES spectrum upon the hole transfer process across the interface. This is surprising at first, because the electron remains rigid in the conduction band during the hole transfer process, and also because any relaxation mechanism is typically expected to cause an overall decrease of the measured electronic energies. However, we do not observe a free photoelectron, but the blue-shift is a direct consequence of the correlated nature of the Coulomb-bound electron-hole-pair.

Compared to the electron transfer occurring on a timescale of sub-100fs, we find both in experiment and theory that the hole transfer is considerably slower and occurs rather on a timescale of a few picoseconds. This can be traced back to different relaxation pathways: In the case of the electron transfer, optically excited intralayer excitons are subject to a relaxation cascade via layer-hybridized KX excitons to the lowest interlayer exciton states. In contrast, the hole transfer occurs via layer-hybridized FX excitons. Since the A valleys are three-fold degenerate, while there is only one T valley, the density of states for the electron transfer pathway is more efficient. Furthermore, the exciton energy difference between the initial optically excited intralayer exciton and the final interlayer exciton is roughly 200 meV larger in the case of the hole transfer, further contributing to a slower transfer dynamics of holes.

The provided insights present an important step forward in microscopic understanding of the technologically important charge transfer process in van der Waals heterostructures.

References:
Two dimensional (2D) transition metal dichalcogenides (TMDs) have received increasing attention because of their optical and electronic properties, including enhanced light-matter interaction, strongly bound excitons, exciton Rydberg states, multiparticle excitonic complexes, and valley-selective circular dichroism [1]. Some of these properties are exploited in the realization of prototypical optoelectronic devices with improved performances and decreased size. Multiple layers of TMDs can also be stacked to form vertical heterostructures (HS) with tailored electronic and optical properties. Most of TMD-based heterobilayers have type II band alignment leading to fast charge separation and formation of interlayer excitons (ILX) with low-power few-cycle light pulses available today. We also provide a novel approach to investigate the properties of these materials.

Excitons in two-dimensional transition metal dichalcogenides emerged as a unique nanoscale platform offering strong light-matter coupling, spin-valley locking and exceptional tunability. Moreover, their properties and optical response change drastically in the presence of free charges, leading to the formation of new quasiparticles known as trions or Fermi polarons. The physics of such Bose-Fermi quasiparticle mixtures have attracted considerable interest in the scientific community. However, there are limitations to how fast the optical response of these states can be manipulated, restricting the majority of applications to a static regime.

Here, we show how to overcome this challenge by using low-energy photons in the THz frequency range. We demonstrate the conversion of trions into excitons in two-dimensional materials on ultrafast timescales of a few picoseconds by applying short THz pulses after the optical excitation. Monitoring the time-resolved photoluminescence dynamics, a strong quenching of the trion population induced by the THz radiation is observed, accompanied by a simultaneous decrease of the exciton emission. The process is highly sensitive to the energy of the THz photons, that has to match the trion binding energy of the material. Furthermore, the observed switching is found to be highly reproducible when both the THz power and the time delay between optical and THz pulses are tuned. Our results provide a promising experimental tool for fundamental research of light-emitting excitation mixtures and offer pathways towards technological developments of nanophotonic devices based on atomically thin materials.

4:35 PM *QT01.02.06
Ultrafast Processes in Atomically Thin Semiconductors Stefano Dal Conte; Politecnico di Milano, Italy

In doped semiconductors, optically excited electron-hole pairs (i.e. excitons) can be treated as an impurity coupling to a Fermi sea. Atomically thin semiconductors provide a rich playground to explore the Fermi polaron problems where the electrons and excitons further acquire a valley index. The attractive interaction between the exciton and Fermi sea leads to an energetically favorable state --- the attractive polaron --- as well as a higher energy repulsive polaron, a metastable state that eventually decays into attractive polarons. Here, we study the emergence and evolution of attractive polarons and repulsive polarons in MoSe₂ and WSe₂ monolayers as the electron doping density increases. Using two-dimensional coherent electronic spectroscopy (2DCES), we follow the changes in resonant energy, oscillator strength, and quantum decoherence of the AP and RP branches. Because of their different band structures, polarons in MoSe₂ and WSe₂ monolayers exhibit distinct quantum dynamics and coupling mediated by valley index. Because of the large oscillator strength associated with quasi-particles, their intrinsic dephasing dynamics occur on sub-picosecond time scales. On the other hand, long-lived population and valley dynamics have been reported in previous experiments. We attribute such dynamics from a few hundred picoseconds to a few nanoseconds to dark-to-bright exciton conversion processes.

We gratefully acknowledge funding by the Department of Energy, Office of Basic Energy Sciences under grant DE-SC0019398 and the Welch Foundation grant F-1662 for sample preparation. Collaborations are enabled by National Science Foundation via MRSEC grants DMR-1720595 and DMR-2308817.
QT01.04.01
Terahertz Parametric Amplification of a Coherent Magnon Mode
Zhuquan Zhang and Keith A. Nelson; Massachusetts Institute of Technology, United States

Parametric amplification is a ubiquitous process in nonlinear systems where a specific parameter can be varied to amplify a coupled degree of freedom. In condensed matter systems, parametric amplification of collective excitations allows one to study non-equilibrium order-parameter physics and potentially control material properties. In this study, we use a pair of intense terahertz (THz) pulses to coherently excite two distinct coherent magnon modes in an antiferromagnet and find that the lower frequency magnon mode is amplified by driving the higher frequency mode. The nonlinear excitation pathway of this parametric downconversion process is confirmed by two-dimensional THz spectroscopy measurements. Our work provides crucial insights into nonlinear magnonics in antiferromagnets, extending the frontiers of spintronics and magnonicics into the ultrafast nonlinear regime.
Spin-phonon coupling enables the mutual manipulation of phonon and spin degrees of freedom in solids. In this study, we reveal the inherent nonlinearity within this coupling. Using a paramagnet as an illustration, we demonstrate the nonlinearity by unveiling spontaneous symmetry breaking under a periodic drive. The drive originates from linearly polarized light, respecting a mirror reflection symmetry of the system. However, this symmetry is spontaneously broken in the steady state, manifested in the emergence of coherent chiral phonons accompanied by a nonzero magnetization. We establish an analytical self-consistent equation to find the parameter regime where spontaneous symmetry breaking occurs. Furthermore, we estimate realistic parameters and discuss potential materials that could exhibit this behavior. Our findings shed light on the exploration of nonlinear phenomena in magnetic materials and present possibilities for on-demand control of magnetization.

10:00 AM BREAK

10:30 AM QT01.04.05

Extreme Nonlinear Opto-Magnonic Effects in a Layered Magnetic Semiconductor Geoff Diederen1, John W. Cenker1, Jordan Fonseca1, Sinabu Pumelo1, Youn Jue Bae2, Daniel Chica1, Xiaoyang Zhu3, Xavier Roy3, Di Xiao1,1, Yafei Ren4 and Xiaodong Xu1,1; 1University of Washington, United States; 2Cornell University, United States; 3Columbia University, United States; 4University of Delaware, United States

The nonlinear dynamics of collective excitations offer both intriguing fundamental phenomena and significant practical applications. A prime illustration is the field of nonlinear optics, where diverse nonlinear frequency mixing processes are central to advancing photonic technology. Demonstration of these frequency mixing processes in magnons holds considerable potential for practical applications in magnonics, an emerging frontier of spintronics and an important platform for developing quantum transducers and wave-based computing beyond traditional paradigms. In this talk, I will demonstrate the optical generation and detection of abundant magnonic frequency mixing processes in the antiferromagnetic semiconductor CrSBr by employing above-gap pump pulses to launch coherent magnons and optically measuring them via strong magnon-exciton coupling. The data shows a series of magnon sidebands arising from high-harmonic generation and, when breaking the system symmetry, the mixing of discrete magnon modes to produce sum and difference frequency generation (SFG & DFG). Further, we demonstrate control over the DFG in CrSBr by rotating an external magnetic field to tune its frequency over a broad range. This tuning allows us to push the DFG mode into resonance with one of the fundamental magnon modes, where we can controllably induce parametric amplification. These findings herald the opening of a new domain in nonlinear opto-magnonic coupling, offering innovative functionalities for hybrid quantum magnonics.

10:45 AM QT01.04.08

Photoexcited Electron Spin Resonance Properties of CrSBr Lovia Ofori1, Eric Walter2, Luis Martinez1, Xavier Roy3 and Srinivasa Rao Singamaneni1, 1University of Texas at El Paso, United States; 2Pacific Northwest National Laboratory, United States; 3University of Washington, United States

The recent discovery of two-dimensional (2D) magnets offers excellent opportunities for the exploration of low-dimensional magnetism and for the development of novel magnetoelectric, magnetooptic, and spintronic devices. CrSBr is an air-stable antiferromagnetic semiconductor and gained a great deal of attention in the community for its novel magneto-optical properties. In this work, we present our recent findings on the electron spin resonance (ESR) properties of quasi-2D CrSBr upon photoexcitation as a function of temperature and time across the magnetic phase transition. We noticed that ESR spectral properties (line shape, g-factor, line width, and signal intensity) are strongly modified upon photoexcitation which infers the tunability of magnetic interactions. Our work demonstrates the unique importance of employing photons in tuning the magnetic properties and interactions of 2D van der Waals magnets.
First-Principles Machine-Learning Quantum Dynamics at 0K in SrTiO3: Light-Induced Ultrafast Ferroelectric Transition

Francesco Libbi1, Lorenzo Monacelli2, Anders Johansson1 and Boris Kozinsky1; 1Harvard University, United States; 2EPFL, Switzerland

Low temperature nonequilibrium quantum dynamics in crystals is extremely challenging, and has not been possible to perform on materials of realistic complexity. In this work we develop a novel technique, the time-dependent self-consistent harmonic approximation (TDSCHA [1]), and use it to simulate the quantum dynamics in SrTiO3 at 0K. We combine TDSCHA with state-of-the-art machine learning force fields to accelerate calculations by multiple orders of magnitude compared to first principles dynamics.

We study the light-induced ferroelectric transition in SrTiO3, where nuclear quantum fluctuations play a major role in stabilizing the paraelectric phase at low temperatures. Our approach allows for an unprecedented description of the light-induced ferroelectric transition due to the absence of ad-hoc parameters, paving the way to the development of next-generation ultrafast nonvolatile memories.


Spatially Heterogeneous Structural Dynamics of NdNiO3 Thin Films

Dynamic Control of Macroscopic Phases via Thermal Quench in 1T-TaS2

Alberto De la Torre; Northeastern University, United States

In materials with competing order parameters, quenching across a phase transition can lead to the system being trapped in a long-lived metastable phase, even if it is not the global free-energy minimum. Examples of this phenomenology can be found over multiple energy and length scales - from the evolution of the known Universe to supercooled liquids [1]. 1T-TaS2, a layered dichalcogenide, is a unique platform for studying dynamic phase transitions in quantum materials [2]. Upon quenching 1T-TaS2 after excitation with an ultrafast laser pulse, a low-temperature metallic metastable phase (H-CDW) emerges [3], which is different from any of the charge density wave (CDW) phases characterizing its thermodynamic phase diagram. I will show that a new metastable insulating phase with similar scattering signatures to the H-CDW [4] can be stabilized by intermediate quenching rates [5]. I will discuss the implications of this new phase in the controversy surrounding the presence of Mott physics and the role of c-axis correlations [6] in the equilibrium ground state of 1T-TaS2.


Probing Exciton Dynamics and Dispersion in C60 Using TR-ARPES

Rysa J. Greenwood1,2, Alexandra Tully1,2 and Sarah Burke1,2; 1Quantum Matter Institute, Canada; 2The University of British Columbia, Canada

In organic semiconductors, photoexcitation generates strongly bound excitons which recombine quickly (generally 10’s – 100’s of femtoseconds). To achieve efficient charge separation in these materials it is necessary to drive the dissociation of the exciton prior to recombination. This is one of the limiting factors for organic photovoltaic (OPV) devices today. The mechanisms that result in efficient charge separation in these materials are still not well understood. Therefore, to better advise device design it is necessary to gain a deeper understanding of both the dynamics and delocalization of excitonic states that occur post-photoexcitation with femtosecond resolution.

While the ultrafast response of organic semiconductors has been studied using all-optical techniques for a number of years [1], a lack of momentum resolution has limited understanding of their delocalization and symmetry. Time-resolved, angle-resolved photoemission spectroscopy (TR-ARPES) is a powerful technique that allows a user to visualize the energy-momentum landscape of a material and monitor how the material responds to photoexcitation with femtosecond resolution. Recent developments in TR-ARPES (or similar techniques) are enabling investigation of organic semiconductors because of its capability to directly map the momentum dependent dispersion of the excitonic states with high temporal resolution [2-4].

Here, I show the capability to probe the fate of excitonic states in C60, a prototypical OPV material, using TR-ARPES pumped with 3.1eV light. We have been able to track the dynamics of the excitonic states which decay into each other with lifetimes ranging from hundreds of femtoseconds to tens of picoseconds. Constant energy contours show momentum-space structure of each state across the first Brillouin zone which disperse energy. With this improved angular resolution, we aim to access the extent of delocalization of the excitons in the C60 lattice.


Spatially Heterogeneous Structural Dynamics of NdNiO3 Thin Films

Jiogul Mehna1, Scott Smith1, Nanna Zhou Hagstrom1, Nushrat Naushin1, Spencer Jeppson1, Yu-Hsing Cheng1, Pooja Rao1, Marc Zajać2, Burak Guzeltekin2, Donald Walko2, Tao Zhou2, Haidan Wen2, Martin V. Holt2 and Roopali Kukreja2; 1University of California, Davis, United States; 2Argonne National Laboratory, United States

Rare Earth oxides display insulator-metal transition which is accompanied by a magnetic transition, charge ordering, and a crystal structure change. Laser-excitation drives the transition at ultrafast timescales providing an avenue to understand the role of coupled transitions in causing the transition. We utilized time-resolved x-ray diffraction to study the transition dynamics of epitaxial NNO thin film by observing the photointerduced changes in the (002) Bragg peak. The out of plane lattice parameter contracts for low fluences and expands for high fluences after laser excitation. A thermal model explains experimental trends revealing the potential for controlling structural dynamics via heteropolar strain. Similar recovery timescales of structural and magnetism dynamics indicate a strong magneto-structural coupling is prevalent in the ultrafast recovery process. The change in integrated intensity and FWHM of the (002) peak indicate photointerduced domain dynamics which corroborates an ultrafast conductivity study proposing recovery via nucleation and growth in NNO. We present direct evidence of phase separation using time-resolved nanodiffraction. Spatitemporally resolved characterization clearly shows the spatial heterogeneity of the structural dynamics in nickelates.
The fundamental physics of solids, including two-dimensional (2D) materials, is inherently linked to their electronic band structure. The investigation of the electronic band structure is therefore of paramount significance for understanding, tailoring and discovering new states of matter. In the case of 2D materials, such as graphene and single layer transition metal dichalcogenides, control of the electronic structure can be achieved by altering their surroundings, as the electronic structure of 2D materials is highly sensitive to the surrounding environment. However, robust methods for the determination of the electronic structure are required to ascertain the effects of those alterations. In this talk, I will present time- and angle-resolved photoemission spectroscopy (TR-ARPES) as a technique for the electronic structure studies on the ultrafast, femtosecond scale [1], and as means to achieve control over 2D materials by light [2].

Furthermore, I will introduce an innovative preparation method for 2D materials, kinetic in situ single-layer (KISS) method [3]. Using KISS method, exfoliation of 2D materials can be performed directly in ultra-high vacuum, and large flakes of excellent crystallinity and purity can be obtained. Multiple semiconducting and metallic transition metal dichalcogenides were exfoliated onto Au, Ag and Ge substrates, showing the versatility of the technique, and characterised by ARPES. Importantly, the proposed method is straightforward, simple, and does not require any specialised equipment. This technique is ideally suited for the electronic structure research of air-sensitive 2D materials since the sample preparation process happens entirely in ultra-high vacuum.

References:

5:00 PM QT01.06.01
A Molecular Dynamics of Photo-Excited Ligand Exchange Dynamics in Tungsten-Complexes
Kamrun N. Keya1, Yulun Han2, Wenjie Xia1, Bakhtiyor Rasulev2, Svetlana V. Kilina2, Wenfang Sun3 and Dmitri Kilin4;
1Iowa State University, United States; 2North Dakota State University, United States; 3The University of Alabama, United States

Transition-metal complexes (TMCs) play a pivotal role in areas such as optoelectronics, solar energy conversion, and biomedical applications. In this study, we delve deep into the dynamics of ligand exchange reactions in six distinct W(CO)5(bpy) complexes using time-dependent excited-state molecular dynamics (TDEMSD) based on Rabi oscillations between ground and excited states under optical irradiation. Our objective is to explore the mechanism of how the photo-induced charge transfer dynamics facilitates the mechanistic pathway in which a mix of W(CO)5 and bipyridine (bpy) transfers into a W(CO)3(bpy) complex. Preliminary findings suggest that the photoreactions are facilitated by excited states corresponding more closely to ligand-to-metal charge transfer (LMCT) character. This is photocoactivation, particularly of the LMCT type, that weakens the W-C bonds, thereby facilitating the subsequent dissociation of CO ligands. Consequently, this gives rise to the reactive W(CO)5 radical, which then establishes a coordination bond with the nitrogen of the bpy ligand. At the next stage, second CO ligand desorbs allowing for formation of two stable coordination bonds between tungsten and bpy. Several approaches have been committed to explore the possibility of the subsequent formation of power source. Their performance rivals that of conventional QD-PDs employing thick Pb-chalcogenide QD layers and typical self-powered PDs from previous researches. Furthermore, PDs fabricated on flexible substrates exhibit outstanding mechanical flexibility and device performance, surpassing that of flexible PDs employing alternative semiconductor materials. This realizes a skin-attachable PPG sensors capable of real-time vital sign monitoring.

References:

5:00 PM QT01.06.02
Wearable Health Monitoring with Ultrathin Self-Powered Heavy-Metal-Free Cu-In-Se Quantum Dot-Photodetectors
Jae Hong Jang1, Shi Li2, Jiwoong Yang2 and Moon Kee Choi1;
1Ulsan National Institute of Science and Technology, Korea (the Republic of); 2Daegu Gyeongbuk Institute of Science and Technology, Korea (the Republic of)

Photodetectors (PDs), that transform light signals into electronic signals, are essential components in wearable electronics, finding wide-ranging applications in biological imaging, computer and communication, and health monitoring. In particular, wearable health monitoring devices utilizing photophotoluminescence spectroscopy (PPG) technology, which employs a light source and PDs to measure blood circulation variations, offer significant potential for non-invasive, cost-effective, and continuous real-time monitoring of vital signs and cardiac function. To enable effective real-time vital sign monitoring, PDs must exhibit high specific detectivity (D*), rapid response time, and high mechanical deformability. Consequently, the development of mechanically deformable PDs with superior device performance and response flexible has been a paramount objective. While prior research advanced flexible and stretchable PDs, challenges endure, including limited deformability with thick inorganic films and reduced performance in organic PDs. Furthermore, most photodetectors rely on external power sources to generate photocurrent, restricting the exploration of point-of-care portable systems capable of response independent, wireless, and small-scale operation.

Collodial quantum dots (QDs) are highlighted for PDs, boasting size-tunable electrical and optical properties, high photo-absorption coefficients, narrow emission and absorption bandwidth, and robust photo- and air-stability. Nevertheless, the practical application of QD-PDs in wearable electronics faces challenges. Existing QD-PDs exhibit limited mechanical deformability due to their relatively thick light absorption layers (typically several hundreds of nanometers). Furthermore, the conventional use of toxic heavy-metal-containing QDs, including lead, mercury, and cadmium chalcogenide QDs, raises concerns about impact on human health.

Recently, heavy-metal-free Cu-In-Se (CISE) QDs have been highlighted as a promising material for eco-friendly optoelectronic devices. CISe QDs offer advantageous characteristics, including a direct-bandgap structure, high absorption coefficient, broad absorption range spanning from ultra-velo to near-infrared, stable phase structure, cost-effectiveness, and nontoxicity. However, a dearth of research exists regarding the selection of optimal charge transport materials, specifically for the electron transport layer (ETL) and hole transport layer (HTL) materials, tailored to CISe QD-PDs. The electron mobility of typical ETLs is generally three orders of magnitude higher than that of general HTLs, causing the charge imbalance and recombination of generated electrons and holes, leading to poor device performance. Therefore, the development of high-quality HTLs is essential to achieve high-performance CISe QD-PDs.

In this study, we present ultrathin self-powered CISe QD-PDs for the wearable PPG-based health monitoring system. We constructed PDs with CISe QDs capped with iodide ions as ultrathin light absorption layers (~40 nm), p-type colloidal MoS2 nanosheets blended with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) as HTLs, and n-type ZnO nanoparticles as ETLs.

Fabricated ultrathin PDs (~120 nm except electrodes) feature high D* of 2.10×10^11 Jones, linear dynamic range of 102 dB, and spectral sensitive region from 250 to 1,050 nm at 0 V bias. These PDs utilize built-in potential created through the photocurrent effect, facilitating the efficient separation and transfer of generated electron–hole pairs without requiring an external power source. Their performance rivals that of conventional QD-PDs employing thick Pb-chalcogenide QD layers and typical self-powered PDs from previous researches. Furthermore, PDs fabricated on flexible substrates exhibit outstanding mechanical flexibility and device performance, surpassing that of flexible PDs employing alternative semiconductor materials. This realize skin-attachable PPG sensors capable of real-time vital sign monitoring.
Ultrafast Exciton Dynamics in 2D Van der Waals Nanostructures: Probing The Hot Exciton Relaxation of Size-Controlled & Well-Dispersed Graphene Nanoflakes

**QT01.08.02**

10:00 AM *QT01.08.01* 
Controlling The Ultrafast Optical Properties of Graphene with Ionic Liquid Gating

Eva A. A. Pongia; CNR-IFN, Italy

Single-layer graphene is endowed with broadband optical absorption, largely dependent on the Fermi energy. Ionic liquid gating allows to tune the Fermi energy to hundreds of eV and control its optical response in the near-infrared and THz ranges. Transient absorption measurements in the near-infrared reveal that also the out-of-equilibrium optical properties can be largely tuned using ionic gating. By varying the Fermi energy via electrostatic gating, the sign of the transient optical response of graphene is switched while the recovery dynamics significantly slows down due to the quenching of the relaxation of the hot electrons through the emission of optical phonons. The electrostatic control of the recovery dynamics and of the sign of differential transmission, opens intriguing perspectives for applications of graphene as a tunable saturable absorber for generation of tunable near-infrared pulses or alternatively as optical limiter or logic gates. Moreover, ionic gating is exploited to conceive compact optoelectronic devices acting in the THz range as amplitude modulators, saturable absorber mirrors and frequency tuners. The large control of the THz optical response is used to compensate the cavity dispersion of a multimode THz quantum cascade laser and induced stable operation as frequency comb for metrological applications.

References

[1] S. Michela dell'Acqua et al., physica status solidi (b) 259, 2100566 (2022)

## 9:30 AM BREAK

SESSION QT01.08: Ultrafast Dynamics in 2D Materials II
Session Chairs: Chiara Trovatello and Ursula Wurstbauer
Thursday Morning, April 25, 2024
Room 420, Level 4, Summit

10:00 AM *QT01.08.02* 
Ultrafast Exciton Dynamics in 2D Van der Waals Nanostructures: Probing The Hot Exciton Relaxation of Size-Controlled & Well-Dispersed Graphene Nanoflakes

Elisa Cassette1, Sébastien Quistrebert1, Daniel Medina-Lopez2, Stéphane Campidelli2 and Jean-Sébastien Lauret3; 1LuMFin - Université Paris-Saclay, ENS Paris-Saclay, CNRS, CentraleSupelec, France; 2NIMBE/LICSEN - Université Paris-Saclay, CEA, CNRS, France

Graphene nanostuctures, such as graphene quantum dots (G-QDs), graphene nanoribbons (G-NRs) and carbon nanotubes (C-NTs), combine the unique mechanical and electronic transport properties of sp²-hybridized carbon materials and the optical properties of direct semiconductors provided by the optical gap resulting from the reduction of dimensionality. Among them, the recent developments within the well-known synthesis of G-QDs though bottom-up approach [1] have led to exceptionally well-controlled nanostuctures in terms of size, shape and dispersion [2]. The resulting graphene nanoflakes provide tunable emission in the red range, with fluorescence quantum yield close to one. Furthermore, these nanostructures have revealed to be promising stable emitters of single photons, as shown in our laboratory [2-5].

Here we use transient absorption of 30 fs temporal resolution with polarization-controlled configuration to probe the hot exciton relaxation (internal conversion, Sn → Tn), here the suppressed aggregation in the position of the steady-state photoluminescence peaks), the dynamics of relaxation were unveiled. The resulting relaxation times range from 100 fs to 175 fs.

These results allowed to discuss the mechanism of relaxation, with the effect of the length of the graphene nanoflakes and of the fluence excitation [Quistrebert et al., in preparation].

References


10:45 AM *QT01.08.03* 
Hot Carrier Cooling and Trapping in Atomically Thin WS2 Probed by Three-Pulse Femtosecond Spectroscopy

Tong Wang1, Tom Hopper1,2 and Artem Bakulin1; 1Imperial College London, United Kingdom; 2Stanford University, United States

Transition metal dichalcogenides (TMDs) have shown outstanding semiconducting properties which make them promising materials for next-generation optoelectronic and electronic devices. These properties are imparted by fundamental carrier-carrier and carrier-phonon interactions that are foundational to hot carrier cooling. Recent transient absorption studies have reported
ultrafast timescales for carrier cooling in TMDs that can be slowed at high excitation densities via a hot-phonon bottleneck (HPB), and discussed these findings in the light of optoelectronic applications. However, quantitative descriptions of the HPB in TMDs, including details of the electron-lattice coupling, and how cooling is affected by the redistribution of energy between carriers, are still lacking. Here, we use femtosecond pump-push-probe spectroscopy as a single approach to systematically characterize the scattering of hot carriers with optical phonons, cold carriers, and defects in a benchmark TMD monolayer of polycrystalline WS₂. By controlling the interband pump and intraband push excitations, we observe, in real-time (i) an extremely rapid “intrinsic” cooling rate of ≈18 ± 2.7 eV/ps, which can be slowed with increasing hot carrier density, (ii) the depreciation of this HPB at elevated cold carrier densities, exposing a previously undisclosed role of the carrier-carrier interactions in mediating cooling, and (iii) the interception of high energy hot carriers on the sub-picosecond timescale by lattice defects, which may account for the lower photoluminescence yield of TMDs under above band-gap excitation conditions.

11:00 AM *QT01.08.04
Revealing Ultrafast Phonon-Mediated Inter-Valley Scattering by Simulating Transient Absorption and High Harmonic Spectroscopies Aaron Kelly Max Planck Institute, Germany
Processes involving ultrafast laser driven electron-phonon dynamics play a fundamental role in the response of quantum systems in a growing number of situations of interest, as evidenced by phenomena such as strongly driven phase transitions and light driven engineering of material properties. In this presentation we will discuss how these processes can be captured in real-time from a computational perspective, focusing on simulating the transient absorption spectra and high harmonic generation signals associated with processes such as valley selective excitation under strong driving, and phonon-mediated intra-band charge carrier relaxation. We will show that the multi-trajectory Ehrenfest dynamics approach, implemented in combination with real-time time-dependent density functional theory and tight-binding models, offers a simple and efficient method to study ultrafast electron-phonon coupled phenomena in solids under diverse pump-probe regimes which can be easily incorporated into the majority of real-time ab-initio software packages.

11:30 AM *QT01.08.05
Quantum Floquet Engineering with an Exactly Solvable Tight-Binding Chain in a Cavity Dante Kennes RWTH Aachen University, Germany
Recent experimental advances enable the manipulation of quantum matter by exploiting the quantum nature of light. However, paradigmatic exactly solvable models, such as the Dicke, Rabi or Jaynes-Cummings models for quantum-optical systems, are scarce in the corresponding solid-state, quantum materials context. Focusing on the long-wavelength limit for the light, here, we provide such an exactly solvable model given by a tight-binding chain coupled to a single cavity mode via a quantized version of the Peierls substitution. We show that perturbative expansions in the light-matter coupling have to be taken with care and can easily lead to a false superradiant phase. Furthermore, we provide an analytical expression for the groundstate in the thermodynamic limit, in which the cavity photons are squeezed by the light-matter coupling. In addition, we derive analytical expressions for the electronic single-particle spectral function and optical conductivity. We unveil quantum Floquet engineering signatures in these dynamical response functions, such as analogs to dynamical localization and replica side bands, complementing paradigmatic classical Floquet engineering results. Strikingly, the Drude weight in the optical conductivity of the electrons is partially suppressed by the presence of a single cavity mode through an induced electron-electron interaction.

SESSION QT01.09: Ultrafast Dynamics in 2D Heterostructures
Session Chair: Niccolò Macciaferri
Friday Morning, April 26, 2024
Room 420, Level 4, Summit

8:30 AM QT01.09.02
Microscopic and Spectroscopic Study on the Superfluorescence of Quasi-2D Perovskite Aaron Weldenborg1, Ryan Munter1, Francisco Freire Fernandez2, Teri W. Odom2 and Jae Yong Suh2, 1Michigan Technological University, United States; 2Northwestern University, United States
Halide perovskites have seen a surge in interest in optoelectronic devices beyond their uses in solar cells and batteries. By using buffer molecules in fabrication, it is possible to inhibit the growth of perovskites along one dimension, creating a few layers thick film called quasi-2D perovskite. With a sufficiently high excitation power at room temperature, quasi-2D perovskite exhibits the phenomenon of superfluorescence in which emitters undergo cooperative spontaneous emission. Our quasi-2D perovskite thin-films have shown pulsed emission of enhanced decay rate, an indicator of superfluorescence. Moreover, we perform scanning transmission electron microscopy on the samples to corroborate the quadratic dependence of output intensity on the number of emitters. We find that the formation of a superlattice plays a significant role in generating the superfluorescence of quasi-2D perovskite.

8:45 AM *QT01.09.03
Bidirectional Phonon Emission in Two-Dimensional Heterostructures triggered by Ultrafast Charge Transfer Archana Raja Lawrence Berkeley National Laboratory, United States
Atomically thin van der Waals crystals like graphene and transition metal dichalcogenides allow for the creation of arbitrary, atomically precise heterostructures simply by stacking disparate monolayers without the constraints of covalent bonding or epitaxy. While these are commonly described as nanoscale LEGO blocks, many intriguing phenomena have been discovered in the recent past that go beyond this simple analogy. In this talk, I will describe how we use ultrafast electron diffraction to uncover the role of layer-hybridized electronic states as a powerful route to control ultrafast energy transport across atomic junctions [1]. We measure the simultaneous heating of both WS2 and WS2 in a WS2/WS2 heterobilayer on a picosecond timescale after selective excitation of the WS2 monolayer. This observation cannot be explained purely by phonon transport across the interface. Through first-principles calculations, we identify electronic states hybridized across the heterostructure that allow phonon-assisted interlayer transfer of photoexcited electrons, which leads to bidirectional phonon emission and simultaneous heating of both the layers.


9:30 AM BREAK

SESSION QT01.10: Polaritronics in Quantum Materials
Session Chair: Niccolò Macciaferri
Friday Morning, April 26, 2024
Room 420, Level 4, Summit

10:00 AM QT01.10.01
Unveiling The Efficient Charge Transfer Cascade in Band-Tailored Two-Dimensional WS₂/ Ni Doped CsPbI₃ Heterosystem Himanshu Bhat1, Tanmay Goswami1 and Hirendra N. Ghosh2; 1Institute of Nano Science and Technology (INST), Mohali, India; 2National Institute of Science Education and Research (NISER), India
Band structure modulation in heterostructure has emerged as a highly effective strategy for fabricating advanced optoelectronic devices. In this work, we have designed a CsPbI₃-WΣ₂ (CsPbI₃-WΣ₂) heterostructure and employed transient absorption (TA) spectroscopy to gather a comprehensive understanding of charge carrier dynamics. TA study demonstrated the charge delocalization at the interface of CI and WS₂. Due to the quasi-type II integration of CI and WS₂, the charge separation in this heterosystem is not very effective, which would restrict their utilization in photovoltaic applications. Further improve the charge separation, Ni atoms were introduced as dopants into CI nanoctystals. Ultraviolet electron spectroscopy (UPS) suggested that the homovalent doping elevated the band position of CI and resulted in a type II band configuration with WS₂. TA analysis revealed the spontaneous carrier’s separation in band-modulated heterosystem due to the isolation of electrons and holes in discrete semiconductors. These spectroscopy findings were correlated with the optoelectronic performance of heterostructure-based devices. Enhanced charge separation within a doped heterosystem leads to superior optoelectronic performance compared to undoped heterosystems. Our findings showed that the band level of engineering encourages the segregation of charge carriers at the hetero-interface, which would be extremely impactful for designing heterostructure-based optoelectronic systems.

10:15 AM QT01.10.03
Light-Matter Coupling with Bound States in the Continuum in Van der Waals Metasurfaces

Luca Sorinto1, Stefan A. Maier2,3 and Andreas Tittel1; *Ludwig-Maximilians-University Munich, Germany; 1Monash University, Australia; 2Imperial College London, United Kingdom

The extraordinary properties of layered van der Waals (vdW) materials, like hexagonal boron nitride (hBN) and Transition Metal Dichalcogenides (TMDs), make them an appealing platform to investigate and engineer light-matter interactions at the nanoscale. When reduced to atomically thin monolayers, they display attractive characteristics, such as strongly bound excitons and optically addressable spin defects, while in their bulk form they exhibit significant optical anisotropy and possess high refractive index values greater than 4, surpassing common semiconductor materials. This makes vdW materials highly desirable for achieving low-loss optical resonances and for vertically stacking different materials for developing novel all-dielectric nanophotonic structures.

Here, we exploit the concept of quasi-bound states in the continuum (qBIC) to create high-quality optical resonances in dielectric metasurfaces made of hBN and TMDs. Our method is entirely monolithic, using only van der Waals materials, and achieves optical resonances with Q factors exceeding $10^7$ through a two-step fabrication process. We demonstrate spectral tuning across the entire visible spectrum in hBN qBIC metasurfaces [1], and enhance light-matter coupling with intrinsic spin defects in hBN [2]. We observe a remarkable 25-fold increase in photocurrent intensity and spectral narrowing of defect emissions, with a linewidth below 4 nm full width at half-maximum. Furthermore, our platform offers exciting possibilities for strong light-matter coupling, as seen in the recent anti-crossing behavior between qBIC resonances and intrinsic excitations in monolithic TMD WS$_2$ metasurfaces, achieving Rabi splitting values up to 116 meV under ambient conditions [3]. Our results illustrate how combining qBIC photonic metasurfaces with van der Waals materials paves the way for novel hybrid nanophotonic platforms and room temperature polaritonic devices.


10:30 AM QT01.10.04
Optical Imaging of Ultrafast Phonon-Polariton Propagation through an Excitonic Sensor

Shan-Wen Cheng1, Ding Xu1, Haowen Su1, James M. Baxter1, Luke N. Holtzman2, Kenji Watanabe3, Takashi Taniguchi1, James Hone1, Katayun Barmak2 and Milan Delor1; 1Department of Chemistry, Columbia University, United States; 2Columbia University, United States; 3National Institute for Materials Science, Japan

Hexagonal boron nitride (hBN) hosts phonon polaritons (PhPs), hybrid light-matter states that facilitate electromagnetic field confinement and exhibit long-range ballistic transport. Extracting the spatiotemporal dynamics of PhPs usually requires tour-de-force experimental methods such as ultrafast near-field infrared microscopy. Here, we leverage the remarkable environmental sensitivity of excitons in two-dimensional transition metal dichalcogenides to image PhP propagation in adjacent hBN slabs. Using ultrafast optical microscopy on monolayer WS2/hBN heterostructures, we image propagating PhPs from 3.5 K to room temperature with sub-picosecond and few-femtometer precision. Excitons in WS2 act as transducers between visible light pulses and infrared PhPs, enabling visible-light imaging of PhP transport with far-field microscopy. We also report evidence of excitons in WS2 co-propagating with hBN PhPs over several microns. Our results provide new avenues for imaging polariton excitations over a large frequency range with extreme spatiotemporal precision, and new mechanisms to realize ballistic exciton transport at room temperature.

10:45 AM QT01.10.05
Polaron Dynamics of The Photo-Induced Hidden Metallic Phase in La$_{2/3}$Ca$_{1/3}$MnO$_3$

Shiyu Fan1, Feng Jin1,2,3, Umesh Kumar2, Brandon Yalin1, Jiemin Li1, Taehun Kim1, Vivek Bhartiya1, Yanhong Gu6, Valentina Bisogni1, Sobhit Singh7, Wenbin Wu3,4,2 and Jonathan Pelliciari1; 1Brookhaven National Laboratory, United States; 2University of Science and Technology of China; 3Anhui Key Laboratory of Condensed Matter at Extreme Conditions, China; 4Hefei National Research Center for Physical Sciences at the Microscale, China; 5Rutgers, The State University of New Jersey, United States; 6The University of Tennessee, Knoxville, United States; 7University of Rochester, United States

Creating new “hidden” phases that have no analog in thermodynamic equilibrium is becoming increasingly important in condensed matter physics. The use of ultrafast laser with femtosecond pulses and variable fluence allows to trigger such quantum phase transition as appealing some of the hidden phases can be long-lived, with a lifetime of hours or weeks, and reversible with temperature sweeper or even for ultra laser pulses. However, investigating and understanding the microscopic interactions in these hidden phases are still on the early stage due to the lack of high-end spectroscopic techniques that are sensitive to all degrees of freedom, precluding the development of designing high performance devices. Here, by combining the femtosecond ultrafast laser as a switching knob with the state-of-the-art ultrahigh-resolution resonant inelastic X-Ray Scattering as a probe, we reveal the phonon and polaron dynamics, as well as the evolution of crystal-field excitations across the insulating to photoinduced hidden metallic phase transition in a strained La$_{2/3}$Ca$_{1/3}$MnO$_3$ thin film. Upon the ultrafast excitation, the Jahn-Teller distortion is suppressed due to the strain relaxation induced by the increasing tunnelling of the Mn$^4+$ electric moments. This renormalizes the energies of the polaron and Mn$^{4+}$ excitations, ultimately leading to the formation of a metastable long-lived ferromagnetic metallic phase. Our results demonstrate that the electronic properties of the mesoscopic photoinduced hidden phase evolve with laser fluence, as an evidence of the systematic softening of the polaron binding energy and Mn$^{4+}$ excitations, consistent with the trend extracted from the bulk phase comparison. However, the spectral weight of the phonon and polaron is different compared to the metallic as-grown film, proving that the photo-induced phase is unique and distinct from the bulk metallic phase. Our findings indicate the strength of electron-photon keys that play the key role to determine the conductivity of manganites.

11:00 AM QT01.10.06
First-Principles Quantum Electrodynamics Theory of Light-Matter Interactions at All Coupling Strengths

Yu Zhang and Xinying Li; Los Alamos National Laboratory, United States

This presentation introduces VT-QEDHF, a novel first-principles quantum electrodynamics method developed to understand light-matter interactions at any coupling strength. The intersection of QED with materials science has catalyzed significant advancements in manipulating materials properties. Traditional computational approaches, while effective, have been limited by their applicability to specific coupling regimes. Our work breaks away from the limitations of conventional approaches, offering a universal and efficient way to study light-matter interactions across various coupling regimes. Our findings open up new possibilities for researching and manipulating material properties via light-matter couplings.

11:15 AM QT01.10.07
A Composite Electrodynamic Mechanism to Reconcile Spatiotemporally Resolved Exciton Transport in Quantum Dot Superlattices

Rongjia Yang1,2, Trevor Roberts1, Rafaela M. Brinn1, Alexander Choi1, Ha Park1, Chang Yan1,2, Justin Ono1,4, Ke Xu1, Paul Alivisatos1,4 and Naomi S. Ginsberg1; 1University of California, Berkeley, United States; 2The Hong Kong University of Science and Technology (Guangzhou), China; 3Shanghai Jiao Tong University, China; 4The University of Chicago, United States

Quantum dot (QD) solids are promising optoelectronic materials; further advancing their device functionality depends on understanding their energy transport mechanisms. The commonly invoked near-field Förster resonance energy transfer (FRET) theory often underestimates the excitation hopping rate in QD solids, yet no consensus exists on the underlying cause [1–3]. We elucidate a mixed near-field FRET and far-field emission/reabsorption mechanism excitonic energy transport by combining time-dependent exciton energy and exciton diffusivity measurements in a heterogeneous QD superlattice (QDSL) [4]. We first quantitatively characterize the heterogeneous energetic landscape of CdSe/Te/CdS QDSL monolayers by extracting inhomogeneous and intrinsic spectral components of QDs by single-particle emission spectroscopy [5]. We next track the time-dependent decay of the mean exciton energy by time-resolved emission spectrum (TRES) upon QDSS photoexcitation. The enhanced dynamic redshift occurring in the QDSLs relative to the solution phase QDs immediately following excitation indicates excitons, on average, sample progressively lower-energy QDs as they explore the spatiotemporal energy landscape. Finally, we measure exciton transport by monitoring the spatiotemporal expansion of the photoluminescence intensity and find that exciton propagation dynamics and exciton hopping rates manifest monotonically with time-dependent exciton emission depletion (TRUSTED) microscopy [6]. The result is that the data may be fitted to a simple model of the TRUSTED protocol [6] to determine migration parameters, such as diffusion. We use all three types of experimental results to constrain parameters in a kinetic Monte Carlo simulation, and we find that FRET theory is incompatible with the TRUSTED and TRES results simultaneously. This approach is unique because we connect the exciton energy and diffusion dynamics directly, which puts stringent test on the existing FRET theory. We show that only introducing far-field emission/reabsorption terms that allows hops well beyond the nearest neighbors, can the model reproduce both all three experimental results. Our inclusion of far-field coupling was inspired by Andrews et al. [7], who originally wrote down how the energy transfer rate between donor and acceptor TDM can most generally be written as a dipole-dipole coupling expansion, where $\beta$ represents the FRET rate and dominates in the near-field. The far-field term (scales with $r^{-2}$) dominates when $r$ is much greater than $\lambda/2a$.

The explanation of our own multimodal study also addresses a longstanding paradox in exciton transport within QD solids, i.e., the typically-employed FRET near-field model has repeatedly fallen short of explaining experimental results despite being perpetuated as a standard. We furthermore showed how our model reconciles the original report of this paradox from Tisdale and co-workers [1]. Overall, this work yields a much-needed unified framework in which to characterize transport in QD solids and new principles for device design.
Understanding spin-to-charge conversion (SCC) allows efficient control and manipulation of the spin degree of freedom, which can pave the way for next generation spintronic devices. Unlike conventional transport-based measurements, terahertz (THz) emission spectroscopy offers great advantages including the capability of measuring transient charge currents with sub-picosecond time resolution. Using THz emission spectroscopy, we observed the ultrafast spin current injection at the interface between a ferromagnetic (FM) material and a chiral two-dimensional (2D) perovskite via inverse Rashba-Edelstein effect. In summary, we observed strong magnetic field- and polarization-dependence in both phase and intensity of the emitted THz signal, implying the great tunability in these chiral 2D perovskites for spintronic application. These results present a promising way to control charge and spin interconversion at perovskite/ferromagnetic interfaces and future spintronics devices. The unique asymmetry in THz emission due to SCC at chiral 2D perovskite/FM (i.e. (R-MBA)PbI\(_3\)NiFe and (S-MBA)PbI\(_3\)interface) distinguishes them from three-dimensional perovskite materials which only exhibit symmetric THz emission. In this talk, I will discuss the measured THz emission signals including both the forward and backward THz emission (reflected at the air/substrate interface). The forward emission signal exhibits a \(\pi\)-phase shift when the in-plane magnetic field flips its sign, whereas the backward signal exhibits no phase shift at all. In addition, we also observe the asymmetry in THz emission intensity. Specifically, the THz emission intensity of the forward emission signal decreases by almost two-fold when the in-plane magnetic field reverses, while the backward emission signal increases by two-fold when the field direction reverses. Such asymmetry in THz emission can be explained with an in-plane momentum shift of the Rashba bands induced by the ultrafast laser pump.

3:15 PM QT01.12.02
Quantum Material Research through Femtosecond Electron Crystallography, Spectroscopy and Microscopy
Chong-Yu Ruan, Michigan State University, United States

The major potential advantage in using electron scattering data, compared to X-ray, is that electrons can be focused using an electromagnetic lens; thus, both images and diffraction patterns can be utilized for structural analysis under the same platform. Importantly, the different modalities are controlled by the post-specimen optics and aperture placement with additional sets of lenses. The lens combination offers great flexibility in creating either image, diffraction, or even spectroscopic signals from a large field of view or data for the microanalysis of small regions. Injecting ultrafast time resolution into the typical TEM modalities will not only allow ultrafast imaging and diffraction patterns to be obtained for studying material processes, but also the delicate control of timing between the pump and probe pulses can create a new contrast mechanism at various stages of the material’s responses. Especially, the recent successful implementation of high precision control of electron probe dynamics enables the technologies to perform in the 10s femtosecond regime, opening new possibility of studying control-feedback mechanism.

We will discuss the uses of dynamical contrast to enhance the imaging and crystallography capabilities for the understanding of the evolutionary processes set forth from different types of pulses in quantum materials. The evolutionary processes are probed through combined approach of ultrafast spectroscopy, diffraction, and microscopy that are conducted in situ to piece together information. Using vanadium dioxide nanocrystals and transition-metal dichalcogenide (TMDC) thin layers as examples, we demonstrate how the multi-modality ultrafast electron platform may provide useful new information regarding quantum material state evolution at different spatial and temporal scales. Through joint structure and spectroscopy probes we identify the common presence of nanoscopic transition intermediate as the cornerstone for the system’s successful descend into the eventual state and adopting its functionality.

In the studies of TMDC (TaS\(_2\), TaSe\(_2\)) first focusing on the dynamics on the ps and sub-ps timescale with time-domain contrasts over the optical signals and selected Bragg peaks, we observe that under different pump conditions different types of phonon modes in the hosting lattice of the charge-density-wave materials may be activated. Upon entering the nonthermal control, these phonon modes are hybridized with the emerging density-wave state observed through the dynamical crystallographic patterns. The transition becomes stepwise with the formation of nanoscopic domains that lock the emergent order with the host lattice in various formation. Remarkably, upon varying the pump power, the timescale for the multi-step structural can be tuned by more than one order of magnitude. In the case of VO\(_2\), multi-critical behavior also emerges but here we show the thermal and non-thermal controls manifest in different types of behavior. For the nonthermal control, in which, the initial step of ultrafast spectroscopic insulator-to-metal transition is observed over sub-100 fs timescale where the emergence of a nanoscopic excitonic polaron domain is simultaneously captured by the diffraction signals. Such evolution is different from the insulator-metal transition obtained under the thermal regime of control where no such polaronic domain is identified. These results indicate that the functional controls in correlated electron crystals may be more nuanced due to their sensitivity to more than one type of control parameter and our multi-perspective results may shed insight to address some highly debated open questions regarding these materials.

The work was funded by the U.S. Department of Energy, Grant DE-FG0206ER46309. The experimental facility was supported by U.S. National Science Foundation, Grant DMR 1625181.

3:45 PM QT01.12.03
Spatiotemporal Imaging of Waveguide Nonlinear Optics
Ding Xu and Milan Delor, Columbia University, United States

Non-linear optical conversion is an essential aspect of modern photonic applications, and major efforts target the realization of efficient nonlinear processes in compact waveguides for miniaturization. Van der Waals structures, renowned for their pronounced light-matter interactions and nonlinear susceptibilities, have emerged as promising platforms to realize such nonlinear waveguides, but optimization requires precise knowledge of their linear and nonlinear optical properties, which are notoriously difficult to extract in highly anisotropic microstructures. I will describe an approach we developed to extract the optical properties and phase-matching conditions of nonlinear materials by directly imaging light propagation and harmonic conversion within van der Waals waveguides with extremely spatiotemporal resolution. Although it is generally assumed that waveguided light remains out the reach of far-field microscopy, our approach, based on far-field ultrafast microscopy, leverages strong light-matter interactions even beyond the total internal reflection barrier, an unprecedented feat. We focus on slab waveguides of 36-MoS\(_2\), which were recently found to exhibit highly efficient second harmonic generation. We show that spatiotemporal imaging of both fundamental and second harmonic waves provides several self-consistent methods to determine the phase-matching angle, mode profiles, harmonic generation efficiency and losses in nonlinear waveguides without any a priori knowledge of material properties. Our approach thus enables rapid identification of promising materials and optimization of waveguide structures for efficient harmonic generation and optical modulation in nanophotonic architectures.

4:00 PM QT01.12.04
Ultrafast Infrared-Light-Driven Symmetry Control in Crystalline Materials
Zhiren He and Guru Khalsa, University of North Texas, United States

The interplay between structure, symmetry, and function is a fundamental and long-standing paradigm in materials physics. It dictates how we access physical properties, reveals hidden order, and guides both our search for, and the engineering of, new physical phenomena. Recent technological advances have enabled sub-picosecond manipulation of structure through the far-from-equilibrium drive of phonons — the mechanical modes of crystalline materials — using mid- and far-infrared light. How can we leverage these structural changes to induce new symmetries and functionalities?

In this talk, I will discuss our theoretical exploration of light-driven control of symmetry in crystalline materials via direct excitation of phonons. Focusing on strategies for tailored optical control of elusory symmetries and orders, I will demonstrate that new symmetries and length scales can emerge, that chemical environments not observed near equilibrium can be prepared, and that known or hidden phase boundaries may be traversed.

References

SESSION QT01.12: Light-Matter Coupling in Quantum Materials II
Session Chairs: Veronika Policht and Chiara Trovatello
Friday Afternoon, April 26, 2024
Room 420, Level 4, Summit
Quantum Defects in 2D Materials for Terahertz Technologies

Su Ying Quek; National University of Singapore, Singapore

The emergence of stable terahertz (THz) sources and other THz optical components has spurred the development of many applications. However, THz technologies have thus far not been well integrated into the quantum regime. In this work, we predict that transition metal substitutional defects in two-dimensional transition metal dichalcogenides (TMDs) can serve as quantum defects for terahertz technologies. Central to this prediction is the finding that the zero field splittings between the spin sublevels in these defects are in the sub-terahertz to terahertz range. These zero field splittings are orders of magnitude larger than those found in other common quantum defects, due to the large spin-orbit coupling in these TMD systems. Based on the symmetries of the quantum states as well as first principles calculations of the optical transition energies, we identify defects that can serve as spin qubits, either through resonant excitation or through intersystem crossing channels. Such spin qubits are expected to have a longer spin coherence time compared to spin qubits with smaller zero field splittings. We further propose defects that can potentially be tunable quantum sources of terahertz radiation. Our research broadens the scope for advancements in quantum computing and information science, and lays a foundation for their integration with THz technologies.

Funding Acknowledgement:
Supported by the Singapore Ministry of Education under grant number MOE2018-T3-1-005.

References:

8:45 AM *QT01.13.03
Non-Linear Light-Matter Interactions in Quantum Materials
Su Ying Quek; National University of Singapore, Singapore

Non-linear optical phenomena are at the heart of many important technologies and spectroscopic techniques. In order to fundamentally understand, and predict, non-linear optical properties in quantum materials, it is necessary to incorporate the physics of excitons, or bound electron-hole pairs. In this work, we develop and implement a theory for the second-order optical susceptibility that takes into account excitonic effects with a first principles GW-Bethe-Salpeter-Equation (GW-BSE) approach. Using this theory, we elucidate the impact of excitons on sum-frequency generation and spontaneous parametric down-conversion in niobium oxydihalides (NbOX2, X = Cl, Br, I) [1], a material of significant current interest in non-linear optics [2]. We also predict difference-frequency generation effects in quantum materials. In addition to shift current effects (the zero-frequency response), we consider the generation of terahertz pulses due to difference frequency mixing from incoming laser pulses. Our work provides a framework to predict and understand the non-linear effects arising from continuous-wave and ultrafast laser light incident on quantum materials.

References:

9:15 AM *QT01.13.04
Ultrafast Thermodynamic Phenomena Involving Photons, Electrons and Phonons in (Twisted) Quantum (Meta)Materials
Klaas-Jan Tielseoij1,2; 1Eindhoven University of Technology, Netherlands; 2Catalan Institute of Nanoscience and Nanotechnology, Spain

Quantum materials exhibit several exciting ultrafast physical phenomena that are moreover potentially technologically useful. This is particularly true for quantum materials with massless Dirac electrons, such as graphene and topological insulators. When light is absorbed in these materials, electron heating occurs through electron-electron interactions on a 10-100 fs timescale, followed by electron cooling, typically involving the emission of phonons on a picosecond timescale. We have exploited these ultrafast thermodynamics, and the heat-induced decrease in terahertz (THz) absorption, to generate bandstructure effects that are particularly efficient in quantum metamaterials that consist of a quantum material and a metallic grating [2]. Thanks to an efficient "Coulomb cooling" mechanism between surface and bulk electronic states in topological insulators [3], we have recently demonstrated that the ultrafast thermodynamics can give rise to third-order terahertz harmonic generation approaching the milliwatt regime [4]. These results establish quantum (meta)materials as an excellent material platform for nonlinear terahertz photonics, with possible applications in next-generation wireless communication systems, among others.

Whereas these ultrafast thermodynamics in graphene and topological insulators are relatively well understood, this is not the case for twisted bilayer graphene near the magic angle. Using time-resolved photocurrent measurements, we have studied these ultrafast dynamics and found that the electron cooling dynamics in twisted bilayer graphene near the magic angle is very distinct from the dynamics in monolayer or non-twisted bilayer graphene. Specifically, the cooling time in near-magic twisted bilayer graphene is a few picoseconds all the way from room temperature down to 10 K, whereas these ultrafast thermodynamics in twist bilayer graphene becomes increasingly slow for lower temperatures. We ascribe this ultrafast cooling in magic-angle twisted bilayer graphene to Umklapp-assisted electron-photon cooling, facilitated by the moiré pattern in twisted bilayer graphene [5]. Whereas Umklapp scattering is a very common phenomenon for phonons, it is very rare to observe such scattering processes for electrons. These results establish twist angle as control knob for steering the cooling dynamics and flow of electronic heat, and have possible implications for the development of ultrafast detectors operating at cryogenic temperatures, among others.

References:
Using High-Pressure Conditions to Access Novel Structures and Engender Magnetic Control in Layered Lanthanide Materials

A rational approach to designing the next generation of quantum magnetic materials requires hypothesis-driven synthesis. Yet, the complex phase space of solid-state systems and the small energy scales that determine magnetic order are such that subtle changes in composition can drastically change the structure and properties of the resulting material. In comparison, pressure provides an incrementally tunable vector, serving to increase orbital overlap and leading to more significant covalent and metallic interactions. In this work, we describe our multimodal approach combining high-pressure synthesis with spectroscopy and calculations to bring new chemical insight into the discovery of layered materials containing lanthanides primed to exhibit exotic magnetic behaviors. To realize promising synthetic targets, we turned to both traditional solid-state techniques as well as high-pressure experiments in diamond anvil cells. We note an approach combining high-pressure synthesis with spectroscopy and calculations to bring new chemical insight into the discovery of layered materials containing lanthanides primed to exhibit exotic magnetic behaviors. To realize promising synthetic targets, we turned to both traditional solid-state techniques as well as high-pressure experiments in diamond anvil cells.
Antagonistic Pairs: A Pathway to The Discovery of New Quasi-Low Dimensional Materials

Tyler Slade; Ames Laboratory, United States

A foundational goal of materials chemistry is to develop general design principles for synthesizing materials with targeted structural motifs and physical properties. We propose that pairs of strongly immiscible elements, referred to here as antagonistic pairs, can be used to reliably produce ternary compounds with low or quasi-reduced dimensionality intrinsically built into their crystal structures. Many pairs of elements offer essentially no miscibility, of which examples are Co-Pb, Cr-La, and Fe-Ag. The heart of our work is to leverage third elements that are mutually compatible with any given immiscible pair to form stable ternary compounds containing that pair. When such ternary compounds can be made, we discuss how the strong immiscibility of the antagonistic pair is remarkably preserved in the ternary crystal structures, with the third element separating the immiscible atoms into spatially separated substructures. Quasi-low dimensional structural units, such as chains or sheets, are the natural consequence of the immiscible atoms seeking to avoid close contact in the solid-state. Finally, we present the growth and characterization of single crystals of several new, 3d transition metal containing, ternary compounds based on antagonistic pairs and which feature quasi-2D structural motifs, concluding with an overview of their magnetic and transport properties.


Work at Ames National Laboratory was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. Ames National Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358.

1:30 PM QT02.02.01
Helical Light Emission from a Moiré Chern Magnet
Xiaodong Xu; University of Washington, United States

Twisted MoTe₂ bilayer is an emerging fractional Chern insulator with spontaneous time reversal breaking. As semiconducting transition metal dichalcogenides famously exhibit spin-valley locking and circularly polarized valley-selection optical rules, a natural question arises as to how the interaction induced ferromagnetism couples to the optical response. Here, we demonstrate that the degree of circular polarization (DOCP) in the trion photoluminescence at zero magnetic field reaches near unity in the anomalous Hall metal phase, with the helicity controlled by the magnetization direction. Spin-valley Hall resistance is shown to tune the emission helicity, establishing the electric current as an additional control of the PL helicity. We further show that the PL DOCP is a sensitive probe of the integer and fractional quantum anomalous Hall effects, the putative zero-field composite fermi liquid state, as well as their electric-field-driven topological quantum phase transitions. The unprecedented optical properties of this system promise to have profound implications for spintronics, valleytronics, and topological-optoelectronic devices.

2:00 PM QT02.02.02
Optics as a Probe and Control of Spin/Valley Order in Topological Moiré Magnet
MoTe₂
Eric Anderson; Xiaodong Xu; Jiaqi Cai; Heonjoon Park; Di Xiao; Liang Fu; Wang Yao; Kenji Watanabe; Takashi Taniguchi; University of Washington, United States; Massachusetts Institute of Technology, United States; The University of Hong Kong, Hong Kong; National Institute for Materials Science, Japan; Kyoto University, Japan

In the past year, near-ÅAA stacked homobilayer moiré MoTe₂ has been established as a robust, gate-tunable ferromagnet upon hole doping of the first moiré valence band. The system’s spontaneous time reversal symmetry breaking enables the realization of an effective Haldane model and flat, topologically nontrivial bands. These unique characteristics of the moiré MoTe₂ system led to observation of quantum anomalous Hall and, for the first time, fractional quantum anomalous Hall states. Here, I discuss our optical measurements of tunable magnetic and topological states in the moiré superlattice. Additionally, I present our more recent studies leveraging the magnetic order in the system to control helical optical emission at zero applied magnetic field. The strong correspondence between the spin, valley, and optical degrees of freedom these results establish suggests that optics is not only a powerful probe of moiré MoTe₂, but could also be promising control knobs to the magnetic state. Beyond the implications for spintronics, valleytronics, and magneto-optical devices, the link between magnetic order and topological index of the FQAH states presents a new path forward in the study of anyon physics – and perhaps, one day, towards topological qubits.

2:15 PM QT02.02.03
Electrical Switching of The Edge Current Chirality in Quantum Anomalous Hall Insulators
Cui-Zu Chang; Yifan Zhao; The Pennsylvania State University, United States

A quantum anomalous Hall (QAH) insulator is a topological state of matter, in which the interior is insulating but electrical current flows along the edges of the sample, in either a clockwise (right-handed) or counter-clockwise (left-handed) direction dictated by the spontaneous magnetization orientation. Such chiral edge current (CEC) eliminates any backscattering, giving rise to quantized Hall resistance and zero longitudinal resistance. In this work, we fabricate mesoscopic QAH sandwich (i.e. magnetic topological insulator (TI)/TI/magnetic TI) Hall bar devices and succeed in switching the CEC chirality through spin-orbit torque (SOT) by applying a current pulse under a suitably controlled gate voltage. The well-quantized QAH states before and after SOT switching with opposite CEC chiralities are demonstrated through four- and three-terminal measurements. Our theoretical calculations show that the SOT that enables the magnetization switching can be generated by both bulk and surface carriers in QAH insulators, in good agreement with experimental observations. Finally, I will briefly talk about the SOT switching-induced topological phase transition between the QAH and axion insulator states.

This work is supported by ARO award (W911NF2210159), AFOSR grant (FA9550-21-1-0177), DOE grant (DE-SC0023113), and Gordon and Betty Moore Foundation’s EPiQS Initiative (Grant GBMF9063 to C.-Z.C.).

2:45 PM QT02.02.04
Observation of Fractional Quantum Anomalous Hall Effect
Heonjoon Park; Jiaqi Cai; Eric Anderson; Yinong Zhang; Jiayi Zhu; Xiaoyu Liu; William Holtzmann; Chaowei Hu; Zhaoyu Liu; Takashi Taniguchi; Kenji Watanabe; Jiun-Haw Chiu; Ting Cao; Liang Fu; Wang Yao; Cui-Zu Chang; David Cobden; Di Xiao; and Xiaodong Xu; University of Washington, United States; National Institute for Materials Science, Japan; Massachusetts Institute of Technology, United States; The University of Hong Kong, Hong Kong; The Pennsylvania State University, United States

The interplay of topology, magnetism, and strong correlation leads to intriguing quantum states of matter. A prominent example is the quantum anomalous Hall effect (QAHE), which displays integer quantum Hall effect at zero magnetic field due to topologically nontrivial bands and intrinsic magnetism. Realizing a similar analogue of the fractional quantum Hall effect at zero field, known as the fractional quantum anomalous Hall effect (FQAHE), has long posed a challenge due to stringent constraints in electron-electron interaction and quantum geometry. Here, we present the experimental observation of FQAHE and electrically tunable topological phase transition in twisted MoTe₂ bilayer using electrical transport measurements. In addition, an anomalous Hall state emerges near the filling factor -1/2. Its behavior mirrors that of the composite Fermi liquid in the half-filled lowest Landau level of a two-dimensional electron gas near high magnetic fields. The direct observation of the FQAHE and associated effects opens the door to exploring charge fractionalization and anyonic statistics at zero magnetic field.

3:00 PM BREAK

SESSION QT02.03: Emerging Kagome and Magnetic Materials
Session Chairs: Zhong Lin and Andrew F. May
Tuesday Afternoon, April 23, 2024
Room 421, Level 4, Summit
The two-dimensional kagome lattice comprised of corner-shared triangles is theoretically expected to host multiple exotic band features such as Dirac points, van Hove singularity and flat bands in its tight-binding model. The intricate interplay of these band features with spin-orbit coupling and electron-electron interactions renders the kagome lattice an exceptionally promising platform for the realization of topological and correlated electronic states. Recently, a growing family of transition metal-based intermetallic materials, known as “kagome metals,” has been found to faithfully realize the anticipated model kagome electronic structure. In this talk, we will focus on the ongoing advancements in the pursuit of topological and correlated phases in binary kagome metals; in particular, we will highlight the band topology in the ferromagnetic phase, the emergence of flat bands as well as non-Fermi liquid behavior in these kagome metals.

References:

4:00 PM QT02.03.02

Above Room-Temperature Ferromagnetism in Van der Waals Material Fe3GaTe2
Chaowei Hu, Jiayi Zhu, Sanae Tominaga, Jordan Fonseca, Yuzhou Zhao, Xiaodong Xu and Jian-Haw Chu; University of Washington, Seattle, United States

The emergence of two-dimensional van der Waals magnets has introduced new prospects for vdW heterostructure and spintronic applications in the past decade. Recently a new member Fe3GaTe2 was found and stood out for its persistent ferromagnetism above room temperature. In this presentation, we will discuss our successful synthesis of single-crystalline Fe3GaTe2, as well as the following bulk characterization, transport, and magneto-optical measurements performed on our single crystal and exfoliated thin flakes. The magnetization and transport studies on the bulk Fe3GaTe2 crystals reveal a high Curie temperature of 355K and the thermodynamic investigations suggest the presence of a strong electron-electron correlation. Layer-dependent magneto-optical studies on thin Fe3GaTe2 flakes further unveil its robust ferromagnetism for room-temperature applications in 2D limits. Our work illuminates the remarkable magnetic properties of Fe3GaTe2, establishing it as a suitable vdW platform for realizing controllable 2D magnetism and spintronic applications in everyday environments.

4:15 PM QT02.03.03

Kagome and Van der Waals Magnetic Topological Materials
Roland K. Kawakami; The Ohio State University, United States

Materials and heterostructures combining magnetic order and band topology are important for science and technology ranging from quantum anomalous Hall effect (QAHE) to highly efficient spin-orbit torque switching. Kagome lattice metals and van der Waals (vdW) heterostructures are two classes of materials that are particularly promising in this regard. The 2D kagome lattice has topological flat bands and Dirac cones inherent in its band structure and these features persist in compounds with layered kagome lattices. Meanwhile, vdW materials encompass 2D ferromagnetism and spin-orbit torque switching. Kagome lattice metals and van der Waals (vdW) heterostructures are two classes of materials that are particularly promising in this regard. The 2D kagome lattice comprised of corner-shared triangles is theoretically expected to host multiple exotic band features such as Dirac points, van Hove singularity and flat bands in its tight-binding model. The intricate interplay of these band features with spin-orbit coupling and electron-electron interactions renders the kagome lattice an exceptionally promising platform for the realization of topological and correlated electronic states. Recently, a growing family of transition metal-based intermetallic materials, known as “kagome metals,” has been found to faithfully realize the anticipated model kagome electronic structure. In this talk, we will focus on the ongoing advancements in the pursuit of topological and correlated phases in binary kagome metals; in particular, we will highlight the band topology in the ferromagnetic phase, the emergence of flat bands as well as non-Fermi liquid behavior in these kagome metals.

References:

4:45 PM QT02.03.04

Half-Magnetization Plateau in The Kagome-Stripe-Lattice Na2Co4(VO)2(OH)2
Yiqing Hao1, Megan Smart1, Jie Xing1, Rongying Jin2, Joseph Kolis3, Duminda Sanjeewa4 and Huibo Cao5; 1Oak Ridge National Laboratory, United States; 2University of South Carolina, United States; 3Clemson University, United States; 4University of Missouri–Columbia, United States

Magnetization plateaus often signify quantum magnetic states arising from geometric frustration and/or quantum fluctuations. Here, we report a half-magnetization plateau in the kagome-stripe lattice (KSL) material, Na2Co4(VO)2(OH)2. Our susceptibility measurements reveal the half-magnetization plateau under the applied field perpendicular to the quasi-one-dimensional stripe direction. To unravel the origin of the magnetization plateau, we used single crystal neutron diffraction to investigate the evolution of magnetic structures with field. At zero field, the ground state magnetic structure is a non-collinear antiferromagnetic order with reduced ordered-magnetic moments on both Co sites. Increasing the magnetic field flips the spins on one of the Co sites to ferromagnetic order, while the spins on the other Co site remain small to zero ordered-magnets despite the strong magnetic field. Such robustness in reducing ordered-magnetic moments indicates strong magnetic frustration and/or quantum fluctuations in this KSL material. Furthermore, aided by the local magnetic susceptibility method using polarized neutrons, we concluded that the resulting ground state and the half-magnetization plateau are likely caused by the Dzyaloshinskii-Moriya (DM) interactions between spins on two Co sites and the strong quantum fluctuations within the 1D Co-spin chain.

The research was supported by the U.S. Department of Energy (DOE), Early Career Research Program Award KC0402020 and used resources at the High Flux Isotope Reactor, a DOE Office of Science User Facility operated by ORNL.

SESSION QT02.04: Emerging 2D Magnetic Materials II
Session Chairs: Dmitry Ovchinnikov and Tyler Slade
Wednesday Morning, April 24, 2024
Room 421, Level 4, Summit

8:30 AM QT02.04.01

Next Level Two-Dimensional Quantum Materials
Xavier Roy; Columbia University, United States

Two-dimensional (2D) materials have received widespread attention in the past two decades due to their remarkable physical, mechanical and chemical properties, and our ability to integrate them into devices. In this seminar, I will present our recent work in the development of the next generation of 2D materials. I will first discuss how magnetic order strongly couples to optical transitions in a new magnetic semiconductor developed in my laboratories, CrSBr. I will then introduce the synthesis and characterization of the first f-electron-based heavy fermion metal, CeSill, that is also a 2D van der Waals (vdW) material. Conceptually, our synthetic design takes a traditional 3D intermetallic heavy fermion compound and slices it into atomically-thin vdW sheets by incorporating iodine into the structure. The resulting material is cleavable and effectively 2D electronically, even in bulk crystals.

9:00 AM QT02.04.02

Intercalation-Induced Magnetic Properties of Quasi-2D Fe3-xGeTe2 Van der Waals Magnet
Srinivasa Rao Singamaneni and Daniel Rascon; The University of Texas at El Paso, United States

Among several well-known transition metal-based compounds, cleavable van der Waals (vdW) Fe3-xGeTe2 (FGT) magnet is a strong candidate for use in two-dimensional (2D) magnetic devices due to its strong perpendicular magnetic anisotropy, sizeable Curie temperature (TC = 154 K), and versatile magnetic character that is retained in the low-dimensional limit. While the Tc remains far too low for practical applications, there has been a successful push toward improving it using external driving forces such as pressure, irradiation, and doping. Here we present experimental evidence of a novel room-temperature (RT) ferromagnetic phase induced by the electrochemical intercalation of common tetrabutylammonium cations (TBA+) into quasi-2D
Metal thiophosphates (MPX₃) have gained recent prominence for their intrinsic magnetic properties. These materials feature a layered, van der Waals structure with \([\text{P}_2\text{X}_6]\)₄ bipyramid anion units surrounded by octahedrally coordinated metal cations. By incorporating different metal cations, a diverse range of magnetic phases can be induced, making MPX₃ compounds promising subjects for condensed matter research into magnetic phases. Remarkably, V-based thiophosphates are comparatively understudied except for demonstrating the most stable antiferromagnetic ground state for the homogenous family of compounds, characterized by large exchange parameter. [1] This is largely due to the difficulty of synthesizing the monometallic phase due to the formation of a parasitic VₓSy species. Utilizing a flux method, [2] we have stabilized V in the MPS₃ structure by alloying with Mn, Fe, Co, or Ni. These V-rich compounds are expected to maintain the large exchange parameter while possibly exhibiting magnetic frustration. Herein, we present a thorough investigation of novel \(V_{0.5}\text{Fe}_{0.5}\text{P}_{3}\text{S}_4\) and \(V_{0.5}\text{MnFeCoNiZn}_{0.5}\text{P}_{3}\text{S}_4\) thiophosphates including a study of structure, vanadium oxidation state, and chemical homogeneity. Elemental studies have confirmed the single crystal stoichiometry of these mixed cation systems. This is corroborated by structural refinement showing lattice expansion with increased alloying. Other mixed bimetallic thiophosphate systems demonstrate an inhomogeneous distribution of cations, resulting in heterostructures in the case CuInP₂S₆ or large composition fluctuations between exfoliated flakes in FeCo₃S₄[1]. [3] Conversely, electron energy loss spectroscopy (EELS) of \(V_{0.5}\text{MnFeCoNiZn}_{0.5}\text{P}_{3}\text{S}_4\) reveals a remarkable homogeneous solid solution which is preferred for future magnetic measurements to determine magnetic moment alignment. Additionally, we were able to clarify the oxidation state of V in these materials using bulk and nanoscale spectroscopy techniques. We confirm a mixed V²⁺ and V⁵⁺ state and observe a trend towards increasing V²⁺ as the system is alloyed from bimetallic to high entropy. Finally, we present synthesis techniques to grow phase pure V-rich thiophosphate powders and centimeter scale crystals to target both catalysis and magnetic measurements. Our findings highlight entropy engineering as a useful method towards stabilizing vanadium rich thiophosphates and provide in-depth chemical characterization which is vital for applications of V-rich thiophosphates in next generation electronic devices.

The recent discovery of magnetic van der Waals materials opens a new paradigm in solid-state research, offering an exploration of magnetism at the nearly atomistic limit, with an impact on the development of newly emerging spintronic, memory and information devices. In particular, antiferromagnetic (AFM) materials are catching special attention at the current time, due to their low stray magnetic field, and fast spin response (in the THz). The talk will include a thorough investigation of the fundamental magnetic properties and their coupling to the electronic nature of two representative materials: MnPS$_3$ and FePS$_3$. With a single AFM layer, the metals are positioned in a honeycomb arrangement. The AFM character is generated via a spin-exchange interaction among metal next neighbours (NNs), when the metal spins are mainly oriented normally to the layer plane arranged either in Néel or zigzag configurations. It is important to note that second and third NNs intralayer interactions are not negligible in the MPX$_2$ layers, governed by super-exchange AFM coupling through the metal(d)-chalcogen(p) bonding. An interlayer interaction adds small tuning with weak super-super-exchange interaction, which despite being weak, may change the magnetic properties by having either AFM or FM stacking or by inducing a magnetic torque.

A MnPS$_3$ layer with a Néel magnetic configuration and lack of spin-orbit coupling was a suitable platform for examining the contribution of the long-spin-exchange interaction. The study implemented dilution of the Mn content (forming alloyed compounds with the general chemical formula MaxZn$_{1-x}$S$_3$), examining the sustaim of AFM arrangement down to a composition of x=0.5, hence, supporting the weight of 2$^{nd}$ and 3$^{rd}$ spin-exchange coupling to the long-range magnetic ordering. A FePS$_3$, having a zigzag magnetic configuration, represents a case with a pronounced distortion of the honeycomb symmetry, due to local distortion around a metal site by a strong spin-orbit coupling. The two examples mentioned here showed a strong correlation between the magnetic ordering and the optical transitions, showing obvious changes in the photoluminescence at the Néel temperature (a point possessing a magnetic transition from AFM to paramagnetic phase), as well as an optical polarization character along the magnetic directionality. It was mainly distinct in the appearance of an exceptionally sharp emission line in the FePS$_3$ single layer with a strong linear polarization along the zigzag direction.

The accompanied DFT calculations simulated the spin-exchange coupling process and its impact on the electronic band structure (will be shown at the presentation by a short movie). Furthermore, the theoretical calculations exposed a fundamental character in which the electronic transitions show a hybrid property between local metal transitions and band-edge transitions. The exploration of these fundamental points is an ongoing process at the current moment.

Acknowledgement: The authors express their gratitude to the collaborators in the project: Dr. Milosz Rybak and Prof. Magdalena Birowska (Warsaw University) and Dr. Thomas Brune and Prof. Thomas Heine (The University of Dresden).

SESSION QT02.05: Disorder and Magnetism in 2D Materials
Session Chairs: Chaowei Hu and Andrew F. May
Wednesday Afternoon, April 24, 2024
Room 421, Level 4, Summit

2:00 PM QT02.05.02
Near Room-Temperature Intrinsic Exchange Bias in an Fe Intercalated ZrSe$_2$ Spin Glass Zhizhi Kong and Kwabena Bediako; University of California, Berkeley, United States

Exchange bias is a magnetic phenomenon commonly manifested as the hysteresis-loop shift when a system hosting certain magnetic heterointerfaces is cooled under an applied external magnetic field. Despite the extensive use of the exchange bias effect, particularly in magnetic multilayers, for the design of spin-based memory/electronics devices, a comprehensive mechanistic understanding of this effect remains a longstanding problem. Recent work has shown that disorder-induced spin frustration might play a key role in exchange bias, suggesting new materials design approaches for spin-exchange materials that harness this effect. Here, we design a spin glass with strong spin frustration induced by magnetic disorder by exploiting the distinctive structure of Fe intercalated ZrSe$_2$, where Fe(II) centers are shown to occupy both octahedral and tetrahedral interstitial sites and to distribute between ZrSe$_2$ layers without long-range structural order. Notably, we observe behavior consistent with a magnetically frustrated and biodegenerate ground state in these Fe$_{0.17}$ZrSe$_2$ single crystals, which persists above room temperature. Moreover, this magnetic frustration leads to a robust and tunable exchange bias up to 250 K. These results not only offer important insights into the effects of magnetic disorder and frustration in magnetic materials generally, but also highlight as design strategy the idea that a large exchange bias can arise from an inhomogeneous microscopic environment without discernible long-range magnetic order. In addition, these results show that intercalated TMDs like Fe$_{0.17}$ZrSe$_2$ hold potential for spintronic technologies that can achieve room temperature applications.

2:30 PM BREAK

SESSION QT02.06: Electronic and Magnetic Phases in Emerging Materials
Session Chairs: Zhong Lin and Daniel Pajerowski
Wednesday Afternoon, April 24, 2024
Room 421, Level 4, Summit

3:30 PM QT02.06.01
Single Crystal Growth and Magnetic Anisotropic Study of SmCrGe$_3$ with Cr Linear Chain Mingyu Xu$^1$, Weiwei Xie$^1$ and Daniel P. Phelan$^1$; $^1$Michigan State University, United States

Mingyu Xu$^1$, Xianglin Ke$^2$, Sergey L. Bud'ko$^3$, Paul C. Canfield$^3$, Weiwei Xie$^1$*

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3. Division of Materials Science, Ames Laboratory, Ames, IA, 50010

SmCrGe$_3$ was reported in the polycrystalline, which has ferromagnetic order occurring at 155 K [1]. To study the magnetic behaviors of SmCrGe$_3$, herein, the single crystals of SmCrGe$_3$ were grown using high temperature flux method. According to the single crystal X-ray diffraction, SmCrGe$_3$ crystallizes in the hexagonal LaCrGe$_3$-type structure with Cr linear chain along the c-axis, which forms the face-sharing Cr-centered octahedra aligned along the c-axis. Compared with itinerant magnet LaCrGe$_3$, SmCrGe$_3$ offers the opportunity to understand the interaction between localized 4f election and itinerant electron in this quasi-one-dimensional system and the role of interaction played in domain pinning changing [2], which may explain “one domain” behavior in LaCrGe$_3$ single crystal. Transport, magnetization, and specific heat measurements are taken. SmCrGe$_3$ behaves as a hard ferromagnetic material, which is different from other RECrGe$_3$ (RE = La - Nd). Coercivity as the function of temperature and field-dependent pinning change are given, and the results will be discussed in detail.
Unravelling Quantum Phases in The Shastry-Sutherland Lattice

Session Chairs: Yunqiu Kelly Luo and Dmitry Ovchinnikov

4:00 PM QT02.06.02
Unravelling Quantum Phases in The Shastry-Sutherland Lattice

Huibo Cao1, Kyle Ma1, Brianna Billingsley2, Madalynn Marshall3 and Tai Kong1; 1Oak Ridge National Laboratory, United States; 2The University of Arizona, United States

The Shastry-Sutherland lattice consists of a two-dimensional orthogonal arrangement of spin dimers. By varying the ratio of intra-dimer and inter-dimer interactions, the rich phase diagram can emerge, encompassing various exotic quantum states. Single-ion and exchange magnetic anisotropies can further diversify the phased diagram and give rise to quantum states beyond the traditional antiferromagnetic Heisenberg Shastry-Sutherland lattice model. Neutron scattering is an important technique for characterizing magnetic states. Here, I will introduce our recent studies using neutron scattering to unravel the quantum states of spin dimers in the rare-earth (RE) Shastry-Sutherland lattice compound Ba2Fe12As2 (RE=Nd, Ce, and Pr).

The research was supported by the U.S. Department of Energy (DOE), Early Career Research Program Award KC0402020 and used resources at the High Flux Isotope Reactor, a DOE Office of Science User Facility operated by ORNL.

4:15 PM QT02.06.03
Structural and Electronic Phases of 2D Transition Metal Dichalcogenides

Oleg Yazyev; Ecole Polytechnique Federale de Lausanne, Switzerland

Layered transition metal dichalcogenides (TMDs) of chemical composition MX2 (M = transition metal; X = S, Se, or Te) represent a broad family of materials with diverse electronic properties, including metals, insulators, as well as more complex states such as the charge-density-wave (CDW) and superconducting phases. More recently, the possibility of realizing single- and few-layer TMDs has brought the two-dimensional (2D) forms of these materials into the spotlight of prospective application in electronics, optoelectronics and beyond [1]. In my talk, I will review the “periodic table” of TMDs attempting to reveal systematic trends and develop chemical intuition across this family of 2D materials. Using a Wannier function approach, I will address the relevance of the crystal and ligand fields in determining the relative stability of 1T and 1H polymorphs as a function of the filling of the d-shell in 2D TMDs [2]. Then, I will present a unified picture of lattice instabilities in metallic TMDs that describes both the CDW phases and the strong-coupling scenario resulting in the formation of metal-metal bonds (as e.g. in the dimerized 1T' phases) [3]. In the rest of my talk, I will focus on topological and magnetic phases of TMDs. The 1T'-phase of Mo and W TMDs that have recently been shown to host the topologically non-trivial quantum spin Hall (QSH) insulator phase. The robustness of the QSH phase as well as the topological edge states [4] and interface states at the well-ordered 1T'-1H lateral heterojunctions will be discussed in conjunction with recent experiments on 1T'-WSe2 [5]. I will also cover our recent discovery of magnetic ordering and magnetoresistive switching in metallic few-layer and insulating single-layer PtSe2 [6,7].

2. D. Pasquier and O. V. Yazyev, 2D Materials 6, 025015 (2019);

4:45 PM QT02.06.04
Probing The Local Properties of Co-Honecomb Magnets as an Avenue to Understanding Their Complex Magnetic Behaviour

Megan B. Rutherford1, Dalmau Reg-i-Plessis2, Daniel Shaw3, Austin Ferrenti4, Solveig S. Aamlid1, Graham King5, Tyrel McQueen4, Kate Ross3, Kenji Kojima6,1 and Alannah Hallas1; 1The University of British Columbia, Canada; 2ETH Zürich, Switzerland; 3Colorado State University, United States; 4Johns Hopkins University, United States; 5Canadian Light Source, Canada; 6TRIUMF, Canada

In the field of frustrated magnetism, the relationship between the crystal structure and its magnetic properties has been a fruitful area of research for decades. A problem that has tormented materials scientists for an equal length of time, is the effect of small structural perturbations on the overall magnetic behaviour of a sample. An example of the interconnectedness of disorder sensitivity with rich magnetic phase spaces can be seen in well-studied examples of honeycomb magnets like \(\text{Ru}_3\text{Sn}_2\), where large differences in its physical characteristics emerge from subtle variations in stacking. A less well-understood example of this type of phenomena can be seen in the material BaCo2(PO4)2 where the Co\(^{2+}\) ions form a highly frustrated, undistorted honeycomb lattice of Co\(^{2+}\) that are well separated by Ba and PO\(_4\) spacer layers, hence this material is highly 2-dimensional. Neutron diffraction of BaCo2(PO4)2 reveals not one, but two distinct short range ordered magnetic states that develop over two successive transition temperatures. In contrast, BaCo2(AsO4)2, which is isostructural to the phosphate, long range orders into a single well-defined magnetic ordered state at low temperatures. Muon spin relaxation (\(\mu\)SR) is a local probe that is uniquely suited to the investigation of multiple coexisting, competing magnetic phases. A comprehensive \(\mu\)SR study has been performed on both the phosphate, and the arsenate for comparison, to determine how these competing magnetic phases develop with changing temperature across the temperature range of interest. The local structure of the material has also been investigated using total x-ray scattering techniques in an attempt to elucidate the origin of the unique magnetic behaviour of BaCo2(PO4)2. The combined evidence from these local probes leads us to conclude that this phase coexistence in BaCo2(PO4)2 is likely a result of synthesis-sensitive polymorphism.

SESSION QT02.07: Poster Session
Session Chairs: Yunqiu Kelly Luo and Dmitry Ovchinnikov
Wednesday Afternoon, April 24, 2024
Flex Hall C, Level 2, Summit

5:00 PM QT02.07.03
Characterization of Alloyed Fe\(_3\)Co\(_{1-x}\)Sn\(_2\) Kagomé-Lattice Films Grown Using Molecular Beam Epitaxy

Anna Li1,2, Prajwal Laxmeesha1,2, Tessa D. Tucker2 and Steven May2; 1University of California, Berkeley, United States; 2Drexel University, United States

Materials in which transition metals form a kagomé lattice have generated interest in recent years due to their unique magnetic and electronic properties. Ferromagnetic Fe\(_3\)Sn\(_2\) is one such example where the Fe kagomé sublattice results in the presence of Weyl fermions and flat bands. Being able to tune Weyl nodes has been an area of immense study, and hole and electron-doping are a potential avenues for changing the position of Weyl nodes in energy and momentum-space, and as a result, as well as moving the Fermi level with respect to the Weyl points with respect to the Fermi level. We performed an experimental investigation on [PM1] the effect of electron-doping in epitaxially grown thin films of Fe\(_3\)Sn\(_2\) through substitution of Co for Fe. We have grown Fe\(_3\)Co\(_{1-x}\)Sn\(_2\) films using molecular beam epitaxy (MBE) at various concentrations of Co (x = 0, 0.1, 0.5, 0.75, 1.0) on Al\(_2\)O\(_3\) (0001) substrates buffered with a thin Co (111)(Si2) wetting layer. The Fe\(_3\)Co\(_{1-x}\)Sn\(_2\) films are capped with CaF\(_2\) to prevent oxidation. Structural characterization of the heterostructures by in situ by reflection high-energy electron diffraction (RHEED) confirms the growth of ordered films, and further surface characterization via x-ray reflectivity and atomic force microscopy identifies smooth surfaces. X-ray diffraction was used to confirm the films have uniform c-axis orientation and that no secondary phases are present, while magnetometry was used to study the magnetic properties of the films. Further, it was observed that both the c-axis parameter and saturation magnetization decreases with increasing Co concentration, in agreement with previous density functional theory calculations (M. Adams et al 2023 J. Phys.: Condens. Matter 35 265801). [PM4] Magnetometry measurements revealed a decrease in saturation magnetization as the Co content was increased. Our results provide the groundwork for further investigation on the changing magnetic properties and electronic band structure in doped alloyed epitaxial Fe\(_3\)Sn\(_2\) heterostructures.

A.W.L. was primarily supported by NSF through the University of Pennsylvania Materials Research Science and Engineering Center (MRSEC) (DMR-1720530).
According to the Mermin-Wagner theorem. Thus, demands for the growth of bulk vdW layered materials to increase its $T_c$ to above room temperature remains challenging.

**Abstract:**
Magnetism in van der Waals (vdW) layered materials has attracted worldwide attention in fundamental condensed matter material research. Magnetism in low dimension materials provides a unique opportunity for tunable magnetic properties that are susceptible to external perturbations. Among all, pressure is a versatile tuning knob. In this work, we present our recent experimental findings collected on Fe$_2$7GeTe$_2$ by employing SQUID magnetometry, Raman spectroscopy, and synchrotron-based XMCD measurements as a function of applied pressure. We observe that the saturation magnetization and the Curie temperature decreased as the external pressure increased. The Raman data showed the pressure-induced structural phase transition. This work signifies the application of pressure in tuning the magnetic properties of layered van der Waals magnets.

**5:00 PM QT02.07.05**

**Pressure-Dependent Magnetic and Optical Properties of Fe$_2$7GeTe$_2$**
Ruby Olmos$^1$, Gilberto Fabbris$^2$, Rahul Rao$^3$, Michael A. Susner$^3$ and Srinivasa Rao Singamaneni$^1$; $^1$The University of Texas at El Paso, United States; $^2$Argonne National Laboratory, United States; $^3$Air Force Research Laboratory, United States

van der Waals magnets offer a great opportunity for tunable magnetic properties as they are susceptible to external perturbations. Among all, pressure is a versatile tuning knob. In this work, we present our recent experimental findings collected on Fe$_2$7GeTe$_2$ by employing SQUID magnetometry, Raman spectroscopy, and synchrotron-based XMCD measurements as a function of applied pressure. We observe that the saturation magnetization and the Curie temperature decreased as the external pressure increased. The Raman data showed the pressure-induced structural phase transition. This work signifies the application of pressure in tuning the magnetic properties of layered van der Waals magnets.

**5:00 PM QT02.07.06**

**Epitaxial Growth and Magnetic Properties of Kagomé Metal FeSn/Elemental Ferromagnet Heterostructures**
Pranjay Laxmesh$^1$, Tessa D. Tucker$^2$, Rajeev Kumar Rai$^2$, Shuchen Li$^3$, Myoung-Woo Yoo$^1$, Eric A. Stach$^3$, Axel Hoffmann$^4$ and Steven May$^1$; $^1$Drexel University, United States; $^2$University of Pennsylvania, United States; $^3$University of Illinois at Urbana-Champaign, United States

Binary kagomé compounds $T_{mx}^c$ (T=Mn, Fe, Co; X=Sn, Ge; $mn=3:1, 3:2, 1:1$) have garnered significant interest due to the coexistence of topological band crossings and flat bands stemming from the geometry of the metal-site kagomé lattice. In order to harness these distinctive electronic band features for potential applications in spintronics, it is imperative to grow high-quality heterostructures. In this work, we detail the synthesis of Fe/FeSn and Co/FeSn bilayers on c-axis-oriented Al$_2$O$_3$ substrates, achieved via molecular beam epitaxy. The use of elemental buffer layers (Fe and Co) facilitates the growth of smooth and continuous FeSn films, while also enabling the formation of heterointerfaces between elemental ferromagnetic metals and antiferromagnetic kagomé metal FeSn. Structural characterization using high-resolution X-ray diffraction, scanning electron microscopy and transport measurements revealed the FeSn films were flat and epitaxial with well defined interfaces. Rutherford backscattering spectrometry was used to confirm the stoichiometric window where single phase FeSn films are stabilized, while transport and magnetometry measurements were conducted to verify metallicity and magnetic ordering in the bilayers. We observe exchange bias in both bilayer systems, affirming the existence of antiferromagnetic order in FeSn, thus opening possibilities for further investigations into interfacing magnetism in kagomé heterostructures and the potential integration of these materials into spintronics devices.

Work at Drexel University and the University of Illinois at Urbana-Champaign was supported by the National Science Foundation, grant number ECCS-2031870. Work at University of Pennsylvania was supported by University of Pennsylvania Materials Research Science and Engineering Center (MRSEC) (DMR-2309043).

**5:00 PM QT02.07.07**

**Synthesis of Mn-Doped Bi$_2$Te$_3$ via Chemical Vapor Deposition**
Matthew E. Metcalf$^1$, Bamidele O. Onipede$^1$, Shaan Dia$^2$, Alexander Giagso$^1$ and Hui Cai$^1$; $^1$University of California, Merced, United States; $^2$Carleton College, United States

Doping a topological insulator with magnetic elements can produce magnetic ordering within the material, breaking the time-reversal symmetry of the surface electronic states. Without this symmetry, topological insulators can exhibit many exotic quantum phenomena that are of theoretical interest and not well studied, including the quantum anomalous Hall effect, chiral Majorana modes, and topological magnetoelectric effects. In this work, we synthesized Mn-doped Bi$_2$Te$_3$, a topological insulator doped with a magnetic element, using atmospheric pressure chemical vapor deposition (CVD) and characterized our samples with optical microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. The optimal values and acceptable ranges of several CVD growth parameters were determined by systematically varying each parameter one at a time. By utilizing CVD to synthesize Mn-doped Bi$_2$Te$_3$, this work demonstrates a simple, scalable, and low-cost process that offers precise control over the stoichiometry of grown crystals and opens the door to the production of high-quality atomically thin crystals–features which make CVD a useful and promising technique for future studies of magnetic topological insulators.

**5:00 PM QT02.07.08**

**Strong Above Room Temperature Intrinsic Magnetism of Freestanding Layered CrTe$_2$ Crystal**
Lihua Zhang$^1$, Kim Kisslinger$^1$, Saji Park$^1$, Seng Huat Lee$^2$, Yu Wang$^2$, Zhiqiang Mao$^2$, Neha Dhillon$^2,3$, Weichang Lin$^3$, Zonghuan Lu$^3$, Toh-Ming Lu$^3$, and Gwo-Ching Wang$^3$; $^1$Center for Functional Nanomaterials, Brookhaven National Lab, United States; $^2$2D Crystal Consortium, Materials Research Institute, The Pennsylvania State University, United States; $^3$Physics, Applied Physics and Astronomy Department, Rensselaer Polytechnic Institute, United States

Abstract: Magnetism in van der Waals (vdW) layered materials has attracted worldwide attention in fundamental condensed matter material research. Magnetism in low dimension materials has many exciting emerging properties and great potential for applications in low power spintronics, quantum computing, data storage, etc. Most monolayer (ML) vdW materials have been demonstrated to have Curie temperatures ($T_c$) below 300 K [1] or near room temperature [2]. This is because thermal fluctuations destroy the long-range magnetic order in a ML material according to Mermin-Wagner theorem. Thus, demands for the growth of bulk vdW layered materials to increase its $T_c$ to above room temperature remains challenging. Only recently, bulk 1T-CrTe$_2$ crystal of nm size was synthesized from K deuteration of CrTe$_2$ and its room temperature $T_c$ (310 K) was reported [3]. In this work, we present synthesized CrTe$_2$ crystals made from a similar method. We present our structure, chemical stoichiometry, vibrational, and magnetic properties of free standing CrTe$_2$ crystal measured by transmission electron microscopy (TEM), X-ray diffraction (XRD), electron backscatter diffraction (EBSD), energy dispersive X-ray spectroscopy (EDS), Raman scattering, superconducting quantum interference device (SQUID), and surface magneto-optical Kerr effect (SMOKE) techniques. TEM and XRD show CrTe$_2$ has crystalline layered structure with (0001) out-of-plane orientation with bulk lattice constants. EBSD shows a six-fold hexagonal crystal symmetry. EDS and Raman spectra show correct stoichiometry of 1 to 2 for Cr to Te ratio. All data support the synthesized crystals are of high quality. The temperatures dependent magnetization shows a phase transition at a $T_c$ (317 K) above room temperature. The critical exponents extracted from the critical field range are consistent with the classic 3D Ising model's prediction. SQUID measurement of CrTe$_2$ crystal at room temperature shows hysteresis loops with low coercivity (~20 Oe). Since the $362 nm$ laser wavelength's penetration depth depends on the laser incident angle, the probing depth is within sub-tens of nm below surface, therefore the magnetic hysteresis loop measured by SMOKE is effectively from ultrathin layers of the CrTe$_2$ crystal.

Acknowledgements: This work is supported by the Center for Functional Nanomaterials, Brookhaven National Laboratory under DE-SC0012704, Penn State 2D Crystal Consortium –Materials Innovation Platform under NSF DMR-2039351, and the NYSTAR Focus Center at RPI, C180117.

References:

**5:00 PM QT02.07.09**

**Diffuse Scattering in The Chiral Magnet BaCoSiO$_4$**
James W. Beare$^1$, Huibo Cao$^1$, Chenyang Jiang$^1$, Zachary Morgan$^1$, Feng Ye$^1$, Yongqiang Cheng$^1$, Erxi Feng$^1$, Xiaojian Bai$^2$, Xianghan Xu$^3$ and Sang-Wook Cheong$^1$; $^1$Oak Ridge National Lab, United States; $^2$Louisiana State University, United States; $^3$Rutgers, The State University of New Jersey, United States

In certain chiral magnets, a chiral arrangement of magnetic spins breaks both time reversal and spatial inversion symmetry, forming a toroidal moment. This symmetry breaking allows for the magnetoelectric effect, making these materials promising candidates for device applications. In BaCoSiO$_4$, Co ions form hexagonal layers in which magnetic interactions between the nearest
five Co neighbors, as well as the antisymmetric DM interaction, are all important, leading to a complicated competition between interactions on this frustrated lattice. The ground state structure can be explained by a trimerization of Co ions into one-dimensional moments which form three interpenetrating sublattices, one of which has a toroidal moment opposite to the other two. Along with the frustration due to antiferromagnetic interactions within triangular trimers, there is structural short-range order which may contribute to additional frustration. In this talk, I will present diffuse scattering results which give insight into the short range magnetic and structural order within the material. Modeling both types of short-range order within the paramagnetic phase will improve our understanding of this exotic magnet.

The research was supported by the U.S. Department of Energy (DOE), Early Career Research Program Awards KC0402020 and KC0402010, and used resources at the HFIR and SNS, DOE Office of Science User Facilities operated by ORNL.

5:00 PM QT02.07.10
Pillars of Discovery: Two Novel Divalent Transition Metal Germananates as Potential Multiferroics Megan Smart1, Jie Xing1, Colin McMillen2, Joseph Kolis2, Fankang Li1 and Huibo Cao1; 1Oak Ridge National Laboratory, United States; 2Clemson University, United States

The pursuit of novel magnetic materials has driven inorganic crystal chemistry towards many exciting discoveries, from rare earth magnets to hexaferrites to elusive quantum materials such as spin liquids. One material class of interest are multiferroics, which combine the desirable properties of ferromagnetism and ferroelectricity, the latter of which requires crystallization in a polar space group. High-quality single crystals of inorganic oxides can be grown via hydrothermal synthetic methods using magnetic ions such as Co2+ and Cu2+, with non-magnetic Ge4+ as a building block. Two such compounds were hydrothermally synthesized, Ba$_2$Rh$_2$Co$_5$O$_{15}$ (1) and Sr$_2$K$_2$Cu$_3$Ga$_2$O$_{12}$ (2), which crystallize in the acentric, polar space group P6$_3$cm. The polar feature of the unit cell is the ‘pillar’ propagating along each vertex on the c-axis. These pillars contain alternating trimers of TM$^2$ (TM = Co, Cu) in tetrahedral and trigonal pyramidal geometries, and are separated by a central germanate cluster. With the conditions for ferroelectricity met, initial magnetic studies were performed, and their results are presented here.

The Co-germanate shows two magnetic transitions in the susceptibility measurements, both suggesting magnetic short-range order. The compound does not have structural disorder, therefore the magnetic short-range order likely originates from magnetic frustration. Two successive transitions possibly represent dimensionality cross-over transitions. The neutron scattering studies are underway to uncover the nature of magnetic transitions and phases in Ba$_2$Rh$_2$Co$_5$Ge$_2$O$_{15}$.

*The research was supported by the U.S. Department of Energy (DOE), Early Career Research Program Award KC0402020 and used resources at the HFIR, DOE Office of Science User Facilities operated by ORNL.

5:00 PM QT02.07.11
Quantum Criticality in Spin Dimer System BaNd$_2$ZnS$_5$ Kyle Ma1, Brianna Billingsley2, Madalynn Marshall3, Xiaojian Bai3, Barry Winn3, Cristian Batista4, Tai Kong2 and Huibo Cao1; 1Oak Ridge National Laboratory, United States; 2The University of Arizona, United States; 3Louisiana State University, United States; 4The University of Tennessee, Knoxville, United States

We investigated the partial-disordered state of the Shastry-Sutherland system BaNd$_2$ZnS$_5$ utilizing the time-of-flight inelastic neutron scattering spectrometer HYSPEC at the Spallation Neutron Source (SNS) of the Oak Ridge National Laboratory (ORNL). Through modeling the field evolution of low-energy spin excitations up to 4T, we uncovered that the disordered states result from a delicate balance between the external magnetic field and antiferromagnetic (AF) inter-dimer Ising interactions. The intra-dimer interaction is predominantly Ising along the ordered moment direction, with a slight mixing of J$_+$ and J$_-$. Paramagnetic measurements ranging from 0 to 4T of the order parameters of the ferromagnetic (FM) and antiferromagnetic (AFM) phases at 40mK were conducted using the DEMAND diffractometer at the High Flux Isotope Reactor of ORNL. The order parameter displays characteristics indicative of a quantum critical point and can be effectively modeled using semi-classical treatment based on SU(4) coherent states. Although the longitudinal mode can not be quantitatively characterized, its presence is essential to explain the observed data, suggesting that the puzzling metamagnetic transition originates from the ordered antiferromagnetic state transitioning to the disordered quantum paramagnetic state.

SESSION QT02.08: Ultrafast Imaging and Control of Magnetism
Session Chair: Dmitry Ovchinnikov and Veronika Sunko
Thursday Morning, April 25, 2024
Room 421, Level 4, Summit

9:15 AM QT02.08.02
Exciton Transport in Van der Waals Antiferromagnet CrSBr Florian Dimmerker1,2, Sofia Terres1, Ksenia Mosina2, Zdenek Sofer3, Akashdeep Kamra3, Mikhail M. Glazov4 and Alexey Chernikov1; 1Institute of Applied Physics and Würzburg-Dresden Cluster of Excellence, Germany; 2Department of Inorganic Chemistry, Czechia; 3Departamento de Física Teórica de la Materia Condensada and Condensed Matter Physics Center (IFIMAC), Spain; 4Ioffe Institute, Russian Federation

The recent discovery of magnetic excitons – a rare type of optical excitation that emerges from spin-polarized electronic states in magnets – raises important questions about elemental interactions between excitons, magnons, and light. The prototypical layered antiferromagnetic semiconductor CrSBr and its strongly bound excitons are a critical platform to address such questions. In this contribution, we present the results of a study of the spatial transport of this intriguing type of exciton with particular focus on the role of magnetic order. We demonstrate highly non-linear exciton transport with unusual temperature dependence that culminates in substantially enhanced exciton propagation at the antiferromagnet-to-paramagnet phase transition. Observations of anomalous and effectively negative transport further indicate the substantial coupling of excitonic, vibronic, and magnetic degrees of freedom.

9:30 AM QT02.08.03
Spin-Orbit Torque in Magnetic Heterostructures: Exchange Interactions and Ultrasensitive Sagnac Magneto-Optic Interferometry Thow Min Jerald Cham1, Saba Karimeddiny1, Orion Smedley1, Reiley Dorrnan1, Xiuyu S. Zhang1, Avalon Dismukes2, Daniel Chaica2, Andrew F. May3, David A. Muller3, Xavier Roy3, Daniel C. Ralph3 and Yunquu Kelly Luo1; 1Cornell University, United States; 2Columbia University, United States; 3Oak Ridge National Laboratory, United States; 4University of Southern California, United States

In this two-part talk, we will first present our recent progress in advancing spin-orbit-torque metrology by adapting an ultrasensitive Sagnac magneto-optic interferometry originally developed for time-measurement symmetry breaking in exotic superconductors, and applying it for the first time to measuring spin-orbit torques. We will introduce the concept of Sagnac interferometry with an ultrahigh Kerr sensitivity of ~ 5µRad/√Hz and describe how such high sensitivity allows quantitative measurements of spin-orbit torque by sensing current-induced small-angle magnetization tilting. This method is especially advantageous for insulating magnets for which conventional transport spin-orbit torque metrology can be disrupted by magneto-thermal artifacts, but it can also be applied widely to broad classes of magnets regardless of conductivity and small net magnetization.

Secondly, we will present our recent work in identifying the gigahertz antiferromagnetic resonances within the easy-axis van der Waals (vdW) magnet CrSBr and understanding how their magnetic order. We demonstrate highly non-linear exciton transport with unusual temperature dependence that culminates in substantially enhanced exciton propagation at the antiferromagnet-to-paramagnet phase transition. Observations of anomalous and effectively negative transport further indicate the substantial coupling of excitonic, vibronic, and magnetic degrees of freedom.


10:00 AM BREAK

10:30 AM *QT02.08.04
Spin-Orbit Torque in Magnetic Heterostructures: Exchange Interactions and Ultrasensitive Sagnac Magneto-Optic Interferometry Thow Min Jerald Cham1, Saba Karimeddiny1, Orion Smedley1, Reiley Dorrnan1, Xiuyu S. Zhang1, Avalon Dismukes2, Daniel Chaica2, Andrew F. May3, David A. Muller3, Xavier Roy3, Daniel C. Ralph3 and Yunquu Kelly Luo1; 1Cornell University, United States; 2Columbia University, United States; 3Oak Ridge National Laboratory, United States; 4University of Southern California, United States
Parametric optical nonlinearities are critical to a wide spectrum of photonic technologies, from optical parametric oscillators to frequency combs to quantum information processing. Optical nonlinearities also play a powerful role in the fundamental properties of electronic structure, including the symmetries of electronic structure. Optical nonlinearities are generally very small in conventional materials as they depend on higher order effects. Parallel to these technical needs, the field of topological materials has seen the prediction and discovery of a large number of massless, three-dimensional linear dispersion systems known as Dirac and Weyl semimetals. It was soon realized that these materials may offer a rich new material phase space for extending the nonlinear effects of graphene including the role of topology and Berry connection. In this context, I will present our recent work on predicting the optoelectronic and nonlinear properties of Dirac and Weyl semimetals with an emphasis on figures of merit (FoMs) that we will evaluate for these new Weyl and Dirac semimetals that capture the confinement and nonlinearity to describe the second and third order susceptibilities and electro-optic coefficients of the materials. Next, I will discuss our recent results on the multiphoton spectroscopy of a dynamical axion insulator. Here, the axion receives contributions from the collective motion of electrons, leading to a nonlinear topological magnetoelectric effect. Identifying this collective axion response faces a number of major experimental difficulties, which necessitate a theory-predicted smoking gun signature. We demonstrate a two-step protocol for the unambiguous optical identification of the collective axion mode in such a system. First, we show how collective oscillations of the axion mode can be induced by two-photon absorption or stimulated Raman spectroscopy, with the magnetoelectric nature of the excitation manifesting in the polarization dependence of the excitation beams. Second, we show how the axion oscillations can be converted to signature manifestations in the time-resolved Kerr-rotation, which again carries signature polarization dependence due to the magnetoelectric nature of the coupling. Looking ahead, I will discuss how collective responses in topological quantum materials can be unambiguously identified in nonlinear electrodynamical probes, as well as identify potential avenues for intersections with particle physics in axion electrodynamics.

11:00 AM QT02.08.05
Scalable One-Dimensional Excitons in a Van der Waals Magnet
Veronika Sunko
Symmetry-Breaking Pathway towards The Unpinned Broken Helix
1:30 PM
Yamakawa1,2, Yue Sun1,2, Rafael M. Fernandes3, Jian Rui Soh4, Dharmalingam Prabhakaran5, Andrew Boothroyd5, James G. Analytis1,2, Joel Moore1,2 and Joe Orenstein1,2; 1UC Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States; 3University of Minnesota, United States; 4Institute of Physics, École Polytechnique Fédérale de Lausanne, Switzerland; 5King's College London, United Kingdom; 6Radboud University, Netherlands; 7University of Chemistry and Technology Prague, Czechia; 8University of Regensburg, Germany
The discovery of two-dimensional (2D) van der Waals magnets has greatly expanded our ability to create and control nanoscale phases. A unique capability appears when a 2D magnet is also a semiconductor, which features tightly bound excitons with large oscillator strengths and potential tunability with magnetic field. While crystalline and geometric anisotropy can lead to anisotropic 2D (black phosphorus) and even 1D excitons (carbon nanotube), the superior excitonic properties do not easily scale up with increasing layer number/system size. Here we report scalable 1D excitons in the 2D A-Type antiferromagnetic semiconductor CrSb from few-layer to the bulk limit. The 1D confinement originates from a combination of in-plane crystalline anisotropy and inter-plane magnetic anisotropy. Magnetic confinement of the 1D excitons is established through the layer dependence and temperature dependence of the exciton properties, and further corroborated with ab initio theory calculations. Our work establishes a novel avenue towards the large-scale application of emergent functionalities of low-dimensional materials.

11:15 AM QT02.08.06
Fast Light-Driven Domain Walls in a Parent Cuprate
Kyle Seyler
Symmetry-Breaking Pathway towards The Unpinned Broken Helix
11:45 AM
Kyle Seyler
University of Arizona, United States
Quantum materials exhibit fascinating phenomena when perturbed on short time scales or viewed at small length scales. For example, ultrafast light pulses can induce nonequilibrium behaviors that are thermally inaccessible. In addition, rich mesoscopic heterogeneity often exists in equilibrium, including the presence of domain walls that lie at the interface between different domains. Merging direct spatial imaging with ultrafast time resolution therefore has tremendous potential to reveal intriguing light-induced domain wall dynamics but is often experimentally challenging. In this talk, I will show how ultrafast optical pulses can be harnessed to both image and dynamically manipulate the antiferromagnetic domain walls in a variant of the parent cuprates. In particular, I will highlight our discovery that antiferromagnetic domain walls can be driven to fast speeds by intense circularly polarized laser pulses. These results provide an unprecedented view of domain wall dynamics in quantum materials.

11:45 AM QT02.08.07
Anil Rajapitamahuni
Angle-Resolved Photoemission Spectroscopy Studies of Flat Bands in Rhombohedral Graphene
Yiping Wang1, Youn Jue Bae1, Andrew Millis1, Mikhail Katsnelson5, Mark van Schilfgaarde3, Kseniia Mosina6, Zdenek Sofer6, Alexey Chernikov2, Rupert Huber2, Yaoxiong Zhu1, Xavier Roy1 and D. Basov1; 1Columbia University, United States; 2Technische Universität Dresden, Germany; 3National Renewable Energy Laboratory, United States; 4King’s College London, United Kingdom; 5Radboud University, Netherlands; 6University of Chemistry and Technology Prague, Czechia; 7University of Regensburg, Germany
The emergence of interaction driven phases in the twisted two-dimensional (2D) van der Waals heterostructures is due to the presence of van Hove singularities or flat bands where Coulomb repulsion energies dominate the kinetic energy of electrons. However, the correlated phenomena in twisted systems are extremely sensitive to angle disorder and strain, making them hard to achieve for experimental reproducibility. In this regard, graphene multilayers with rhombohedral or ABC stacking offers a different route to achieve flat bands. In this work, we have systematically studied the electronic structure of ABC stacked multilayer graphene via high resolution angle resolved photoemission spectroscopy (ARPES). Few-layer (4 - 120) graphene flakes are directly exfoliated on to highly conducting Si (100) substrates using blue tape. We then identified ABC stacked flakes via Raman spectroscopy measurements. The thickness of the flakes is determined via atomic force microscopy (AFM). Synchrotron-based micro-ARPES experiments revealed intense flat bands around the K point, close to Fermi level (E_F)
The presence of the flat bands over a large, measured photon energy range (44 -235 eV) confirms their surface origin. From the energy distribution curves (EDCs) stacks a curvature in the Fermi surface is determined via atomic force microscopy (AFM). Synchrotron-based micro-ARPES experiments revealed intense flat bands around the K point, close to Fermi level (E_F)

SESSION QT02.09: Imaging and Control of Magnetism
Session Chairs: Ahmet Avar and Kyle Seyler
Thursday Afternoon, April 25, 2024
Room 421, Level 4, Summit
1:30 PM QT02.09.01
Symmetry-Breaking Pathway towards The Unpinned Broken Helix
Veronika Sunko1,2, Elizabeth Donoway2, Thais Trevisani1,2, Alex Liebman - Pelaez1-2, Kohtar Yamaoka1-2, Yue Sun1-2, Rafael M. Fernandes3, Jian Rui Soh4, Dharmalingam Prabhakaran5, Andrew Boothroyd5, James G. Analytis1,2, Joel Moore1,2 and Joe Orenstein1,2; 1UC Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States; 3University of Minnesota, United States; 4Institute of Physics, École Polytechnique Fédérale de Lausanne, Switzerland; 5University of Oxford, United Kingdom
The search for materials exhibiting novel emergent properties relies on identification of their characteristic symmetries. A prominent example are materials in which magnetic symmetries promote topological phases, and consequently quantized responses to external stimuli. EulnA2Sb4, attracted attention when ab-initio calculations predicted that it hosts the elusive axion insulator state, based on the assumption of a simple collinear antiferromagnetic structure. Recently, scattering measurements revealed a much more intricate magnetic ground state, characterized by two coexisting magnetic wavevectors, reached by successive thermal phase transitions. The proposed magnetic phases were a spin helix and a state with penetrating helical and antiferromagnetic order, termed a broken helix. The symmetries of both deduced phases protected the axion state.
In this talk I will show results of magneto-optical experiments which are not compatible with the magnetic structures deduced by scattering. I will further demonstrate how combining the experimental information from scattering and symmetry-sensitive optics with an analysis based on group theory allowed us to uniquely identify the magnetic structure associated with each of the two phases. We find that the higher temperature phase hosts a nodal amplitude-modulated structure rather than a helix, characterized by a variation of magnetic moment amplitude from layer to layer, with the moment vanishing entirely in every third Eu layer. The lower temperature structure is similar to the broken helix, but with one important difference: the relative orientation of the magnetic structure and the lattice is not fixed, resulting in an unpinned broken helix. As a result of the consequent breaking of rotational symmetry, the axion phase is not generically protected in EulnA2Sb4 but we show that it can be restored if the magnetic structure is tuned with externally applied uniaxial strain. Finally, I will present a spin Hamiltonian that identifies the
interactions needed to account for the complex magnetic order in EuIn$_2$As$_2$, and how they arise from coupling to itinerant degrees of freedom.

Taken together, our results emphasize the power of a multimodal approach combining scattering experiments and symmetry-sensitive optical probes in identifying complex magnetic structures, as well as identifying EuIn$_2$As$_2$ as a remarkably tunable platform for exploration of magnetic symmetries.

2:00 PM QT02.09.02
Ferromagnetism in a Monolayer 2D Metal-Organic Framework [Fazouna Isufi Neziri]$^{1,2}$, Karl-heinz Emel$^{1,3}$ and Christian Wäckerlin$^{4,5}$; 1Universität Zürich, Switzerland; 2Swiss Federal Laboratories for Materials Science and Technology, Switzerland; 3The Czech Academy of Sciences, Czechia; 4Swiss Federal Institute of Technology Lausanne, Switzerland; 5Paul-Scherrer-Institut, Switzerland

Motivated by applications in information and energy technology, the search for new materials with stable long-range magnetic ordering continues. In this respect, metal-organic magnets, being built by coordination of metal-atoms with suitable ligands, have attracted significant attention in the recent years. Nanoscale magnetic materials with reduced dimensionality promise very interesting applications in information technology, e.g. information storage, information processing (spintronics) or quantum computing. The Mermin-Wagner theorem establishes that in systems with dimensions $D \leq 2$, governed by the isotropic Heisenberg exchange with short-range interactions, continuous symmetries cannot break spontaneously at finite temperatures. Only in presence of a significant magnetic anisotropy that counteracts random spin reorientations (or non-Heisenberg exchange interactions), ferromagnetism at low dimensions can occur. In this work, we show the existence of ferromagnetic coupling in a 2D metal-organic framework (MOF) consisting of Ni atom centers and tetracyanoethylene (TCNE) ligands on a Au(111) surface. Scanning tunneling microscopy (STM) shows a well-ordered MOF after co-deposition of Ni and TCNE. Analyses based on x-ray magnetic circular dichroism (XMCD) measurements reveal a strong out-of-plane magnetic anisotropy and a square like hysteresis loop with a coercive field of 1 T. Origin of such 2D ferromagnetism will be discussed.

2:15 PM QT02.09.03
Structural and Electronic Properties of Ti- and Ca-Doped Hexagonal TbInO$_3$
Kuntal Taluk$^{1}$, Nabaraj Pokhrel$^{1}$, Yang Zhang$^{2}$, Johanna Nordlander$^{2}$, Ismail El Baggari$^{2}$, Julia Mundy$^{2}$ and Elizabeth Nowadnick$^{2}$; 1University of California, Merced, United States; 2Harvard University, United States

Magnetic frustration combined with strong quantum fluctuations can create a quantum spin liquid ground state in that material. Doped spin liquids, which may host novel properties such as fractionalized charges and unconventional superconductivity are of fundamental interest and may hold promise for quantum computing applications. However, understanding what happens to added charge carriers in doped spin liquids remains a challenging problem. Recent research has demonstrated that hexagonal ferroelectric TbInO$_3$, characterized by anisotropic exchange interactions, substantial spin-orbit coupling, and $f$-electron magnetism, is a candidate spin liquid material. Low-dimensional frustrated magnetism in TbInO$_3$ arises from its layered crystal structure, consisting of nonmagnetic layers of corner-sharing InO$_6$ trigonal bipyramids alternating with layers of magnetic Tb$^{3+}$ ions arranged in a distorted triangular lattice featuring two distinct Tb sites. In this work, we employ density functional theory (DFT) calculations together with scanning transmission electron microscopy (STEM) imaging to investigate the effects of doping hexagonal TbInO$_3$ thin films via chemical substitution. We explicitly introduce Ti$^{4+}$ for electron doping and Ca$^{2+}$ for hole doping, systematically exploring various dopant concentrations and configurations. We investigate the evolution of the structural and ferroelectric properties of electron- and hole-doped TbInO$_3$, finding good agreement between changes to lattice parameters and atomic displacement amplitudes from our DFT calculations and STEM measurements. We also combine DFT calculations of the density of states with electron energy loss spectroscopy measurements to probe the evolution of the electronic structure of TbInO$_3$ upon Ti$^{4+}$ and Ca$^{2+}$ substitution. This research provides new insight into the structural and electronic properties of doped TbInO$_3$ and their implications for conductivity in low-dimensional frustrated magnetic states.

Funding acknowledgement: This material is based upon research supported by Air Force Office of Scientific Research (MURI Grant No. FA9550-21-1-0429).

2:30 PM QT02.09.04
Inelastic Neutron Scattering of The Spin-Liquid Candidate Ba$_3$ZnRu$_2$O$_9$ and Diluted Ba$_3$Zn(Ru$_{0.1}$Sb$_{0.9}$)$_2$O$_9$
Luke Cording$^{1}$, Jiawei Liu$^2$, Jun You Tan$^3$, Kenji Watanabe$^3$, Takashi Taniguchi$^3$, Barbaros Ozyilmaz$^2$ and Ahmet Avsar$^2$; 1Oak Ridge National Laboratory, United States; 2Argonne National Laboratory, United States; 3University of Missouri–Columbia, United States

Ba$_3$ZnRu$_2$O$_9$ (BZRO) is a 6-H perovskite compound with layers of $S=3/2$ Ru$^{5+}$ dimers arranged in a triangular lattice. There is no evidence of long-range magnetic order at temperatures as low as 37 mK, which suggests a potential spin liquid ground-state. [1] Inelastic neutron scattering results are presented from from BZRO (powder, crystal arrays) and the diamagnetic doped Ba$_3$Zn(Ru$_{0.1}$Sb$_{0.9}$)$_2$O$_9$. The BZRO shows highly dispersive excitations with no magnetic Bragg peaks. So, contrary to prior suggestions that a similar compound, Ba$_3$CaRu$_2$O$_9$, consists of magnetic dimers with negligible inter-dimer interactions, these data show that BZRO clearly deviates from a dimer model. Different analysis techniques of the correlations are illustrated, including coarse-graining the system so that dimers are local entangled units.


2:45 PM BREAK

SESSION QT02.10: Spintronic Devices Based on 2D Materials
Session Chairs: Marco Gibertini and Yungui Kelly Luo
Thursday Afternoon, April 25, 2024
Room 421, Level 4, Summit

3:15 PM *QT02.10.01
Superlative Spin Transport in Two-Dimensional Black Phosphorus
Luke Cording$^1$, Jiawei Liu$^2$, Jun You Tan$^3$, Kenji Watanabe$^3$, Takashi Taniguchi$^3$, Barbaros Ozyilmaz$^2$ and Ahmet Avsar$^2$; 1Oak Ridge National Laboratory, United States; 2Argonne National Laboratory, United States; 3University of Missouri–Columbia, United States

Exploitation of the intrinsic spin of an electron, spintronics, facilitates the development of multifunctional and novel devices which could play an important role in the Beyond-CMOS era. Two-dimensional (2D) crystals and their van der Waals heterostructures are particularly promising for spintronics device applications due to their unique properties, including strong responses to field effect gating and proximity interactions, which may enable new functionalities that are not possible with conventional bulk materials [1].

Two-dimensional black phosphorus is a promising material for semiconducting spintronics research due to its high charge mobilities, low atomic mass, and puckered crystalline structure, which are expected to lead to anisotropic spin transport with nanosecond spin-lifetimes. In this presentation, I will introduce ultra-thin BP as a unique platform for studying rich spin-dependent physics. Firstly, I will show that BP supports all electrical spin injection, transport, precession and detection up to room temperature [2]. Then, I will present our recent findings on the impact of field effect gating and proximity interactions, which may enable new functionalities that are not possible with conventional bulk materials [1].


3:45 PM *QT02.10.03
Graphene has weak spin-orbit coupling and no magnetic order. But when placed in contact with a strong spin-orbit coupling material, such as a TMDC, or a ferromagnet, such as Cr2Ge2Te6, Dirac electrons acquire strong spin-orbit and exchange coupling, respectively. Such proximity effects render graphene suitable for spintronic applications that require spin manipulation. In addition, graphene with strong spin-orbit spin interactions can host novel topological states.2) Fascinating new phenomena appear when bilayer graphene gets encapsulated by a TMDC from one side, and a ferromagnet from the other. The resulting, so-called ex-sto-tic structure,3 offers spin swap functionality: switching spin-orbit and exchange coupling on demand by the gate. In this talk, we will review recent developments in the proximity phenomena in graphene, and present some recent theoretical results on the control of the proximity spin-orbit and exchange coupling by twisting the van der Waals layers. I will show that the signature proximity spin-orbit coupling in graphene—valley Zeeman coupling—can be efficiently tuned by the twist angle4), and that proximity exchange coupling can be switched by the twist angle, and even morph from ferromagnetic to antiferromagnetic.5) Finally, I will also discuss the emergence of new correlated phases in AB bilayer and ABC trilayer graphene6) due to the presence of proximity spin-orbit and exchange couplings. Support from DFG SPP1244, SFB 1277, FLAGERA 2DSOTECH, and EU 2DSPINTECH is acknowledged.

References

10:45 AM • QT02.10.04
The Fabrication and Characterization of Spintronic Terahertz Emitter Using Magnetic/Non-Magnetic Bilayer with Nanometer Thickness Mikihiko Nishitani, Kohei Ejiri, Shinya Isosaki, Ruochen Dai, Shojiro Nishitani and Makoto Nakajima; Osaka University, Japan

The response time of electrons below the fermi energy in solids to electromagnetic waves is known to be on the order of femtoseconds. As a result, the energy transfer between electromagnetic waves and spins is ultrafast, at the terahertz frequency.1) Similarly, spin currents generated by spin polarization are described according to the LLG equation, i.e., the time dynamics of magnetization, and spin currents are expected to have a response time equivalent to that of electrons in the solid to electromagnetic waves. Furthermore, the effect of those spin currents being converted into electric currents by spin-orbit interactions or other effects is known as the inverse spin Hall effect, and the response time of those phenomena is also on the order of sub-picoseconds.2)

In 2013, Kampfrath et al. reported the emission of terahertz waves by femtosecond laser (photo-energy of 1.55eV) irradiation of magnetic/nonmagnetic bilayers composed of nanometer-thick films.2] Subsequently, those devices were named STE (Spintronic Terahertz emitters (STEs)), which have been actively studied in basic research as well as in application fields. We have been studying STE using ultrashort (several nanometer-thick) bilayers (PtFe, W/Fe, etc.) of nonmagnetic/magnetic materials on inexpensive, large-aperture (large area) substrates such as glass wafers, and the intensity of terahertz radiation by femtosecond laser irradiation is comparable to that of conventionally used nonlinear optical crystal ZnTe, and further advances are being made[3,4]. Specifically, we have been studying: 1) how to efficiently generate spin currents by femtosecond laser irradiation and 2) how to maximize the inverse spin Hall effect at the interface between magnetic and nonmagnetic materials.

In this report, we quantitatively evaluate the spin Hall angle, which is the figure of merit of the effect shown in 2) above mentioned, and investigate its relation to the experimental terahertz wave radiation intensity. The spin Hall angle was obtained by analyzing the magnetic field dependence of the spin Hall magnetoresistance, which is used to evaluate spintronic devices, and the terahertz radiation intensity was obtained using our TDS system. The obtained results show a good linear correspondence between the magnitude of the change in spin Hall magnetoresistance and the intensity of terahertz radiation. We plan to reflect these results in the fabrication conditions and in the progress of the technique to further improve the performance of this system.

References

SESSION QT02.11: Imaging of Magnetism in Magnetic Materials
Session Chairs: Eric Fullerton and Zhong Lin
Friday Morning, April 26, 2024
Room 421, Level 4, Summit

8:30 AM • QT02.11.01
Synthesis and Ferroelectric Field Effect Studies of Few-Layer CrCl3 Xiao Hong; University of Nebraska-Lincoln, United States

The van der Waals magnets CrX3 (X = I, Br, and Cl) exhibit highly tunable magnetic properties and are promising candidates for developing novel two-dimensional (2D) spintronic applications. The ability to synthesize atomically thin CrX3 samples and achieve voltage control of their magnetic states is critical for their technological implementation. In this talk, I will present our recent progress in the synthesis and ferroelectric field effect studies of large size few-layer CrCl3 flakes. Using the physical vapor transport technique, we have deposited high-quality CrCl3 flakes down to monolayer thickness on mica. Both isolated flakes with well-defined facets and long stripe samples exceeding 60 μm length have been obtained. High-resolution transmission electron microscopy and Raman studies confirm the high crystallinity of these samples. The tunneling magnetoresistance of graphite/CrCl3/graphite tunnel junctions reveals in-plane magnetic anisotropy and Néel temperature of 17 K of CrCl3. We encapsulate the tunnel junctions with free-standing ferroelectric PbZr0.2Ti0.8O3 membranes and define the polarization state of the top-gate via conductive atomic force microscopy. Ferroelectric polarization reversal leads to nonvolatile modulation of the tunneling current, with an on/off ratio of 106 obtained at room temperature. Compared with the negative tunneling magnetoresistance observed in hBN encapsulated devices, the PZT-gated CrCl3 tunnel junctions exhibit positive tunneling magnetoresistance at low temperatures, suggesting a change of magnetic state. Our study provides an effective strategy to design low power, scalable, flexible 2D nanoelectronics and spintronics.

This work was primarily supported by NSF through Grant No. DMR-2118828 and ERSCoR EQUATE Award No. OIA-2044049, and Nebraska Center for Energy Sciences Research.

9:00 AM • QT02.11.02
STEM Developments: Atomic-Resolution SE Imaging, Fast 4D STEM, Ultra-High Energy Resolution Tracy C. Lovejoy; Nion, United States

A new type of secondary electron (SE) detector designed by Nion for a modern STEM combines SE detection with an atom-sized probe in the operating range 20-200 kV, clean (metal-sealed and bakable) UHV vacuum conditions, and state-of-the-art electron energy loss spectroscopy (EELS) and 4D-STEM capabilities.1,2) Running experience reveals that common S/TEM samples (e.g. MoS2 or metal nanoparticles on a carbon film) that give atomic-resolution annual dark field (ADF) images initially show only surface contamination in the SE signal. We use multiple methods for SE surface cleaning, including resistive heating of the whole sample in a side entry holder (e.g. Protochips) and direct laser illumination of a small spot (20 mm x 40 mm). Direct laser illumination is particularly interesting because the laser light modulates the SE signal in some samples by changing the local charge distribution on the surface.

After cleaning, atomic-resolution SE signals are readily visible. Expanding on previous work with atomic-resolution SE imaging,4) lower operation voltage in a modern STEM avoids knock-on damage and enables atomic-resolution SE studies of 2D materials. We will show two examples: (1) combining atomic resolution ADF, SE, and 4D-STEM to study MoS2 with intentional Vanadium dopants at 60 keV primary energy, and (2) combining atomic resolution EELS and SE analysis to study the origins of the SE signal in a model system that can tolerate very high electron doses -- monolayer graphene with Nitrogen and Boron dopants.

4D-STEM and especially EELS experiments on 2D materials have traditionally been complicated by slow detectors and readout noise. The latest direct detectors avoid readout noise and
achieve high DQE and dynamic range with speed approaching that of traditional single-channel detectors (>10,000 frames/second). Combining these detectors with powerful open-source software for smart acquisition/compression and live processing makes multi-frame (time series) 4D-STEM or EELS imaging possible, bringing significant advantages when changing the sample environment (e.g. heating, cooling, light-, or gas-injection) causes sample drift that makes longer exposures impractical.

Doing these experiments in an instrument capable of <5 meV energy resolution [5] makes possible synergistic experiments such as mapping the absolute temperature of the sample and around the spot illuminated by a laser using electron energy gain spectroscopy [6] and measuring the presence and local bonding configuration of hydrogen in the sample by detecting the “infrared absorption” signal of the H bonds with vibrational EELS [7]. Phonon spectroscopy of surface dopants visible in the SE signal is also very promising.

References

3:00 PM *QT02.13: Devices and Control of Magnetism
Session Chairs: Matthew Daniels and Yunqiu Kelly Luo
Friday Afternoon, April 26, 2024
Room 421, Level 4, Summit

**10:30 AM *QT02.11:03**
**Scanning NV Microscopy** Mathieu Munsch and Peter Rickhaus; Qnami AG, Switzerland

We introduce Scanning NV Microscopy (SNVM) as a non-contact characterization technique to investigate magnetic materials and thin films. We show that SNVM can be used to evaluate MRAM performance at the individual bit level. Magnetic random-access memory (MRAM) is a leading emergent memory technology that is poised to replace current non-volatile memory technologies such as eFlash. However, controlling and improving distributions of device properties becomes a key enabler of new applications at this stage of technology development. Here, we demonstrate magnetic reversal characterization in individual, < 60 nm sized bits, to extract key magnetic properties, thermal stability, and switching statistics, and thereby gauge bit-to-bit uniformity. We showcase the performance of our method by benchmarking two distinct bit etching processes immediately after pattern formation. Finally, we will provide other examples of the applications of SNVM for the study of multiferroics, 2D materials, and magnonics.

**10:00 AM BREAK**
A new frontier in the search for the next-generation electronic, photonic, and spintronic devices is quasi 2D films of transition-metal phospho-trichalcogenides (MPX₃) where “M” is a transition metal and “X” is a chalcogen [1]. Recent studies have reported that MPX₃ structures are one of rare few-layer van der Waals (vdW) materials with stable intrinsic antiferromagnetism (AFM) even at mono- and few-layer thicknesses. The diverse properties of layered MPX₃ materials, tunable by proper selection and combination of the “M” and “X” elements make them an interesting platform for investigating novel low-dimensional device functionalities. The existence of weak vdW bonds between the MPX₃ layers allows one to scale them conveniently to individual atomic planes. The “M” element determines the AFM spin ordering. While Fe₃GeTe₂ shows an Ising-type phase transition at the Néel temperature ($T_N$), NiPS₃ follows XY-phase transitions, respectively. MPX₃ structures are semiconductors in nature and variation in the metal element modifies their bandgap from $-3$ eV to $-3.5$ eV. The latter opens up unique opportunities to design novel electronic and magnonic nanodevices suitable for optoelectronic and spintronic applications. However, the data on the electron transport properties and their interaction with spin ordering in these structures is scarce and requires detailed investigations. MPX₃ materials are highly resistive making electron transport measurements a formidable challenge in conventional lateral device structures. To overcome this challenge, we fabricated vertical h-BN/MPX₃ heterostructures where with different MPX₃ components hosting various AFM spin orderings. In this presentation, we report the results of our temperature-dependent cross-plane electrical transport and noise measurements. The low-frequency noise spectroscopy was used to detect the magnetic phase transitions [2]. In vertical h-BN/Fe₃GeTe₂ devices with the active layer characterized by the Ising-type spin order, we observed a combination of two Lorentzian bulges appearing in the overall $1/f$ noise envelope at close to $T_N$. These two features were attributed to the generation-recombination (G-R) and magnetic phase transition. The noise measurements of the vertical devices with both Fe₃GeTe₂ and NiPS₃ active layers, characterized by the Ising and XY AFM spin orders respectively, revealed multiple noise peaks near the magnetic phase transitions. The intensity of the noise peaks in NiPS₃ was significantly higher than that in the Fe₃GeTe₂ device. The comparison of noise characteristics for devices fabricated with two materials of different AFM spin ordering shows a strong dependence of noise on the particular magnetic spin direction and suggests a strong interplay of the magnetic and electrical properties in these AFM materials.

F.K. and A.B.B. acknowledge funding from the National Science Foundation (NSF), Division of Material Research (DMR) via the project No. 2205973 "Controlling Electron, Magnon, and Phonon States in Quasi 2D Antiferromagnetic Semiconductors for Enabling Novel Device Functionality.”


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Low-Frequency Electronic Noise Characteristics of Vertical Quasi-Two-Dimensional Antiferromagnetic Semiconductor Devices Subhajit Ghosh, Zahra E. Nataj, Fariborz Kargar and Alexander B. Balandin*

Department of Electrical and Computer Engineering
University of California, Riverside, United States

Abstract

Magnetic topological insulators and, so far, the largest reported for 2D magnets. The hitherto unobserved THE under zero magnetic field could provide a platform for the writing and electrical detection of TST aiming at energy-efficient devices based on vdW ferromagnets.
Liquid phase exfoliation (LPE) has become an important production technique for colloidal dispersions and solution-processable inks of a range of materials due to its versatility and applicability to a broad range of material classes. While mass production is possible, samples are inherently polydisperse and aspect ratios of lateral size/thickness are limited due to scission.
Two-dimensional, organic-inorganic hybrid perovskites (2DHPs) are stoichiometric compounds composed of alternating sheets of corner-sharing, metal-halide octahedra and organoammonium cationic layers. We study 2DHPs containing single lead iodide layers separated by intervening substituted, phenethylammonium (PEA) cations with the chemical structure of (x-PEA)2PbI4, where x = F, Cl, Br, or CH3. These 2DHPs form type-I heterojunctions in which excitons and carriers are strongly confined to the lead halide layers with exciton binding energies > 150 meV. We use x-ray diffraction and variable-temperature steady-state and time-resolved absorption and photoluminescence (PL) measurements to uncover the correlation between their structure and photophysical properties. (PEA)2PbI4 excitonic absorption and PL spectra at 15 K show splittings into regularly spaced resonances every 40–46 meV.1 Anti-Stokes hot exciton PL is observed at the same energy as the optical absorption resonance. Replacing a single atom in the para position of the PEA-cation phenyl group increases its length and therefore the interlayer spacing, but leaves the cross-sectional area unchanged and results in structurally similar metal halide frameworks.2 As the cation length increases, the absorption spectra broaden and blueshift, but the PL spectra remain invariant. In the ortho position with progressively larger cations increasingly distorts and strains the inorganic framework.3 Ortho substitutions change the number of and spacing between the discrete excitonic resonances and increase the hot exciton PL by >10X. By correlating the atomic substitutions on the cation with changes in the excitonic structure, we show that the origin of the discrete excitonic resonances is consistent with a vibronic progression caused by strong exciton-phonon coupling to a phonon on the organic cation. We also show evidence of the structure-dependent formation of exciton polarons.4 The properties of 2DHPs can be tailored by the selection of the cation without directly modifying the inorganic framework.5,6


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Structure-Property Engineering in The 2D Hybrid Perovskite Family

8:45 AM

*QT03.02.09
Towards In-Plane Control of Neutral Exciton Flux in Semiconducting 2D Materials

Hassan Lamsaadi1, Dorian Beret2, Ioannis Paradisanos3, Pierre Renucci2, Delphine Lagarde2, Marie Xavier2, Bernhard Urbaszek4, Ziyang Gan5, Antony George6, Kenji Watanabe7, Andrey Turchanin5, Takashi Taniguchi7, Laurent Lomb2, Nicolas Combe1, Vincent Paillard1 and Jean-marie Pounir1.

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For a wide range of next-generation applications in excitonic circuits, quantum optics and optoelectronics, neutral excitons in semiconducting 2D materials need to be controlled. Until now, and in particular in transition metal dichalcogenides, such control has been achieved through the local strain gradient engineering. However, the charge-neutral nature of the dominant exciton types in such materials limits their interaction with external electric or magnetic fields, still making their manipulation a challenging task. Recently, we demonstrated efficient unidirectional transport of excitons from high-gap to low-gap material at room-temperature in high-quality lateral heteromonomer [1]. Tip enhanced Raman and Photoluminescence spectroscopies (30nm resolution) performed on high-quality heteromonomers reveal that excitons generated inside the high-gap material are able to pass through the junction before recombining inside the low-gap material, while propagation in the opposite direction is forbidden. Going further, we have shown that the abrupt change in exciton energy and effective mass has resulted in a strong Kapitza resistance-like effect, allowing excitons to be accelerated locally at the junction as they move from high-gap to low-gap material while being blocked in the opposite direction [2]. This effect causes a strong discontinuity in the excitonic density profile at the junction. As a result, a quenching of high-gap material-related PL is observed while low-gap material-related PL is enhanced near the junction. Finally, by using µ-Photoluminescence(µ-PL) imaging combined with a simulation-based statistical approach of randomly moving excitons through specific geometries of a high-quality CVD-grown MoS2-WSe2 heterolayer, we demonstrated that the exciton Kapitza effect enhances the exciton diffusion length, and is able to focus and confine excitons down to sub-wavelength dimensions [3]. We believe that our work provides new tools for manipulating neutral excitons in flat semiconducting 2D materials and will enable the incorporation of lateral heteromonomers in next-generation excitonic devices.

References


SESSION QT03.03: 2D Halide and Chalcogenides Semiconductors III – Synthesis
Session Chairs: Cherie Kagan and Alexander Urban

Wednesday Morning, April 24, 2024
Room 444, Level 4, Summit

8:45 AM *QT03.03.01
Structure-Property Engineering in The 2D Hybrid Perovskite Family

David B. Mitzi; Duke University, United States

Two-dimensional hybrid organic-inorganic perovskites (2D HOIP) semiconductors based on metal halide frameworks offer unprecedented opportunity to tailor structural and materials properties using the full flexibility afforded by the realms of inorganic and organic chemistry,1 and such tunability offers wide-ranging potential for applications including solar cells, light-emitting devices, detectors, transistors and advanced computing devices. This talk will focus on examining the role that the organic cation plays in tuning one or more of the following: 1) self-assembling quantum well structures with predictable energy band offsets and charge carrier response,2,3 2) chirality transfer and symmetry breaking within the inorganic framework,4 and/or 3) melting and glass formation/crystalization kinetics.5,6 Recent examples of such structure-property flexibility highlight the unique versatility and promise of using the organic component to control charge, light and spin within the wide-ranging 2D HOIP family.


9:15 AM *QT03.03.03
Growth of Arbitrary 2D TMDs Nanopatterers via Thermal Scanning Probe Lithography

Giorgio Zambito, Maria Caterina Giordano, Matteo Gardella and Francesco Buatier de Mongeot; University of Genoa, Italy

Two dimensional (2D) materials have emerged as promising platforms for creating new generation, atomically thin devices in various fields, from nanoelectronics and nanophotonic, to quantum technologies and energy conversion [1–3]. These materials are generally manufactured from mechanically exfoliated flakes, which suffer from stochastic positioning and micrometric sizes. The re-shaping of 2D materials is attractive, since it opens interesting possibilities for engineering optoelectronic and photonic responses, as well as it enables the fabrication of devices with optimized geometries. Nanopatterning of exfoliated flakes is generally obtained by subtractive chemical etching methods [4] which, although effective for creating single demonstrative configurations, are not suitable for fabricating scalable devices for real-life applications.

Here we propose a process that allows the direct fabrication of few-layer MoS2 nano-circuits with arbitrary geometries. Our approach combines i) a custom-developed sputtering growth for creating few-layers MoS2 extended films and ii) a high-resolution lithography technique which makes use of a nanoscopic (10nm) hot silicon probe (thermal Scanning Probe Lithography – t-SPL, NanoFrazor). By the accurate manipulation of such hot nanoprobe, transiently heated by Joule effect, we write deterministic nanopaths onto a sacrificial polymer layer; these nanopatterns spread over a large-area substrate are homogeneously coated by few-layer MoS2 by the Ion Beam Sputtering (IBS) of a MoS2 target, leading to MoS2 nano-circuits with complex geometries and in-series scalability. After a proper high-temperature recrystallization process in a controlled atmosphere, these arbitrary MoS2 nano-interconnections are characterized by the means of micro-Raman spectroscopy and Kelvin Probe Force Microscopy (KPFM). The observed vibrational and electronic responses confirm the presence of the stable 2H semiconducting phase confined inside the nano-circuits.

After the fabrication of a proper nano-device configuration, the local electrical transport properties of these MoS2 nano-paths are investigated via conductive - AFM (ResiScope c-AFM), demonstrating the possibility to employ these 2D semiconducting nanocircuits as building blocks of integrated electronics devices.

Finally, we show some preliminary results on alternative applications of t-SPL on 2D materials, such as multilevel patterning of polymer films by 3D grayscale lithography. Indeed, the creation of three-dimensional patterns with arbitrary submicrometric features can serve as a tool to induce and study on-demand strain engineering of 2D materials.


Exciton self-trapping strategy, broadband emission is obtained under room conditions via tuning STE states from dark to bright. Temperature-dependent PL gives insights to the emissive

References


Acknowledgements: CCS acknowledges the Special Account for Research Funding of the University of Crete (grants KA10330 and KA10652), the project “NANO-TANDEM” (MIS 5029191), co-financed by Greece and the European Regional Development Fund, and the Ministry of Science and Higher Education of the Russian Federation (Megagrant no. 075-15-2022-1112) for financial support.

10:30 AM QT03.03.05

Extrinsic Doping and Compensating Defects in The 2D Hybrid Perovskite PEA$_2$PbI$_4$ Gabrielle Koknat, Haipeng Lu, Jin, Yi Yao, Ji Hao, Xixi Qin, Chuanshao Xiao, Ruyi Song, Florian Merz, Markus Rampp, Sebastian Kokott, Christian Carborgo, Tianyang Li, Glenn Teeter, Matthias Scheffler, Jörgen R. Berney, David B. Mitzi, Jeffrey Blackburn, Volker Blum, and Matthew C. Beard. Duke University, United States; National Renewable Energy Laboratory, United States; The Hong Kong University of Science and Technology, Hong Kong; Lenovo HPC Innovation Center, Germany; Max Planck Computing and Data Facility, Germany; The NOMAD laboratory at the Fritz Haber Institute of the Max Planck Society, Germany

2D hybrid organic-inorganic perovskites (HOIPs) are exciting materials for optoelectronic device applications due to their high degree of chemical and structural tunability. The ability to electronically dope these materials via incorporation of extrinsic dopants is essential for control over carrier concentrations. Conversely, the presence of intrinsic defects can negatively impact electronic doping efficiencies. Here, we present a systematic study of intrinsic point defects and extrinsic dopants (e.g., Bi, Sn [PRX Energy, 2, 023010 (2023)], both in isolation and as combined defects, in phenylethylammonium lead iodide (PEA$_2$PbI$_4$). Using spin-orbit coupled hybrid density functional theory (DFT) and supercell models up to 3,383 atoms in size, we pinpoint the expected positions of dopant-derived electronic levels in the bandgap. Complementary experimental findings reinforce hypotheses of compensation mechanisms and limiting factors derived from DFT.

10:45 AM QT03.03.06

Intergditation and Hydrogen Bonding in Benzotriazole-Based 2D Layered Perovskites: a Study of Organic Non-Covalent Interactions Arthur Mauport, Jesús Cerda Calatayud, Kristof Van Hecke, Davy Deduytsche, Arne Verding, Bart Rutens, Christophe Detavernier, Laurence Lutsen, Claudio Quarti, Wouter Van Gympel, David Beljonne, and Dirk Vanderzande. Hasselt University, Belgium; University of Mons, Belgium; Ghent University, Belgium; IMEC, Belgium

Extensive research in the past decade has shown that hybrid perovskites might become a cornerstone in the future global energy economy. Although three-dimensional 3D perovskites have been receiving a lot of research attention, their 2D layered counterparts have also been proven valuable to the field. In state-of-the-art 2D layered perovskites, alkylammonium and phenethylammonium cations are still mostly employed. Although these organic cations stabilize the perovskite, they do not offer valuable properties of their own to complement the attractive optoelectronic properties of the perovskite layers. Synergy could be achieved by choosing larger organic cations with more suitable optoelectronic properties, or by inserting organic charge-transfer complexes or dipole stacks in the organic layers. However, the non-covalent interactions acting within these more advanced organic layers need to be fully understood in order to formulate design rules and structure-property relationships for this novel class of materials.

In this work, benzotriazole-based organic cations have been utilized to obtain the materials in pure form and I will discuss the evolution of important homologous series that constitute the arch types of many related compounds. I will discuss how the optical properties of the materials vary in these systems, focusing of their ability to form stable excitonic states and the peculiar changes that occur in the spectra upon the numerous phase transitions observed in variable temperature experiments. I will conclude my talk by describing potential applications of layered perovskites that can benefit from the presence of stable excitons.

References

[5] A manuscript by the authors on organic non-covalent interactions in 2D layered perovskites is being prepared.

11:00 AM QT03.03.08

Self Trapped Exciton under Ambient Conditions in Two-Dimensional Halide Double Perovskites Triggered by Heterovalent Metal Substitution Chunyang Chi, Andrew B. Wong. National University of Singapore, Singapore; National University of California, Berkeley, United States

Layered double perovskites (LDPs) possess soft lattice and strong exciton-phonon interactions, which represent an emerging class of materials as promising self-trapped exciton (STE) emitters. However, few LDPs have been discovered with observable photoluminescence (PL) under room conditions hindered by the intrinsic parity-forbidden band transition. Herein, manganese (Mn) is incorporated into (PA)$_4$AgInBr$_8$ (PA=CH$_3$(CH$_2$)$_2$NH$_3^+$) to form (PA)$_4$Ag$_{1-x}$Mn$_x$In$_{1-x}$Br$_8$ (0≤x≤1) heterovalent-metal alloyed layered double perovskites. Halogen substitution is applied to characterize tunable optoelectronic properties of LDPs. Highly oriented thin films are fabricated and investigated via X-ray diffraction (XRD) and XPS. With this alloy-induced extrinsic exciton self-trapping strategy, broadband emission is obtained under room conditions via tuning STE states from dark to bright. Temperature-dependent PL gives insights to the emissive behavior and charge-carrier dynamics. The associated Huang-Rhys factors and exciton binding energies show the complexity of excitonic localization in this quantum-well-like structure. This study provides inspiration for designing novel lead-free PL-active perovskites and highlights the significance of understanding the intricate exciton-lattice coupling dynamics in LDPs.

SESSION QT03.04: 2D Halide and Chalcogenides Semiconductors IV – Devices

Session Chairs: Alexey Chernikov and Goki Eda
Achieving long-range ballistic (coherent) electron flow in materials at room temperature is a long-standing goal that could unlock lossless energy harvesting and wave-based information technologies. The key challenge is to overcome short-range scattering between electrons and lattice vibrations (phonons). I will describe several avenues to achieve ballistic transport by harnessing strong interactions between coherent and incoherent excitations in solid-state lattices. The first is to leverage polarization, part-light part-matter quasiparticles resulting from hybridization between photons and semiconductor excitations. The second is to leverage strong electronic and electron-phonon interactions, yielding either highly delocalized excitons or acoustic polarons that are intrinsically shielded from phonon scattering. In all cases, we develop ultrafast optical imaging capabilities enabling us to track the propagation of these quasiparticles with femtosecond resolution and few-nanometer sensitivity over a frequency range spanning the visible to the mid-IR, providing a precise measurement of quasiparticle velocity, scattering pathways, and transition from coherent to incoherent transport.

2:00 PM *QT03.04.02
Optoelectronics of Atomic Dopants in 2D Semiconductors Goki Eda; National University of Singapore, Singapore

Substitutional doping is a versatile approach for tailoring desired functionalities in 2D semiconductors. Unlike conventional semiconductors, dopants in 2D systems often possess a high activation energy due to reduced screening, leading to apparently minor effects on the host's electronic properties, even at relatively high concentrations. In this presentation, we will delve into the distinctive impact of atomic dopants on the optical, electrical, and optoelectrical characteristics of 2D semiconductors in contrast to traditional semiconductors. As an illustrative example, we will demonstrate that a single atomic impurity significantly enhances the local out-of-plane conductivity of 2D semiconductors by up to two orders of magnitude through resonant-assisted tunnelling. This breakthrough enables the rapid quantification of selected impurities in the dilute limit (<10^10 cm^-2) under ambient conditions, leveraging conductive atomic force microscopy. Additionally, we will elucidate how atomic impurities create a narrow impurity band that facilitates in-plane conduction beyond a critical concentration. We conclude by showcasing the photovoltaic effect generated by individual atomic impurity dopes within homolayers of doped transition metal dichalcogenides, as observed using photoconductive atomic force microscopy.


3:30 PM QT03.04.03
Emerging Van der Waals Heterostructures for Ultrathin Solar Cells: Implication of Type-II Band Edge Alignment on Photo-Conversion Efficiency Ponnapa K. Prasanna and Sudip Chakraborty; Harish Chandra Research Institute (HRI), India

The emerging two-dimensional (2D) materials, ZrSe₂ and HfSe₂, have been envisaged to construct the possible van der Waals heterostructures (vdW), for enhancement of solar cell efficiency. We have performed systematic first principles electronic structure calculations to explore the electronic band structures and optical properties of the heterostructures in order to determine the photo-conversion efficiency (PCE). We have considered both H and T phases of ZrSe₂ and HfSe₂ while constructing four different possibilities of heterostructures. From the analysis of band edge alignment, it has been found that the heterostructures are having Type-II band alignment, which helps in boosting the effective separation of electron-hole pairs, paving the way towards their application in materials for ultra-thin excitonic heterojunction solar cells. The electrostatic potential shows a huge difference in the dip which signifies the inbuilt electric field that is generated between two different surfaces therefore enhancing the transfer of electrons and holes between different layers. The optical absorption spectra of the heterostructures cover the wider range of the incident solar energy therefore better utilization of the incident radiation. The results show that the heterostructure formed by the H phase of ZrSe₂/HfSe₂ has attained a maximum power conversion efficiency of over 21%.

3:45 PM QT03.04.04
Spin LEDs Based on a Chiral Halide Perovskite Spin Injector Matthew Hautzinger, Kirstin M. Alberi and Matthew C. Beard; National Renewable Energy Laboratory, United States

The chirality induced spin selectivity (CISS) effect is the selective transmission of electron spin dictated by the handedness of chiral molecules (or structures). Materials exhibiting the CISS effect have great potential in acting as spin injectors, yet there are limited demonstrations of incorporating CISS active materials into spintronic devices. Here, we successfully integrate semiconductor nanowires (or quantum wells) with chiral perovskites using LED emitters. Based on the optical selection rules and conservation of angular momentum, we observe circularly polarized light emission as a result of the spin polarized injection from the chiral perovskite into the semiconductor. The large degree of spin polarization is enabled by the semiconductor-perovskite interface. To further understand what parameters dictate CISS based spin injection efficiency, we have incorporated chiral perovskites with a variety of emitter materials to probe the impact of band offsets, spin lifetimes, and composition. This demonstration opens numerous opportunities to incorporate CISS materials with semiconductors as opto-spintronic technologies and provide some ground rules for achieving high CISS based spin injection efficiency.

4:00 PM QT03.04.05
Ultrathin Chalcogenide Light Harvesters: Charge-Carrier Transport and Fast NIR Photodetectors Robert Hoye; University of Oxford, United Kingdom

Bismuth-based semiconductors have gained increasing attention as potential nontoxic alternatives to lead-halide perovskites.[1] Whilst most attention has been on bismuth-halide-based compounds, there is growing interest in broader families of materials, including chalcogenides, such as AB₂₉ materials (A = monovalent cation; B = Bi³⁺ or Sb³⁺; Z = chalcogen).[2] However, the semiconductors explored thus far have gradually-increasing absorption onsets, and their charge-carrier transport is not yet well understood. The first half of this talk discusses our recent work on cation-disordered NaBiS₂ nanocrystals,[3] which have a steep absorption onset, with absorption coefficients reaching >10⁶ cm⁻¹ just above its pseudo-direct bandgap of 1.4 eV. Surprisingly, we also observe an ultrafast (picosecond-timescale) photocconductivity decay and long-lived charge-carrier population persisting for over one microsecond in NaBiS₂ nanocrystals. These unusual features arise because of the non-bonding Sₚ character of the upper valence band, which leads to a high density of electronic states at the band edges, ultrafast localisation of spatially-separated electrons and holes, as well as the slow decay of trapped holes.

The second half of this talk covers our recent work on AgBiS₂, which also has high absorption strength, such that films only 50 nm thick are required to achieve adequate light absorption. Given the small bandgap of 1.2 eV, we demonstrate the utility of this material in near-infrared photodetectors. We achieve high cut-off frequencies reaching 0.5 MHz at 940 nm wavelength, along with >1 MHz cut-off frequencies in the visible wavelength range. Through detailed characterisation, we reveal the electronic-ionic transport properties of this material, and how these properties can be controlled to achieve fast NIR photodetectors. Finally, we demonstrate the practical application of these devices for heart beat monitoring.[4]

Overall, in this talk, the critical role of cation disorder in these ternary chalcogenide systems is revealed, especially how they influence optical absorption and charge-carrier kinetics.

Non-linear optical responses in 2D transition metal dichalcogenides (TMDs) have attracted increasing attention due to unique layered structures and the ability to generate a series of non-linear van der Waals (vdW) heterostructures. Unique combination of tunable optical properties and high carrier mobility of WS₂, as well as ZnO wide band gap, large exciton binding energy and through evaporation in a sandwich configuration.

In this work, we present controllable variation of the PL signal from chemical vapour deposition (CVD)-grown MoS₂ monolayer films. We demonstrate selective alteration of the MoS₂ PL intensity, bidirectional energy shift and spectral reshaping via superacid treatment or atomic layer deposition (ALD) of a high dielectric constant (high-κ) material. By submerging monolayer MoS₂ in a solution containing the superacidic bis-(trfluoromethanesulfonyl)amide (TFSA), we achieve improvement of the PL character, in agreement with previous reports. 7, 8 We find that superacid treatment induces significant enhancement of the absolute MoS₂ PL intensity, as well as blue shift in the energy of the emission and narrowing of the dominant peak. Conversely, we reveal opposing changes to the MoS₂ PL signal result from deposition of a high-κ dielectric. Grown by ALD, an atop layer of hafnium oxide (HfO₂) or aluminium oxide (Al₂O₃) layer is shown to attenuate the strength of the PL emission from monolayer MoS₂, with an accompanying redshift and broadening of the PL spectrum also observed. Via PL mapping, we confirm the treatment-induced modifications of the PL intensity to be prevalent across the MoS₂ surface following both TFSA and ALD-dielectric treatments. We utilise Lorentzian deconvolution of the PL spectra, coupled with a correlated analysis of the characteristic Raman peaks, to attribute the varying PL changes to differing charge doping and strain effects. 10 This work demonstrates facile control of the PL behaviour of CVD-MoS₂ monolayer films via application of an external chemical or dielectric treatment.

References
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7. S.L. Pain; N.E. Grant; J.D. Murphy, ACS Nano 16, 1260 (2022).

Developing Bismuth Sulphide Pellets for Low-Energy X-Ray Detection
Maja Momburu1, Kavya Reddy Duddapala2, Hugh Holan3, Robert L. Hoye2, Matthew C. Veale3, Laura Fornaro4 and Ivana Aguia4; 1Universidade de la Republica, Uruguay; 2University of Oxford, United Kingdom; 3Science and Technology Facilities Council, United Kingdom; 4Universidad de la Republica, Uruguay

Bismuth-based semiconductor materials are increasing in popularity due to their potential in optoelectronic applications such as solar cells and radiation detection. The latter application has uses spanning many fields, from medicine to homeland security. Given the nature of soft and hard X-rays and gamma radiation, being able to correctly detect their presence and measure them is imperative. In particular, BiSI has been studied for solar cells, especially in film deposition, and for X-ray detection in pellets from nanomaterials. In this work, we present the study of soft X-ray detection in BiSI pellets. BiSI nanorods were synthesized by either a solution or solvothermal method, using mono ethylene glycol as a reaction medium, and Bi₂S₃ and I₂ as reagents. The solution method yielded pure crystalline BiSI nanorods of 200 nm in average width, while the solvothermal method produced a composite of BiSI nanorods and amorphous carbon phases. Pellets were constructed with the powders by cold pressing with a uniaxial press. The orientation of the BiSI nanorods is parallel to the surface of the pellet, evidenced both by SEM and XRD characterization. In the case of the nanocomposite, this orientation is partly disrupted by the spherical nature of the carbon particles. Prototype devices were built by depositing Au contacts through evaporation in a sandwich configuration.

1-V curves were measured both in the dark and under X-ray irradiation. Dark current was measured up to 600 V and the resistivity was two orders of magnitude higher for the nanocomposite versus the pure compound, with values of 10⁸ to 10¹¹ Ω cm, respectively. This is in accordance to the fact that the composite has amorphous structure that limits the conductivity. The response to X-rays of 9 kV in energy was measured up to 20 V, and a linear response was obtained in both cases. When the dose was up to 4.2 μGy s⁻¹ at a fixed voltage of 20 V the current increased linearily. When comparing the two materials, the nanocomposite had a considerably better performance than the pure compound. The amorphous carbon particles lower the dark current, but do not contribute negatively to the photoconduction of the charge carriers generated by the X-rays. A notable advantage of this study is that the bias applied is considerably low with regards to usual operating voltages of direct semiconductor detectors, allowing for the possibility of using these devices in wearable technology, for instance in direct dosimeters. This work presents an easy, scalable and cheap way to produce low energy X-ray detectors with a suitable performance.

Observations and Maps of Second Harmonic Generation on 2D Chalcogenide MoS₂ Monolayers and Single Crystalline Thin Films
Xiaoxuan Fan1,2, Lawrence Mubwika2 and Lian Li2; 1Marshall University, United States; 2West Virginia University, United States

Non-linear optical responses in 2D transition metal dichalcogenides (TMDs) have attracted increasing attention due to unique layered structures and the ability to generate a series of non-linear harmonic waves, such as second harmonic generation (SHG). As an exotic class of atomically thin semiconductors, TMDs have emerged as a new generation of electronic and optoelectronic devices. MoS₂ monolayers and single crystalline thin films were deposited on Si substrates by a high-temperature tube furnace-based physical transport CVD system. MoS₂ monolayers showed SHG signals conducted by a homemade optical microscope system with filters to block the fundamental and higher frequency lasers. It was found that powerful SHG signals can be generated from single crystalline thin films compared to monolayers, indicating that the intensity of the non-linear optical responses is proportional to the number of layers. We have successfully mapped SHG profiles on monolayers and thin films through reflection mode by an optical detector, and the maps are analogous to their optical microscopic images. The mapping technique utilizes the intensity contrast of reflected lasers between the SHG area, which is different from the general area method used by others. Powerful SHG signals are generated from thick single crystalline thin films, potentially enabling immediate applications in optoelectronic devices and SHG light generators.

Understanding The Role of Defects in WS₂ Layer in Contact with ZnO Substrate
Dedi Sutarma and Peter Kratzer; University of Duisburg-Essen, Germany

The remarkable properties of two-dimensional (2D) materials have garnered significant attention in recent years, and understanding their fundamental behavior is critical for developing next-generation optoelectronics. In this study, we investigate the microscopic behavior of a 2D material, WS₂, with ZnO (1 1 0 0) taking the role as the substrate as well as charge injection layer in this van der Waals (vdW) heterostructures. Unique combination of tunable optical properties and high carrier mobility of WS₂, as well as ZnO wide band gap, large exciton binding energy and compatibility with existing fabrication technique, provides an attractive outlook for optoelectronic devices. Specifically, we aim to elucidate the role of native defects in WS₂/ZnO, such as sulphur and oxygen vacancies. Using Density Functional Theory (DFT) calculations, we examine the structural and optoelectronic properties of the WS₂/ZnO including the impact of point defects.
Transition metal dichalcogenide (TMD) monolayers hold great promise for advancing next-generation electronics and optoelectronics. The synthesis of large-area TMD monolayers with a high degree of crystallinity is crucial for enabling mass production and real-world applications. However, the influence of structural defects on the optical properties of these two-dimensional (2D) materials remains unclear. In this study, we demonstrate a method for synthesizing MoSe₂ monolayers with high concentrations of selenium vacancies. Using liquid-assisted chemical vapor deposition and by controlling the duration of the selenium feedstock during synthesis, we were able to introduce selenium vacancies into MoSe₂ monolayer flakes. As the flakes grew, we observed that double-selenium vacancies became more frequent at the edges of the flakes when compared to the central regions, whereas the concentration of single-selenium vacancies remained relatively constant throughout the entire flake of MoSe₂. These observations were confirmed by atomic-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). Furthermore, femtosecond transient absorption spectroscopy revealed a notably accelerated decay rate at the edges of the flakes, implying a higher likelihood of nonradiative transitions related to defects (e.g., double-selenium vacancies). Interestingly, photoluminescence (PL) spectroscopy showed an increase of approximately 40 meV in the energy of emission for both excitons A and B at the flake's edges when compared to the central region. Laser power-dependent PL measurements performed at the edge of the samples indicated a linear power relationship with the emission on the edge, suggesting the nature of a free exciton. Through first-principles density functional theory calculations, we confirmed that the selenium vacancy concentration is correlated with an increased bulk bandgap, which confirmed our observations in the PL measurements. These findings not only unveil the growth mechanism of liquid-assisted chemical vapor deposition on MoSe₂ but also contribute to a better understanding of the role of double-selenium vacancies in tailoring the optical properties of MoSe₂ monolayers.

References
Monolayers of transition-metal dichalcogenides (TMDs) exhibit fascinating properties that make them attractive in optics, electronics, spintronics, and valleytronics, and it is of vital importance to understand and control their morphology and tune their physical properties. However, the origin of their morphology evolution is still highly elusive, which hinders the synthesis of desired morphologies for specific applications. Herein, we report the controlled synthesis and formation mechanism of star-shaped WS2 monolayers by adding trace concentrations of molybdenum using a liquid-phase precursor-assisted approach. Fluorescence imaging and photoluminescence (PL) mapping of six-arm stars revealed bright lines between adjacent arms. To correlate the morphology and optical properties with the microstructure, second harmonic generation (SHG) microscopy and dark-field transmission electron microscopy (DF-TEM) were implemented to confirm the presence of polycrystal domains with a 60° lattice misorientation and a mirror twin grain boundary. Detailed analysis of the grain boundary and molybdenum distribution was assessed using high-resolution, high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The relationship of the growth morphology of WS2 stars and the molybdenum to tungsten ratio of the precursor was also carefully investigated. In corroboration with the experimental results, we further developed a multiscale model which combines density functional theory, ReaxFF based molecular dynamics simulations, a Wulff construction and a phase-field model, which demonstrated that the anisotropy of grain boundary (GB) energy due to molybdenum doping can lead to the star morphologies of WS2. Our study provides further insights into controlling the morphology of crystalline TMD monolayers, with implications for the development of field-programmable semiconductor memristor devices.

References


SESSION QT03.05.12

Self-Powered Photodetectors Based on Ruddlesden-Popper 2D Hybrid Perovskites with Carbazole Derivatives Anna N. Alphenaar, Xiaoyu Zhang and Quiming Yu; Cornell University, United States

Recently, carbazole-based organic cations have attracted the interests of scientists in a variety of fields for their potential application in 2D layered hybrid perovskite solar cells. These materials have demonstrated enhanced stability compared to other 2D and 3D hybrid perovskites which could allow them to achieve the level of self-sufficiency and environmental durability required of commercial solar cells. However, the potential incorporation of these highly efficient materials in photodetection has been largely unexplored. In this study, we synthesized CzEAP, a 2D layered organic-inorganic hybrid perovskite (OIP) containing PbI2 and a large organic ammonium 1-(9H-carbazol-9-yl)ethanaminium iodide (CzEAI) in a 1:2 molar ratio. We developed a series of thin films and devices in the configuration ITO/PEDOT:PSS/(CzEA)2PbI4/MOO3/Ag. Through optimization of the deposition procedure for this perovskite, we constructed novel photodetector devices with a specific detectivity of 6.95 × 10^7 Jones at 485 nm illumination and the ability to operate in a self-powered condition at 0V. The development of highly efficient self-sustaining photodetectors is essential to the progression of a wide range of fields including optical communications, security, video imaging, biomedical imaging, motion detection, and gas sensing.

SESSION QT03.05.14

Strain-Engineered Thermophysical Properties ranging from Band-Insulating to Topological Insulating Phases in β-Antimonene Sumit Kukreti; Indian Institute of Technology Jodhpur, India

Employing strain may lead to unusual modifications in the material’s properties. Low-dimensional materials having large mechanical strength are well suited for strain engineering. In our work, we present the structural, electronic, thermal, and vibrational characteristics along with the phonon and carrier dynamics of β-Sb elemental monolayers for achieving the band-insulating phase at no strain and topological insulating phase at ~15% biaxial strain. The weakened π and σ bonds under strain, leading to anharmonicity in the system. It is further reflected by the drop in lattice thermal conductivity (κT) from 4.5 to 3.1 W m−1 K−1 at ~15% strain, i.e., in the topological phase. Helical edge states at 15% strain and meeting the Z2 invariant criterion confirm the non-trivial topological state. Here we noticed the significant contribution of the out-of-plane A1g vibrational mode in the topological phase compared with the band-insulating phase. Importantly, the dominance of the out-of-plane optical modes contributes significantly to the topological phase along the band edges, which is primarily due to the reduced buckling height under strain. This work provides the microscopic origin of the onset of the topological phase in strained β-Sb monolayers and provides strain-engineered structure–property correlations for better insights.

SESSION QT03.05.15

Charge and Energy Transfer Across the Organic-Inorganic Interfaces of Two Dimensional Lead Halide Perovskites Anupama De and Libai Huang; Purdue University, United States

Creating heterojunctions enables the amalgamation of optimal properties from diverse materials, effectively bypassing individual bottlenecks. The essential photophysical phenomena in these materials are propelled by charge and energy transfer across these heterojunctions, making a comprehensive understanding of these processes imperative for optimizing such systems for energy conversion and harvesting applications. In our work on pyrene-based quasi-2D lead iodide perovskites, we explore how band engineering can instigate the formation of distinctive excited states and diverse optical phenomena. We conduct an in-depth analysis of their underlying mechanisms, also examining their competition with other parasitic processes. For the n=1 perovskite, efficient triplet energy transfer (TET) occurs from the inorganic sublattice to the organic layer, within the Marcus inverted domain. This transfer is driven by quantum tunneling, resulting in rarely witnessed temperature-invariant TET rates. On the other hand, the n>2 perovskite exhibits no TET. Instead, we observe the emergence of long-lived and mobile ‘interlayer’ excitons, originating from ultrafast charge transfer across the organic-inorganic interface.
physical mechanisms of these exciting materials. In this talk, I will overview our most recent results on prototypical structure of layered halide perovskites, vacancy ordered double perovskites, and low dimensional halide perovskite-like materials. I will present the key details of their electronic structure for each type of system that define their experimentally observed optical properties and achieved performances [1,2,3]. In the last part of my talk, I will show our latest findings on the effects of structural dimensionality on the charge carrier transport properties when comparing three-dimensional ABX$_3$ and layered halide perovskites.

References


Acknowledgements
This work was supported through the Center for Hybrid Organic Inorganic Semiconductors for Energy (CHOISE), an Energy Frontier Research Center funded by the Office of Basic Energy Sciences, Office of Science within the US Department of Energy.

References

10:30 AM QT03.06.04

Mechanistic and Electronic Properties of Ge$_2$Sb$_2$Te$_5$ Heterostructures with Different Layer Orderings from Density Functional Calculations
Tomi Ketolainen, Janne Kalikka, Tampere University, Finland

Previous experimental studies suggest that a large contrast in the electrical conductivity of Ge$_2$Sb$_2$Te$_5$ can be achieved also in heterostructures comprising specific sequences of single-layer materials without the amorphous-to-crystalline phase transition. In this work, we explore the effect of different layer orderings on the electrical conductivity and basic electronic properties of Ge$_2$Sb$_2$Te$_5$ heterostructures. We employ the VASP code package based on density functional theory (DFT) along with the DFT-D3 van der Waals correction and B3LYP2P code to compute electronic conductivity for six previously investigated stacking configurations. Furthermore, the lattice parameters, electronic band gaps, and electronic band structures are calculated for our set of 18-atom unit cells by using the DFT method.

Our calculations show that the in-plane (along the atomic layers) electrical conductivity is clearly larger than the out-of-plane (perpendicular to the atomic layers) electrical conductivity. Some
Two-dimensional (2D) metal organic chalcogenides (MOCs) such as silver phenylselenolate (AgSePh) have emerged as a new class of 2D materials due to their unique optical properties. These materials provide a basis for the semiconducting band structure, whilst the organic molecules stabilize the lattice, indirectly controlling the optical properties. These soft and ionic crystals possess many important properties. For example, they can be used as building blocks for the design of novel electronic and optoelectronic devices. In this work, we will discuss the optical properties of AgSePh, focusing on its two-dimensional band structure, and its potential applications in electronics and optoelectronics.
Two-dimensional (2D) lead halide perovskites are a very interesting group of novel semiconducting materials, considered an alternative for applications in photovoltaics and optoelectronics. Their structure can be seen as the "natural" quantum wells, where slabs of metal-halide octahedral units are surrounded from both sides by large organic cations, acting as potential barriers. As a consequence of the quantum and dielectric confinement, the excitation binding energy can reach several hundreds of millielectronvolts, which results in significant splitting of states of the exciton fine structure. This makes them attractive objects for the investigation of exciton physics, since all excitonic effects are greatly enhanced in this system. Significant state spacing and whether or not the lowest excitonic state interacts with photons are also crucial aspects affecting the performance of a device based on 2D perovskites. Gaining a deeper understanding of the exciton fine structure is therefore very important from the point of view of potential applications.

We combine the optical spectroscopy techniques with the use of magnetic field to investigate the exciton fine structure of perovskite compounds with the general formula (PEA)2(MA)n-1PbIn3-xI3+x, where n=1,2 denotes the number of octahedra layers within a slab. For the thinnest quantum wells (n=1) we reveal the full exciton fine structure, including the optically inactive electron-hole gauge factors. This theory requires separate knowledge of dielectric constants for wells and barriers, which we were able to deduce in a self-consistent manner for many materials. Using the results of our theory that we can tell that the most important parameters that affect E0 are well dielectric constant (metal halide layers), barrier length (organic molecules), and exciton reduced mass which we also relate to the MHP octahedral distortion; and we generate a parameter space map of realistically achievable (E0, E0) values. Finally, the dielectric constants required by the theory are between the microwave and optical-frequency dielectric values, indicating that the excitonic interaction is partially screened by phonons.

Layered van der Waals crystals are an exciting class of materials whose properties strongly depend on their thickness. Their structure makes them very sensitive to the interlayer spacing, which allows for the control of the exciton fine structure. In particular, we show that the moiré potential landscape is dynamic down to very low temperatures. Our observations show that the moiré patterns arising from the mismatched lattices of a moiré heterostructures can enable surprisingly efficient transport of energy in the form of excitons, even at low temperatures.
Dynamical Coulomb Screening in Atômically Thin Semiconducting Transition Metal Dichalcogenides

Amine Ben Mhamdi, Dinh Van Tuan, Leonard Geilen, Marko M. Petrlic, Kenji Watanabe, Takashi Taniguchi, Seifiattin I. Tongay, Kai Müller, Nathan P. Wilson, Jonathan J. Finley, Hanan Dery, Matteo Barbone, Technical University of Munich, Germany; Munich Center for Quantum Science and Technology (MCQST), Germany; University of Rochester, United States; National Institute for Materials Science, Japan; Arizona State University, United States

Reduced screening contributes to the particularly strong Coulomb interaction characteristic of 2D materials, which is behind the emergence of exotic quantum many-body phases found therein. While the 2D nature of these material systems complicates the screening description, its understanding is, to date, considered well-established, mainly based on static approaches. Here, we use exciton resonances as probes to study screening in monolayer WSe2, which we embed in dielectric environments with dielectric constants ranging from 5 to more than 1000. At odds with previous reports, we find evidence for an optical bandgap blueshift for larger dielectric constants. We understand the experimental findings by developing a fully dynamical approach to the environment dielectric response. Starting from the 3y model, we take the frequency dependence into account via the dynamical screening function, both in the bandgap renormalization and in the exciton binding energy calculations. While binding energy remains mainly controlled by low-frequency dielectric screening, we find that high-frequency dielectric response is predominant in bandgap renormalization. Our results show that a fundamental understanding of Coulomb interaction in atomically thin materials cannot ignore dynamical effects. The achieved tunability of the optical bandgap by more than 30 meV, together with the qualitatively different theoretical framework developed, offer new opportunities for tuning the optoelectronic properties of 2D semiconductors and advance the study of many-body interactions in layered materials and their heterostructures.

References:
Photonic Ferromagnets: Leveraging Chemistry to Develop New Van der Waals Ferromagnets with Strongly Coupled Spin and Optical Functionalities

11:00 AM

QT03.08.06

Enhanced Circular Dichroism and Polarized Emission in an Achiral, Low Bandgap Bismuth Iodide Perovskite Derivative

Philipp Klement1, Jakob Möbs2, Gina Stuhrmann3, Lukas Gümbel1, Marius Müller1, Johanna Heine2 and Sangam Chatterjee3; 1Justus Liebig University Giessen, Germany; 2Philipps-Universität Marburg, Germany; 3Karlsruhe Institute of Technology (KIT), Germany

Lead halide perovskites and related main-group halogenido metalates exhibit unique semiconductor properties, positioning them as promising candidates for next-generation optoelectronics. Their applications span solar cells, light-emitting diodes, lasers, sensors, and photo-catalysis. The approach of assembling customized building blocks into materials with tailored properties opens doors to explore novel phenomena. Recent advances in incorporating chiral organic cations have given rise to chiral metal-halide semiconductors. These materials exhibit intriguing properties such as chiroptical activity and chirality-induced spin selectivity, enabling the generation and detection of circularly polarized light and spin-polarized electrons for applications in spintronics and quantum information.

However, understanding the structural origin of chiroptical activity presents a challenge due to macroscopic factors and experimental constraints.

In our study, we present an achiral perovskite derivative \([\text{Cu}_3\text{I}_7\text{N}_3\text{O}_2\text{H}]\)\(_2\)\([\text{Bi}_3\text{I}_{11}]\)\(_2\)\(\text{pyz}\)\(\text{pyz}\); \(\text{pyz} = \text{pyrazine};\) \(\text{MCN} = \text{acetonitrile}\), which displays remarkable circular dichroism (CD) arising from the material’s noncentrosymmetric structure. CuBiI features a unique crystal structure as a poly-threaded iodido bismuthate, with \([\text{Bi}_3\text{I}_{11}]\)\(_2\) chains intertwined within a cationic two-dimensional coordination polymer. The material exhibits a low, direct optical band gap of 1.70 eV. Notably, single crystals exhibit both linear and circular optical activity with a substantial anisotropy factor of up to 0.16. Intriguingly, despite the absence of chiral building blocks, CuBiI exhibits a substantial degree of circularly polarized photoluminescence, reaching 4.9%. This value is comparable to the results achieved by incorporating chiral organic molecules into perovskites, typically ranging from 3% to 10% at zero magnetic field.

Our findings shed light on the macroscopic origin of CD and provide valuable insights for the design of materials with high chiroptical activity.


11:00 AM QT03.08.06

Photonic Ferromagnets: Leveraging Chemistry to Develop New Van der Waals Ferromagnets with Strongly Coupled Spin and Optical Functionalities

Kelly M. Walsh, Kimo Pressler, Thom Snoeren, Rachel Smith and Daniel R. Gamelin; University of Washington, United States

Materials with strongly coupled electronic, magnetic, and optical properties are highly desirable for application in next-generation spin-based devices. Magnetic van der Waals materials have been demonstrated to be attractive candidates for archetypal spin-based electronics, but such ferromagnets are often non-emissive or show only broad, nondescript luminescence. Moreover, their chemical parameter space is often largely explored. This presentation will describe the use of composition to develop new van der Waals materials that both are ferromagnetically ordered and show unique optical properties, with strong coupling between the two. In one example, we show that deliberate doping with optical impurities can transform the broad luminescence of the prototypical 2D ferromagnet, CrI\(_3\), into sharp /// luminescence of the lanthanide impurity, sensitized by the CrI\(_3\) host. We show that the impurity spin is pinned to the ferromagnetism of the CrI\(_3\) lattice, reflecting strong dopant-host exchange coupling and providing sensitive magnetic control over lanthanide emission polarization at exceptionally low fields. In another example, we have developed solution routes to growth of ferromagnetic 2D perovskites with complex compositions. These materials show strongly temperature-dependent absorption whose intensity reflects coupling to thermally populated 2D magnons. We also show that the air stability of these compounds can be increased dramatically through composition tuning. These demonstrations illustrate the ability to leverage the chemical tunability of layered 2D materials to access new and unusual magneto-optical functionalities.

SYMPOSIUM QT04

Superconducting Materials

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Materials Research on REBCO Superconductors to meet Application Requirements
Venkat Selvamanickam

2:00 PM
Vortex Pinning in Complex Heterogeneous Microstructures in REBCO Thin Films Formed by High-Density Artificial Pinning Centers
Kana Matsumoto1,2,3, Tomoya Hori1,2,3, Yutaka Yoshida1,2,3 and Ataru Ichinose4,3; 1Kyushu Institute of Technology, Japan; 2Nagoya University, Japan; 3JST-CREST, Japan; 4CRIEPI, Japan

Development of REBCO coated conductors is in progress, and it is desired to improve the superconducting current-carrying capability for equipment applications at operating temperatures near 20 K and 65 K. For this purpose, appropriate introduction of artificial pinning centers (APCs) into REBCO thin films is effective, and higher concentrations of APCs are needed. For example, the main pinning center in NbTi metallic wires is the α-Ti normal-conducting precipitate, with an upper limit of about 25-30% in volume fraction. However, the upper limit for the volume fraction of APCs in REBCO thin films is much lower. If it is possible to introduce APC in REBCO thin films up to the same level as the volume fraction of α-Ti, higher Jc performance is expected to be achieved. At present, it is known experimentally that the upper limit of APC concentration in REBCO thin films is about 5-10%. The reason for this is thought to be the increase in epitaxial distortion, formation of various lattice defects, and oxygen deficiency at the interface due to the introduction of APC, as well as the reduction of the superconducting current path due to the complex structure. Under such a complex and inhomogeneous structure, it is very difficult to find the optimal APC distribution for high magnetic field applications by a conventional screening method. We first investigate the microstructure of REBCO thin films near the upper limit of APC concentration and the degradation of superconducting performance caused by epitaxial distortion, in order to obtain clues for solving the upper limit problem of APC volume fraction. In this study, GdBCO thin films with BHO nanorods were fabricated on IBAD-CeO2 substrates by PLD method. The PLD targets were 4.0, 4.5, 5.0, and 5.5 wt% BHO-doped GdBCO, and the PLD conditions were as follows: deposition temperature 760–840°C, oxygen partial pressure 300 mTorr, distance between substrates 60 mm, laser frequency 10 and 100 Hz, and laser energy 300 mJ/pulse. The sample was subjected to structural analysis by XRD, evaluation of superconducting properties such as Jc and Tc by PPMS, and microstructural observation by TEM and STEM. Degradation of Jc properties was observed along with a decrease in Tc at higher BHO concentration. Interestingly, in the films fabricated at 10 Hz, the BHO nanorods collapsed and a BHO layered structure appeared. Elemental mapping by STEM confirmed that these were BHO additives. The collapse of the nanorod structure clearly causes degradation of the c-axis Jc property. This structural transition from nanorods to layers is considered to depend on the competition between the release of strain energy stored in the thin film and the kinetic process of thin film nucleation and growth. To quantitatively evaluate the origin of the above structural transition, epitaxial strain energy was analyzed based on micromechanics theory. Furthermore, vortex pinning simulation using TDGL (time-dependent GL) was performed to evaluate the elementary pinning forces at the complex APC interface, and the optimized APC structures to be considered in the future were discussed.

2:00 PM
Materials Research on REBCO Superconductors to meet Application Requirements
Venkat Selvamanickam; University of Houston, United States

REBCO superconductors are in great demand now for many applications, particularly compact fusion. While these superconductors are being implemented in prototype devices, several issues remain before they can be widely used in commercial applications. Cost, capacity, uniformity, mechanical properties, and quench damage are the main issues of concern. High and uniform critical current to reduce cost, high growth rates to increase capacity and reduce cost, alternate conductor architectures for improved strength, flexibility, and defect tolerance are ongoing areas of research. Progress in these areas at the University of Houston will be discussed in this presentation.

2:30 PM
Development of Novel Methodologies for Better Understanding and Manufacturing of REBCO Coated Conductors by Integrating High Throughput Magnetic Microscopy and Machine Learning
Takanobu Kiss1,2,3, Juntao Yao1,2, Sarah Paone1,2, Genda Gu2 and Qiang Li1,2,; 1Kyushu University, Japan; 2Nagoya University, Japan; 3JST-CREST, Japan; 4CRIEPI, Japan

Recent advances in manufacturing techniques have made it possible to obtain commercial RE1Ba2Cu3O7-α (REBCO, RE: Rare Earth) coated conductor (CC) tapes having a length of several 100 m. Along with this trend, research on the development of CC applied equipment is also being vigorously promoted in various countries of the world. However, in developing REBCO CC based large-size superconducting equipment, unexpected quenching and lowering of critical current (Jc) and yield at coil-forming are noticed as problem. Technology development for obtaining more stable performance with good reproducibility becomes an urgent issue. The author considers that, as the cause, 1) the behavior of the long CC tape under the practical operation condition is not sufficiently understood, and 2) the problem of the complexity of the manufacturing process. In this study, the local nonuniformity of critical current density (Jc) in the tape-plane of the long CC is measured nondestructive and noncontact manner at high spatial resolution using a re-top high-speed magnetic microscope. Integrating with image analysis by machine-learning (ML), we succeeded in the automated analysis of several thousands of magnetizing current images and clarified the presence of domains of the local nonuniformity in the long tape, which is difficult to be detected by the conventional inspection by local Jc criterion, and obtained detailed information on the Jc lowering domain such as the size, position, and statistical distribution. To
improve the process conditions, we also developed a ML regression model which can quantitatively estimate \( I_c \) obtained by the manufacturing condition through a coupled analysis by high-speed \( L_c \) measuring and ML regression using a combinatorial sample in which the manufacturing condition was systematically changed in the longitudinal direction of the tape. Furthermore, using the Genetic Algorithm on the basis of this ML regression model, we have also succeeded in deriving the combination of control variables, i.e., the production conditions, to maximize the \( I_c \) as output as the solution of the inverse problem. These new methodologies enable us to elucidate the reason for local non-uniformity of long CC tapes, to develop CC tapes with better spatial uniformity, to derive process parameters quickly on PC to maximize the tape performance and are expected to greatly contribute to drastic shortening of lead times for CC tape development and realizing stable tape performance.

Acknowledgements: This work was supported by JSPS KAKENHI Grant Number JP19H05617.

3:00 PM BREAK

3:30 PM QT04.02.04

Ultrafast transient liquid assisted growth of \( \text{YBa}_2\text{Cu}_3\text{O}_x \) coated conductors: why is it a novel process? Xavier Obradors Berenguer1, Teresa Puig1, Lavinia Saltarelli1, Diana G. Franco1, Kapil Gupta1, Elzbieta Pach1, Roxana Vlad1, Aiswarya Kethamkuzhi1, Carla Torres1, Adrià Pacheco1, Silvia Ras1, Albert Queraltó1, Jordi Aguilar1, Daniel Sánchez2, Emma Ghirad2, Ona Mola3, Victor Fuentes4, Laiia Soler5, Julia Jarelo1, Juri Banckewski1, Natalia Chamorro1, Cornelia Pop1, Joffre Gutierrez1, Susana Ricart1, Jordi Farjas2, Cristian Mocuta3, Ramon Yañez4 and Eduardo Solano5; 1Instituto de Material Science of Barcelona (ICMAB-CSIC), Spain; 2Universitat de Girona, Spain; 3SOLEIL Synchrotron, France; 4Universitat Autònoma de Barcelona, Spain; 5Alba Synchrotron, Spain

Coated conductors (CC) of \( \text{REBa}_2\text{Cu}_3\text{O}_7 \) (REBCO, RE= Rare Earth) are an exceptional achievement in materials science which encompassed many scientific and engineering challenges. These superconducting materials have emerged as the most attractive opportunity to reach unique performances at high and low temperatures, particularly at high magnetic fields, while reducing the cost/performance ratio continues to be a key objective for a large scale marketability.

To address the challenge of reducing the cost/performance ratio it is unavoidable to develop ultrafast growth rate processes which will lead to high throughput manufacturing of CCs with high performance. Liquid assisted growth of epitaxial REBCO films appears as a very promising approach to reach growth rates beyond 100 nm/s. We have recently created a novel concept, the Transient Liquid Assisted Growth (TLAG) [1-3], which differs from previous growth paths because it is a non-equilibrium process, i.e. the Ba-Cu-O transient liquid with different stoichiometries leading to the formation of REBCO is not an equilibrium one and its properties can be manipulated through kinetic parameters [4]. We will show that different REBCO (RE=Y, Gd, Dy) films can be grown through TLAG using either the temperature or the PO2 routes and also with different liquid compositions. The TLAG process is fully compatible with the use of preformulated BaMO3 (M=Zr, Hf) nanoparticles to prepare nanocomposite CCs when propionate metalorganic solutions are used in a Chemical Solution Deposition (CSD) route. Finally, we show that the TLAG process can also be extended to other precursors such as amorphous phases deposited by Pulsed Laser Deposition (PLD) at low temperatures [5]. The growth process has been analyzed by in-situ synchrotron X-ray diffraction analysis which have confirmed that ultrafast growth rates (> 1000 nm/s) can be achieved. We will show that high critical current densities have been achieved up to 3.5 MA/cm^2 at 77K in thin films and CCs and the process has been transferred to thicker films and metallic substrates. An overall overview of the features of the TLAG process, as compared to other growth approaches, will be presented [6], together with an outlook of the future potential and the pending challenges of this novel technique.

References


4:00 PM QT04.02.05

Ultra-fast Growth of REBCO Superconducting Thin Films by Transient Liquid Assisted Growth Elzbieta Pach1, Diana G. Franco1, Lavinia Saltarelli1, Carla Torres1, Daniel Sánchez2, Jordi Farjas3, Eduardo Solano3, Cristian Mocuta4, Xavier Obradors Berenguer1 and Teresa Puig1; 1Institut de Ciència de Materials de Barcelona, Spain; 2GRMT, University of Girona, Spain; 3ALBA Synchrotron, Spain; 4SOLEIL Synchrotron, France

Cuprates, \( \text{REBa}_2\text{Cu}_3\text{O}_7 \) (REBCO, RE = Y or rare earth) are the most important class of High Temperature Superconducting (HTS) materials, due to their outstanding properties. They are the superconductors with the highest operational temperature and highest operational magnetic field, hence, nowadays the materials of choice for Coated Conductor (CC) technology in most of the high current applications. The synthesis of REBCO-type superconducting films is compatible with standard chemical solution deposition methods (CSD) and pulsed laser deposition growth (PLD). However, recently, the development of a novel synthesis approach promises the reduction of the cost/performance ratio in the CC field. The, so called "Transient Liquid Assisted Growth" (TLAG) method [1-3] is a high-throughput, ultra-fast, non-equilibrium, kinetic process of growth of REBCO type superconducting films and coated conductors compatible with industrial applications. The understanding of the TLAG process requires application of advanced tools and techniques for its characterization and optimization. Therefore, development of a specialized instrumentation for the characterization and optimization of TLAG process in real time and in real conditions by synchrotron radiation based in-situ X-ray Diffraction, was achieved. This new instrumentation allows to follow the dynamic behavior of the superconducting phase while acquiring the resistance of the sample in real time and in-situ by XRD. Epitaxial REBCO TLAG growth at 1000 nm/s has been reached in superconducting films of 3 MA/cm^2 at 77 K. Furthermore, TLAG growth method was shown to be compatible with introduction of inorganic nanoparticles as vortex pinning centres to increase the performance of such films. In this presentation, I will mainly report on the present understanding of the TLAG process based on the results gathered from the in-situ instrumentation setup.

References:


4:15 PM QT04.02.06

Monte Carlo Simulation of Nanostructure Formation in BMO-Doped REBCO Films Yusuke Ichino1,2, Noriyuki Taoka3, Yoshiyuki Seike1, Tatsuo Mori1, Tomonori Arita1,2, Tomoya Horide1,2 and Yutaka Yoshida1,2; 1Aichi Institute of Technology, Japan; 2Japan Science and Technology Agency, Japan; 3Nagoya University, Japan

When BMO-doped REBCO superconducting thin films (BMO+REBCO films) are prepared by vapor-phase-epitaxy (VPE) such as PLD and MOCVD, BMO self-organizes into nanorods and/or nanoparticles in the REBCO matrix. The other hand, only incoherent BMO nanoparticles are observed in the solid phase growth method such as MOD. These experimental results suggest that the kinetics of the raw material particles at the surface of the thin film crystal growth contribute significantly to the self-organization of BMO. In fact, it is known that BMO exhibits various nanostructures depending on the growth temperature (\( \text{TC} \)), the volume fraction of BMO added (\( \text{VF}_{\text{BMO}} \)), and the deposition rate (\( \text{DR} \)) in the VPE. Therefore, we have developed a BMO+REBCO thin film growth simulation considering the kinetics using the Monte Carlo (MC) method to investigate the effect of deposition conditions on the nanostructure and the formation mechanism of nanorods. As a result, the following trends were obtained.

(1) When \( \text{TC} \) is high and \( \text{DR} \) is low, nanorods are formed perpendicular and linear to the substrate surface. In addition, the diameter of the nanorods becomes thicker.

(2) At a lower \( \text{TC} \) and higher \( \text{DR} \) than (1), the nanorods are inclined and their diameters are narrower and their number density is higher.

(3) When \( \text{DR} \) is high enough, nanoparticles consisting of short nanorods are observed.

(4) Even if \( \text{DR} \) is high enough, linear nanorods can be obtained if \( \text{TC} \) and \( \text{VF}_{\text{BMO}} \) are sufficiently high.

The above trends are qualitatively in good agreement with experimental results and reported cases. The time evolution of nanostructure formation can also be observed in the MC simulations. This indicates that nanorods are formed in the following steps. First, crystal nuclei of REBCO and BMO are generated on the substrate surface, from which crystal growth proceeds. Since the volume fraction of BMO is small, the BMO islands are eventually surrounded by the REBCO layer, and BMO can only grow in the direction perpendicular to the substrate surface. This process is repeated, consequently, BMO nanorods are formed. On the other hand, at low \( \text{TC} \) and high \( \text{DR} \), more BMO crystal nuclei are generated, which slows down the growth rate of BMO islands in the vertical direction, resulting in tilted or shortened...

References

Low-Temperature Fabrication of High-Tc NdBa2Cu4O8 Films by Oxygen Partial Pressure Controlled KOH Flux Method Shuei Funaki, Haruki Shigenobu, Eisuke Sasaki and Yasuji Yamada; Shimane University, Japan

To apply coated conductors operated at boiling temperature of liquid nitrogen (77.3 K) to various fields, an improvement of the superconducting properties is required. In the case of REBa2Cu4O8 (RE124), RE: rare earth elements coated conductors, a biaxial orientation of RE123 crystals on substrate and the improvement of a critical current density (Jc) have been greatly conducted. However, this RE123 coated conductor needs a high growth temperature during film fabrication that causes degradation of superconducting properties due to impurity diffusion from metallic tape substrate. Moreover, for the achievement of high critical current (Jc), a particular technique for the fabrication of thick RE123 film is needed. A single crystalline REBa2Cu4O8 (RE124) has been fabricated by a low-temperature phase-growth process using molten alkali hydroxide (KOH) in an ambient atmosphere [1–3]. By this approach, we synthesized biaxial oriented RE124 epitaxial films on NdGaO3 (001) single crystalline substrate at low-temperature of 650°C [4]. Furthermore, by controlling the oxygen partial pressure (pO2), we fabricated biaxial oriented Y123 epitaxial films [5]. The critical temperature (Tc) of Y123 film fabricated at 650°C was 90 K, comparable to that of conventional Y123 films. Recently, we have focused on light RE123 (LRE123), which has potentially high Tc and prepared the Nd123 on SrTiO3 (100) single crystalline substrate with high Tc by a low-temperature crystal growth process using KOH [6]. We succeeded in obtaining biaxially oriented Nd123 films even at a low temperature of 425°C. However, the Tc was dramatically reduced due to the increase of Nd/Ba substitution as the deposition temperature. In high critical current, the Ba composition ratio of the flux to Ba-rich, the Nd123 film was slightly improved, however it was much lower than the conventional Tc [7]. In addition to Ba enrichment of the flux composition, a low pO2 is also reported to be effective in suppressing Nd/Ba substitution in Nd123 [8]. In this investigation, to establish the fabrication method of high-performance RE123 films by feasible simple process, we endeavored to fabricate the LRE123 films on single crystalline substrate at low-temperatures by liquid phase epitaxial growth using KOH flux with controlled pO2. Obtained films of LRE123 (RE=Gd, Sm, Nd, La) fabricated at 700°C in various pO2 of 2x10−1, 1x10−2, 1x10−3 atm showed biaxial orientation of 123 single phase completely, and c-axis length was elongated to the stoichiometric value with decreasing pO2. Moreover, Nd123 films fabricated at 700°C in pO2 1x10−2 atm showed high-Tc onset of ~90 K. From these facts, we succeeded in the fabrication of high-Tc (> 90 K) Nd123 film using KOH flux method at low temperature by controlling of pO2.

References


SESSION QT04.03: Poster Session
Session Chairs: Liangzi Deng and Yusuke Ichino
Tuesday Afternoon, April 23, 2024
Flex Hall C, Level 2, Summit

5:00 PM QT04.03.01
Magnetic ac Susceptibility of Superconducting Ta Films for Quantum Computing Juntao Yao1,2, Chenyu Zhou2, Sarah Paone1,2, Mingzhao Liu2 and Qiang Li1,2, Stony Brook University, United States; Brookhaven National Laboratory, United States

Recently, breakthroughs were reported in the long coherence time (> 0.5 ms) transmon qubit using tantalum films (Ta). Identifying the loss mechanism in Ta films will help further improve the performance of Ta-based superconducting qubits. Here, we report a study of superconducting properties in two sets of Ta films grown on c-cut and a-cut sapphire respectively using contact transport and noncontact ac magnetic susceptibility measurements. Although the resistive transition appears to be similar in both films, we found strikingly different responses in their complex magnetic susceptibilities χ′(ω)χ′′(ω). χ′ in the c-cut films exhibits a sharp peak at superconducting transition Tc and becomes featureless below Tc indicating a strongly coupled superconducting state. In contrast, χ′ in the a-cut films exhibits a broad peak near Tc and a second peak appears below Tc, indicating granular superconductivity behavior. This second peak in χ′ is associated with the hysteresis loss at weak-link-type grain boundaries, which is believed to be a leading source of decoherence in the a-cut Ta films. The derived magnetic loss tangent in the a-cut films is about one order of magnitude higher than in the c-cut films. This study demonstrates that ac susceptibility is an excellent probe for characterizing bulk superconducting properties of the constituent superconducting materials used in qubits.

5:00 PM QT04.03.02

Although nitrogen is approximately four times more prevalent than oxygen in the Earth’s atmosphere, the stability of dinitrogen leads to an order of magnitude fewer known nitrides than oxides. Despite this, many of the known nitrides are important technological materials. Transition metal nitrides (TMNs) in the rocksalt crystal structure are one such example: these chemically stable, high-symmetry superconductors are well suited for epitaxial thin film integration with common substrates. To extend the functionality of TMNs and create epitaxial superconductor–semiconductor heterojunctions, suitable rocksalt-structured nitride superconductors are required. Our team has discovered a series of new rocksalt-structured nitride superconductors with band gaps ranging from E ~0.9-2.4 eV, described as either MgTmN (TM=group 4 transition metal) or Mg TmN (TM=group 5 transition metal). The lattice parameters of these new materials are...
New user accessible capability and the wide range of ongoing and future applications of it. The new capability enables synthesis and characterization of materials at every fabrication step, as well as their integration into quantum devices in a single vacuum cycle, using multiple nanofabrication tools (deposition, oxidation, ion milling), a characterization suite (XPS, ellipsometry, FTIR, OES) and automated robotic system — all combined in an integrated system. This new capability enables synthesis and characterization of materials at every fabrication step, as well as their integration into quantum devices in a single vacuum cycle, using multiple nanofabrication tools (deposition, oxidation, ion milling), a characterization suite (XPS, ellipsometry, FTIR, OES) and automated robotic system — all combined in an integrated system.

In this work, we will present our recent low temperature electronic transport characterization in a high quality InAs quantum well (QW), grown by molecular-beam epitaxy. A specimen of a InAs-Al hybrid devices that are consistent with the observation of TSSs and MQPs. InAs has emerged as a promising material platform to realize topological superconducting states (TSSs) which can host Majorana quasiparticles (MQPs). (1) It can form a highly transparent interface with aluminum (Al, a superconductor); (2) the strength of spin-orbit coupling (SOC) is large and tunable, a key ingredient for realizing TSSs. Indeed, recent work by Microsoft Quantum shows exciting results in InAs-Al hybrid devices that are consistent with the observation of TSSs and MQPs.

Results from this study will provide critical information for the realization of MQPs.

In this study, we found that the K-deintercalation process from K$_2$WS$_2$ is spontaneous, and a non-oxidative acidic reaction environment is sufficient to facilitate the oxidation of WS$_2$; so far, this process has been completed using a strong oxidizer, K$_2$Cr$_2$O$_7$ in dilute H$_2$SO$_4$. A disadvantage of such an indirect reaction. In this study, we will discuss how to access the thermodynamically unfavorable superconducting 2M phase of WS$_2$ as high-quality crystals.

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**Investigating The superconducting and Structural Properties of Trigonal PtBi$_2$ Single Crystals**

Time-Wei Kuo, Layla Smith, Kent Smith, Leroy Salary, Doyle Temple and Wei Pan; Norfolk State University, United States; Sandia National Laboratories, United States

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**Superconducting Materials Exploration for Quantum Devices**

Aidar Kemelbay, Layla Smith, Kent Smith, Leroy Salary, Doyle Temple and Wei Pan; Norfolk State University, United States; Sandia National Laboratories, United States

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**Selective Area Epitaxial Growth of Magnesium Diboride on SiC using Epitaxial Graphene**

Patrick A. Rondonasiki, Chengye Dong, Joshua Robinson, Qi Li and Jian M. Redwing; Pennsylvania State University, United States

Magnesium diboride (MgB$_2$) has a bulk transition temperature ($T_c$) of 39 K, the highest temperature BCS $\lambda$-wave superconductor at ambient pressure, and it has been shown to achieve an upper critical field ($H_{c2}$) larger than 60 T. Furthermore, MgB$_2$ possesses two superconducting energy gaps, a small gap of ~2.3 meV due to the $\lambda$ band and a larger gap of ~7.1 meV due to the $\sigma$ band.
which contributes to the high $T_c$. Access to the desirable $n$ band carriers for proximity coupled superconductivity are largely confined to the $ab$-axes and is not readily available in standard $c$-plane films. Selective area growth of $c$-plane films would allow not only direct growth of superconducting devices, but it also affords the opportunity to fabricate high quality thin film-based lateral devices. To selectively deposit MgB$_2$, a chemically inert masking material is preferred to isolate growth regions to the substrate. Graphene is a 2D material that is highly stable and is chemically inert due to its strong sp$^2$ bonding. Moreover, graphene possesses high mobility, Dirac bands, and has been observed to have a room temperature quantum Hall effect in relatively low magnetic fields. The Josephson effect across graphene has been a subject of intense research recently due to the predictions of exotic states due to its Dirac bands, gate tunability, and even in low Landau level quantum Hall states. However, current studies on this matter mostly utilize low $T_c$ superconductors, such as Nb, and it is therefore desirable to employ higher $T_c$ materials to increase the operational temperatures. The high $T_c$ and $H_c$ of MgB$_2$ make it an ideal candidate to pair with the quantum Hall or fractional quantum Hall effect found in graphene to study the predicted chiral superconductivity.

In this work we present selective epitaxial (SAE) growth of $c$-plane MgB$_2$ by hybrid physical-chemical vapor deposition (HPCVD) using patterned epitaxially grown graphene on semi-insulating 6H-SiC (EG). We find that EG patterned using positive resist photolithography and etched with a $N_2$ plasma restricts MgB$_2$ deposition predominantly to the exposed SiC and allows for fabrication of lateral MgB$_2$-graphene heterostructures. Low surface energy combined with minimal available oxygen bonds prevents Mg from sticking to the graphene and allows high surface mobility of adatoms to the exposed SiC. Thus, this makes graphene a suitable candidate to mask MgB$_2$ growth. The SAE technique also allows for simple and direct synthesis of MgB$_2$ devices, such as thin film nanoribbons for applications as single photon detectors or as other quantum sensors, on a semi-insulating substrate without the contamination and degradation of the superconductor from standard lithography processing after deposition. We have fabricated $5 \mu$m wide by $1 \text{ mm long}$ $c$-plane MgB$_2$ nanoribbons of $30 \text{ nm}$ thickness that retain the bulk $T_c$ of 39 K. Scanning electron microscopy shows that parasitic deposition on graphene is largely limited to photore sist contaminated areas or point and edge defects of the masking material that allow for Mg bonds to form. Furthermore, XPS analysis suggests the graphene is decoupled from the substrate during the MgB$_2$ deposition process, which allows for greater carrier mobility in the graphene. Lastly, the van der Waals bonding of graphene allows for easy physical exfoliation of the mask without damaging the MgB$_2$ device. Thus, this allows for isolation of superconducting devices on the semi-insulating SiC substrate if desired for the device application. Discussions in this talk will include synthesis considerations of developing these structures, such as chemical modification of the graphene during MgB$_2$ deposition, and the electrical properties of as-grown nanoribbons and other devices fabricated.

5:00 PM QT04.03.10 High Energy Analogues to The Superconducting Face Centered Cubic W-Pt Binary Denver P. Strong and Robert J. Cava; Princeton University, United States

We report single phase superconducting face centered cubic (fcc) high entropy alloys (HEAs) synthesized via splat cooling. The single phase materials fall at electron counts in the HEA superconductor alloy family where structural stability and optimal superconducting electron counts clash. The materials’ superconducting properties follow the general trends predicted for metallic alloys. Insights are provided as to why an FCC structure may be stable.

5:00 PM QT04.03.11 Capping Effects in Parent and Superconducting Nd$_{1-x}$Sr$_x$NiO$_2$ Shiyu Fan, Harrison Laboilitra, Qiang Gao, Yanhong Gu, Taehun Kim, Jiemin Li, Vivek Bhartiya, Yueying Li, Jiangfeng Yang, Shengjun Yan, Xingjiang Zhou, Andres Cano, Fabio Bernardini, Yuefeng Nie, Zhihai Zhu, Valentina Bisogni, Antia Botana and Jonathan Pelliciari; 1Brookhaven National Laboratory, United States; 2Arizona State University, United States; 3Chinese Academy of Sciences, China; 4University of Texas, United States; 5National Laboratory of Solid State Microstructures, Jiangsu Key Laboratory of Artificial Functional Materials, China; 6Songshan Lake Materials Laboratory, China; 7CNRS, Universite Grenoble Alpes, Institut Neel, France; 8Dipartimento di Fisica, Università di Cagliari, Italy

The discovery of superconductivity in infinite layer nickelates (Nd$_{1-x}$Sr$_x$NiO$_2$) has attracted a lot of attention. So far, superconductivity in Nd$_{1-x}$Sr$_x$NiO$_2$ is a prerequisite of thin films making the role of substrates and interfaces crucial. On this end, capping has been shown to affect the interface structure highlighting its active role on the electronic and magnetic properties of nickelates. However, only few spectroscopic studies specifically address this topic. Here, we use Resonant Inelastic X-ray Scattering (RIXS) to investigate the influence of the SrTiO$_3$ capping layer on the excitations of Nd$_{1-x}$Sr$_x$NiO$_2$ ($x\approx0$ and 0.2). Spin excitations are observed in Nd$_{1-x}$Sr$_x$NiO$_2$ regardless of capping. While doping softens the spin excitations, capping moderately hardens them in both parent and superconducting samples and increases their spectral weight. Additionally, the hybridization between Ni 3d and Nd 5d orbitals is reduced by capping, as evidenced by a weaker charge transfer peak at 0.6 eV. These observations can be rationalized phenomenologically in the context of the polar discontinuity at the Nd$_2$NiO$_4$/SrTiO$_3$ interface leading to the atomic and electronic reconstruction, possibly extending to the whole film. Finally, our findings uncover the effects of SrTiO$_3$ capping on the spin and charge excitations in Nd$_{1-x}$Sr$_x$O and pave the way for a general understanding of infinite layer nickelates thin films.

5:00 PM QT04.03.12 Memristively Programmable Josephson Junctions Julian Liedtke and Stefan Tappertzehofen; TU Dortmund University, Germany

Superconducting quantum interference devices (SQUIDs) can be used for realization of highly sensitive magnetic field sensors and qubits for quantum computers. SQUIDs rely on Josephson junctions and flux quantization. Achieving ultra-high sensitivity, low noise, and long coherence times demands precise tuning of the junction’s critical current while simultaneously suppressing the sub-gap current. Nb/NbOx/Nb junctions are highly attractive due to the high gap-energy of Nb, which minimizes the sub-gap current. However, the inherent reactivity of Nb with its native oxide introduces considerable variations of the critical current. Today, Al/AIOx/Al and Nb/AIOx/Al/Nb junctions show the best and reliable performance. Nevertheless, even with the application of advanced fabrication techniques like laser annealing or high-voltage electron beam lithography, the critical current variation still extends up to 15% on the wafer level. Here, we introduce an innovative solution by utilizing a memristive Nb/NbOx/Nb heterostructure, serving as a programmable Josephson junction. By resistive switching at room temperature, a filamentary weak link (metallic quantum point contact) or tunneling junction between two electrodes formed, effectively operating as a Josephson junction at cryogenic temperatures. In this proof-of-concept, we analyzed in detail and modeled the electrical and physico-chemical properties of the Nb-based memristors. Particular attention is paid to the quantum charge transport at cryogenic temperatures and the statistical variations of the critical current. We demonstrate reproducible forming and erasing of the filamentary junction, which may transcend the limitations of conventional Nb-based junctions such as stress or degradation. The fundamental transport and switching studies are complemented by advanced spectroscopic and microscopies techniques. These memristively programmable Josephson junctions allow for precise tuning of the junction properties post-fabrication through simple programming steps. This may eliminate the need for sophisticated deposition or patterning techniques and unlock the full application potential of Nb-based superconducting electronics.

5:00 PM QT04.03.14 A Study on Oxygen Post-Annealing of GdBa$_2$Cu$_3$O$_y$ Coated Conductors Irradiated with Low-Energy Ions Toshinori Ozaki, Hiroiyuki Okazaki, Hiroshi Koshikawa, Shunya Yamamoto, Tetsuya Yamakö, Morihisa Saeki, Tetsuuro Sueyoshi and Hitoshi Sakane; 1Kwansei Gakuin University, Japan; 2National Institutes for Quantum Science and Technology, Japan; 3Kyushu Sangyo University, Japan; 4SHI-ATEX Co., Ltd., Japan

High-temperature superconducting coated conductors (CCs) based on REBa$_2$Cu$_3$O$_y$ (REBCO, RE = rare earth) with high current carrying capacity are being developed for use in high magnetic field applications. For these applications, increasing critical current density $J_c$ under magnetic fields is important considerations. The in-field $J_c$ can be improved by the introduction of artificial pinning defects with nano-meter size, which can pin the vortices. The desired defect structures can be created by ion irradiation, which is a promising technique applicable to all superconducting materials. Depending on appropriate ion species and energy, ion irradiation enables the creation of a variety of defects, such as point, clusters and tracks in the materials. Recent studies show low-energy ion irradiation could be a viable option for creating uniform pinning defects in superconducting films. We have reported the effect of low-energy Au-ion irradiation on superconducting properties in GdBa$_2$Cu$_3$O$_y$ CCs. The superconducting transition temperatures $T_c$’s of the GdBa$_2$Cu$_3$O$_y$ films irradiated with 2 and 10 MeV Au-ions decrease gradually with increasing fluence up to about $8 \times 10^{11}$ ions/cm$^2$ and then significantly started to drop. The $J_c$ in the GdBa$_2$Cu$_3$O$_y$ CCs irradiated with 10 MeV Au-ions shows about 70% enhancement at around 3 T and 30 K, indicative of effective pinning defects by the irradiation. In this talk, we will present a study on the oxygen post-annealing of GdBa$_2$Cu$_3$O$_y$ CCs irradiated with 2 and 10 MeV Au-ions. The oxygen post-annealing at 450 °C leads to a recovery of $T_c$, which is close to the pre-irradiation level up to $8 \times 10^{11}$ ions/cm$^2$. We also observe an appreciable recovery of $T_c$ above $8 \times 10^{11}$ ions/cm$^2$, but these $T_c$ values are much less than the one before the irradiation. These results indicate that the oxygen annealing is effective to restore the $T_c$ of the GdBa$_2$Cu$_3$O$_y$ CCs irradiated 2 and 10 MeV Au-ions. We will present self-field and in-field $J_c$ before and after the oxygen post-annealing in the irradiated GdBa$_2$Cu$_3$O$_y$ CCs. We will also report the effect of oxygen post-annealing temperature on superconducting properties of GdBa$_2$Cu$_3$O$_y$ CCs irradiated with 300 KeV He-ions.

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Coupling of superconducting qubits to the external environment through dielectric traps, oxidized surfaces, defects, or inhomogeneous phases can introduce undesired energy levels in form of host two-level systems leading to quantum decoherence. Identifying and eliminating the defects responsible for the decoherence will lead to scalable quantum computers. Recent developments in epitaxial growth of single phase, atomically smooth $\beta$-Nb$_2$N have confirmed superconductivity with a critical temperature $T_c>0.6$ K. [1]. This opens the opportunity for large single-crystal layers to be used in Josephson junctions and enables easier identification of defects in comparison to amorphous and polycrystalline materials.

We investigate an epitaxial transition metal nitride (TMN) Josephson junction with $\beta$-Nb$_2$N/AIN/ $\beta$-Nb$_2$N trilayer structure grown by molecular beam epitaxy (MBE) on c-plane sapphire. We measure non-linear I-V characteristics showing superconducting current across the junction. Hexagonal (non-polar) $\beta$-Nb$_2$N and wurtzite (polar) AlN are symmetry-matched and have only 1.8% lattice mismatch. Here, we use multislice electron microscopy on four-dimensional scanning transmission electron microscopy (4D-STEM) to obtain a three-dimensional reconstruction of the junction and its interfaces with atomic-scale imaging and depth sectioning to show the presence of polarity-inversion boundaries of AlN at $\beta$-Nb$_2$N step edges. [1] Wright, J. et al., Phys. Rev. Mater. 7, 074803 (2023). DOI: 10.1103/PhysRevMaterials.7.074803


Over the past few years, the world has experienced a steadily increasing demand for high-temperature superconducting wires of the second generation (2G-HTS wires). A significant proportion of wires require the exceptional performance under moderate to strong magnetic fields at reduced temperatures of 4-65K. These wires are primarily used in applications such as fusion magnets, rotating machines, and accelerators. Among these, fusion applications are a key driver for the development and manufacturing of 2G-HTS wires, having specific property requirements at 20K and in 15-20T magnetic fields.

In 2023, Faraday Factory Japan (FFJ) supplied over 2,000 kilometers of 4mm wide wires. The technology utilizes an electropolished Hastelloy substrate, alongside technologies involving the formation of an ion-beam assisted MgO (IBAD-MgO) textured buffer layer and pulsed laser deposition (PLD) of superconducting materials. Our research activities aim at improving the deposition process in all stages of the tape fabrication. This presentation will focus on our current research efforts to enhance the quality of the buffer substrate, improve the performance of superconducting materials in strong magnetic fields, and achieve higher uniformity in the Cu and solder layers. Our results have led to produce wires with an engineering critical current density (Je) at 20K and 20T of approximately 900-950 A/mm², with an average piece length of 350 meters. We will also discuss further practical improvements in our 2G-HTS fabrication process, which includes development of the new equipment, improvement of quality management, and addressing the challenges related to the scaling up of daily production.

1:30 PM *QT04.05.01
From LTS through HTS to RTS Paul C. W. Chu, University of Houston, United States

Superconductivity has been an ever-self-reinvigorating discipline since its discovery in 1911. It continues to generate excitement in science, materials, and technologies. One of the obvious hurdles to its full fruition in technology is to bring its transition temperature \( T_c \) to room temperature. In this talk, I shall first briefly review the impressive advancements made in low-temperature superconductivity (LTS) and high-temperature superconductivity (HTS) before the arrival of room-temperature superconductivity (RTS). Accompanying the advancements made in superconductivity science and technology over the last century, a solid experimental framework concerning the search, development, and even authentication of new discoveries has been established. All these can serve as valuable references in the infancy of RTS research. In this spirit, we will comment on the current status of rare-earth hydrides RTS and present our preliminary experimental results from our research on the superconduction of rare-earth hydrides. We conducted independent measurements on the materials synthesized by the methods described in Ref. 2. Four-probe electrical measurements on selected samples in diamond anvil cells show abrupt and reproducible loss of resistance at well-defined critical temperatures and pressures. Magnetic susceptibility measurements show reproducible signatures of field expulsion at similar critical temperatures. The \( T_c \) values from electrical resistance and magnetic susceptibility for these samples agree and are consistent with the previously reported data. On the other hand, new samples prepared with similar procedures exhibit no measurable \( T_c \), but instead show evidence for anomalous metal-insulator transitions that have been well-studied in lanthanide hydrides at ambient pressure (e.g., Ref. 4). Our measurements thus provide direct evidence for near ambient superconductivity in one or more Lu-N-H phases while some phases in the material are not superconducting. We also conducted first-principles DFT and DFT+U calculations to further understand the remarkable properties of these materials. Supercell calculations starting with N-doped \( \text{Fm}-3m \text{LuH}_3 \) reveal configurations such as \( \text{Lu}_2\text{H}_{2.5} \text{N} \) that exhibit novel electronic properties such as flat bands, sharply peaked densities of states (van Hove singularities, vHs), and intersecting Dirac cones near the Fermi energy (\( E_F \)). These electronic properties are present when N substitutes H in the octahedral interstices of \( \text{Fm}3m \text{LuH}_3 \). These structures also exhibit an interconnected metallic hydrogen network, a common feature of high-\( T_c \) superconductor. Electronic property systematics gives an estimate of \( T_c \) for one structure that is well above the critical temperatures predicted for structures considered previously. DFT+U has an especially strong effect on one of the structures considered, enhancing the vHs and flat bands near \( E_F \). These results provide a basis for understanding the electronic properties observed for nitrogen-doped lutetium hydride. Additional work is needed to fully characterize the material, optimize its synthesis, stabilize it at ambient pressure, and accurately determine the range of critical temperatures possible.
Superconductivities in Twisted Interface of Atomically Thin Van der Waals Materials

Philip Kim, Harvard University, United States

Engineering moire superlattices by twisting and stacking two layers of van der Waals materials has proven to be an effective way to promote interaction effects and induce exotic phases of matter. After the discovery of superconductivity and correlated insulators in magic-angle twisted bilayer graphene, several different two-dimensional materials have been used to create twisted two-layer systems and various novel phases. In this talk, we will discuss the emergent electronic states observed in various twisted vdW materials. In the first part, we will discuss superconducting multilayer graphene, including twisted bilayer graphene, twisted trilayer graphene, and twisted quadrilayer graphene with alternative twist angles. In these twisted multilayer graphene systems, we also demonstrate a flat electron band tunable by perpendicular electric fields over a range of twist angles. Several correlated behaviors have been observed, including superconductivity and spontaneously broken symmetry states. In the second part of the talk, we will discuss twisted interfaces between stacked van der Waals cuprate crystals that enable tunable Josephson coupling. Using a novel cryogenic assembly technique, we fabricate high-temperature Josephson junctions with an atomically sharp twisted interface between Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ crystals. We find that near the $45^\circ$-circuit twist angle, we observe two-period Franck-Herzog interference patterns and fractional Shapiro steps at half integer values, a signature of co-tunneling Cooper pairs necessary for high-temperature topological superconductivity.

Spin-Orbit Coupling and Superconducting Stripes in an Oxide Heterostructure EuO/KTO(110)

Xiaohui Chen, University of Science and Technology of China, China

Unconventional quantum states have been realized at the interfaces of oxide heterostructures, where they can be effectively tuned by the gate voltage. Recent studies reveal that the conductive interfaces in the SrTiO$_3$ (STO)-based and KTaO$_3$ (KTO)-based heterojunctions host a surprisingly enriched cascades of intriguing physical phenomena, most notably the emergence of two-dimensional (2D) superconductivity. Such 2D superconductivity is characterized by a Berezinskii-Kosterlitz-Thouless (BKT) transition; its unusual behavior in external magnetic fields and large tunability under varying electric fields render the superconducting oxide interfaces a promising platform for exploring the mechanism of unconventional superconductivity.

In this talk I will introduce our recent progress on the study of the interface between high-quality EuO (111) thin film and KTO (110) substrate. Both oxides are insulating, yet the interface is metallic and shows superconductivity with onset transition temperature $T_c$. The 2D nature of superconductivity is verified by the large anisotropy of the upper critical field and the characteristics of a BKT transition. By applying gate voltages, $T_c$ can be largely tuned with an enhancement of ~70%; such an enhancement can be associated with a boosted spin-orbit coupling (SOC) energy. Further analysis based on the upper critical field ($H_{c2}$) and magnetocconductance reveals complex nature of SOC at the EuO/KTO (110) interface with different dominant scattering mechanisms in the superconducting and normal states. Our results demonstrate that the SOC should be considered an important factor in determining the 2D superconductivity at oxide interfaces.

More interestingly, we discovered a peculiar band-filling-controlled dimension reduction at the superconducting interface between EuO and (110)-oriented KTO. In devices with low carrier densities, electrical transport measurements reveal different $T_c$ and $H_{c2}$ with current applied along the two orthogonal in-plane directions. Theoretical analysis suggests that strong coupling between Ta $5d$ and Eu $4f$ occurs in the low-carrier-density samples, whereas in the high-carrier-density samples (wherein $T_c$ becomes isotropic) such coupling is weakened.

Complemented by experiments of local magnetic susceptibility imaging, our observations imply an unprecedented emergence of unidirectional stripe-like superconducting texture, presumably induced by the ferromagnetic proximity effect; we suggest that the superconducting phase coherence is first established within these “stripes”, leading to the peculiar directional dependence of $T_c$. The realization of such exotic superconducting states provides impetus for the study of novel physics in heterostructures possessing both magnetism and superconductivity.

Enhancement of Superconductivity by Isoelectronic Defects in The Fermi-Hubbard Ladder

Fabio Pablo Mendez-Cordoba$^{1,2}$, Paula Giraldo-Gallo$^1$ and Juan J. Mendoza-Arenas$^3$.

$^1$Universidad de los Andes, Colombia; $^2$Universität Hamburg, Germany; $^3$University of Pittsburgh, United States

In this work we show that superconductivity across a two-leg Fermi-Hubbard ladder can be enhanced by introducing changes of the hopping parameter at specific locations in each leg. Using density matrix renormalization group calculations, we obtain the ground state of the model with repulsive on-site interactions, open boundary conditions and below half filling. We find that modifying the hopping at the position of extremal values of the density Friedel oscillations can strongly increase the value of the superconducting correlations and Luttinger parameter, compared to the homogeneous case. We discuss the mechanism underlying this finding, and experimental platforms where it can be implemented. Ours results provide a possible pathway to enhance the superconducting dome by disrupting the lattice structure without changing the number of charge carriers.

Superconductivity in Thin-film Nickelates: Materials Synthesis

Danfeng Li, City University of Hong Kong, Hong Kong

Developing new techniques to design and discover novel superconductors, especially those with unusual symmetries of superconducting order parameters and/or exotic pairing mechanisms, opens new doors to future applications in quantum devices. The recent discovery of superconductivity in infinite-layer nickelates has engendered revived interest in the study of a cuprate-analog system [1]. Notably, superconducting nickelates display signatures of intriguing similarities and distinctions to the cuprates in their phase diagrams, proximity to strongly correlated electronic phases [2], antiferromagnetic interactions [3], superconducting anisotropy [4], etc. Partially owing to the non-trivial challenges in materials synthesis and their thin-film nature [5], experimental demonstration of the intrinsic properties of this materials family has still been limited. In this talk, I will introduce this new family of superconductors synthesized by a soft-chemistry approach and highlight the key aspects of their electronic and magnetic structure. I will also present our latest developments in synthetic approaches to the nickelate materials system and probing of their distinct features, in a broader context of the unusual role that rare-earth elements and chemical environment play.


Disentangling Symmetry-Breaking Charge Order from Oxygen Order in Infinite-Layer Nickelates

Lona Bhatt$^1$, Christopher T. Parzych$^1$, Kyle Shen$^{1,2}$, Berit Goede$^2$, David A. Muller$^{1,3}$ and Lena Koukouritaki$^{1,3}$.

$^1$Cornell University, United States; $^2$Max Planck Institute for Chemical Physics of Solids, Germany

As a 3$d$ analogue to the cuprates, the recent discovery of superconductivity in infinite-layer nickelates has provided a promising direction to understand high-temperature superconductivity and its competing orders [1,2]. Despite their similarities in crystal structure and valence electron configuration, the cuprates and nickelates are distinguished by significant differences in $T_c$ and competing ground states [3]. In cuprates, charge density waves break symmetry and compete with superconductivity at low temperature, while in nickelates charge order has been relatively...
We synthesized polycrystalline samples, La$_3$Ni$_2$O$_7$ and La$_4$Ni$_3$O$_{10}$, via solid-phase reaction and Hot Isostatic Pressing process from La$_2$O$_3$ and NiO [4]. Samples are characterized by powder X-ray diffraction and reveal the presence of excess oxygen which order with 3a$_0$ periodicity, a period similar to that of previously reported charge order. Associated oxygen octahedral rotations and accompanying periodic lattice distortions (PLDs) of Nd and Ni sites are present in regions with oxygen ordering. Superlattice peaks which arise from these structural distortions enable mesoscale visualization of the excess oxygen ordering using electron nano-diffraction. We find that the ordering is not uniform across the film but exists in dispersed domains. No superlattice peaks are observed in areas outside of ordered excess oxygen domains, suggesting that the signatures of charge order in NdNiO$_3$ reflect the presence of excess oxygen rather than intrinsic correlation effects. This work exemplifies the unique capability of a highly localized and sensitive probe, such as electron ptychography, to directly differentiate and disentangle exotic phases arising in finely tuned systems such as nickelates.

Exploration of Superconductivity in Layered Perovskite Nickelate La$_4$Ni$_3$O$_{10}$ under High Pressure

Yoshikiko Takano; 1,2 National Institute for Materials Science, Japan; 2University of Tsukuba, Japan

Recent discovery of superconductivity in layered perovskite nickelate La$_4$Ni$_3$O$_{10}$ (Tc~80K) attract much attention due to its high superconducting transition temperature (Tc) and similarity of crystal structure to high-Tc cuprate [1]. And its mechanism of superconductivity is expected to be unconventional [2]. La$_3$NiO$_2$ corresponds to the n = 2 case of the Ruddlesden-Popper phase represented by the general formula of La$_{n-1}$Ni$_n$O$_{3n+1}$, and it has two layers of NiO$_2$ plane. In general, Ruddlesden-Popper phase has two-dimensional crystal and electric structure which is suitable for appearance of superconductivity for instance KC$_4$Na$_2$Nb$_4$O$_{19}$ [3]. Particularly, La$_4$Ni$_3$O$_{10}$ is corresponding to n = 3 case of the Ruddlesden-Popper phase having three layers of NiO$_2$ plane. Due to the similarity between these materials, we expect the possibility of superconductivity in La$_4$Ni$_3$O$_{10}$ under high pressure [4].

We synthesized polycrystalline samples, La$_3$Ni$_2$O$_7$ and La$_4$Ni$_3$O$_{10}$ via solid-phase reaction and Hot Isostatic Pressing process from La$_2$O$_3$ and NiO [4]. Samples are characterized by powder X-ray diffraction and thermogravimetry. High pressure was generated with Diamond Anvil Cell with boron-doped diamond electrodes designed for four-terminal resistance measurement [5]. Cubic boron nitride powder was used as a pressure-transmitting medium.

References

La$\text{N}_3\text{Ni}_3\text{O}_{10}$ displays metallic behavior across all measured pressures, with a slight upturn observed at temperatures below approximately 100 K. At 32.8 GPa, a drop in resistance suddenly appears below 5 K. With increasing the pressure beyond 46.2 GPa, the drop of resistance becomes significant. And the temperature where the resistance begins to drop elevated up to 79.2 GPa. Magnetic field dependence of resistance was measured at 69.4 GPa. As the magnetic field increases, the drop of resistance becomes smaller. Therefore, the drop in resistance is most likely to be the result of a superconducting transition of La$\text{N}_3\text{Ni}_3\text{O}_{10}$ [4].

References:

10:30 AM QT04.07.02

Pressure-Induced Superconductivity and Phase Transitions in Thermoelectric Material (Bi, Sb)$_2$Te$_3$ (Liangzi Deng$^1$, Clayton Halbert$^2$, Busheng Wang$^3$, Melissa Gooch$^1$, Daniel J. Schulze$^1$, Xin Shi$^1$, Trevor Bontke$^1$, Ting-Wei Kuo$^{1,4}$, Shaowei Song$^1$, Nilesh Salke$^2$, Russell J. Hemley$^2$, Eva Zurek$^3$, Hung-Duen Yang$^4$, Zhiheng Ren$^1$, Xiao-Jia Chen$^1$ and Ching-Wu Chu$^1$; $^1$University of Houston, United States; $^2$University of Illinois Chicago, United States; $^3$University at Buffalo, United States; $^4$National Sun Yet-Sen University, Taiwan

BixSb$_{2-x}$Te$_3$ is a thermoelectric material with a high room-temperature figure of merit, which can be further enhanced through the application of pressure. Recently, we discovered pressure-induced superconductivity up to ~9 K in this system, and the variation in its superconducting transition temperature with pressure indicates possible phase transitions. Systematic X-ray diffraction measurements conducted at room temperature and pressures up to ~50 GPa reveal two distinct structural phase transitions. Our experimental results also suggest possible topological electronic transitions induced by pressure. In addition, our theoretical calculations have helped us verify and shed light on the structural and electronic phase transitions driven by pressure, as well as the underlying mechanisms responsible for the emergence of superconductivity in this system.

10:45 AM QT04.07.03

Superconducting Properties of Transition-Metal Nitrides from First Principles: Prospects for Strain and Isotope Modification of Superconducting Critical Temperatures (Betal Pamuk$^1$ and Guru Khalaria$^2$; $^1$Cornell University, United States; $^2$University of North Texas, United States)

Epitaxial integration of metallic and superconducting transition metal nitrides into the Group IIIA-nitride semiconductor family opens new avenues for low-temperature electronics and quantum information systems. A challenge for superconducting devices in the nitride platform arises due to the incompatibility between the hexagonal GaN crystal structure and the cubic NbN phase, the main focus of existing experimental work. This incompatibility leads to twin domains that may hamper device design and functionality. Furthermore, due to epitaxial lattice mismatch, the superconducting material may be strained by several percent. Here we use first-principles theory to explore the structural polytypes of NbNx to gather insights into the microscopic physics at play in their metallic and superconducting properties. We focus this work on the prospect of using strain and isotopes to modify electron-phonon interactions and superconducting properties. We discuss the limitations of the theoretical approximations and present our results within the framework of current experimental capabilities. We weigh the desired properties against the constraints imposed by structural symmetry dictates of domains, aiming for the development of domain- and defect-free epitaxial devices.

11:00 AM QT04.07.04

Effect of Metamaterial Engineering on The Superconductive Properties of Ultrathin Layers of NbTiN (Michael S. Osofsky$^1$, Vera Smolyaninova$^1$, Grace Yong$^1$, Will Korzi$^1$, Anne-Marie Valente-Feliciano$^2$, David Beverstock$^{2,3}$, Joseph Prestigiacomo$^3$ and Igor Smolyaninov$^{3,6}$; $^1$United States Naval Research Laboratory, United States; $^2$University of Maryland, United States; $^3$Saltena LLC, United States)

The electronic transport and optical properties of high quality multilayers of NbTiN/AIN with ultrathin NbTiN layers were characterized. The anisotropy of the dielectric function of the multilayers confirmed their hyperbolic optical metamaterial properties. The superconductive transition temperature, $T_c$, of these engineered superconductors was enhanced up to 32% compared to the $T_c$ of a single ultrathin NbTiN layer while the resistivity per NbTiN layer remained unchanged. We have demonstrated that this $T_c$ increase can be attributed to enhanced electron-electron interaction in superconducting hyperbolic metamaterials. The measured critical fields are high and have anomalous temperature dependence in the perpendicular to the magnetic field direction. These results demonstrate that the metamaterial engineering approach can be used to enhance $H_c2$.

SESSION QT04.08: Novel Materials III—Topological Materials

Genda Gu and Juntao Yao
Thursday Afternoon, April 25, 2024
Room 445, Level 4, Summit

1:30 PM QT04.08.01

Experimental Signatures of Higher Order Topology (Richard Deblock, Laboratoire de Physique des Solides, France)

In second-order topological insulators (SOTIs), the bulk and surfaces are insulating, while the edges or hinges conduct current in a quasi-ideal (ballistic) manner, insensitive to disorder. As in the case of quantum spin Hall edges of 2D topological insulators, the current should not be transported without dissipation by counter-propagating ballistic helical states with spin orientation locked to momentum. These edge or hinge states open up many possibilities, ranging from dissipation-free charge and spin transport to new avenues for quantum computing. Bismuth, although a semi-metal, has been shown to belong to this class of materials. In our group, we have studied Josephson junctions based on crystalline Bi nanowires and found that they exhibit robust sawtooth current phase relations in a high magnetic field, which is the signature of one-dimensional ballistic edge states. We also demonstrated the topological nature of Andreev states through the dissipative microwave response in a phase-biased configuration. More recently, in a SQUID constructed from a bismuth ring, we have identified the parity relaxation rate by exploring the statistics of the switching current. In order to find different topological insulators with reduced contribution from bulk non-topological states, we are now exploring the quantum transport properties of WTe$_2$, which has been shown to exhibit a quantum spin Hall effect in the few-layer limit, and Bi$_3$Te$_5$. The latter material is a SOTI with a high bulk band gap.

2:00 PM QT04.08.03

Searching for Ideal Topological Superconductors in Pb-Sn-In-Te System (Genda Gu, Ruidian Zhong, John A. Schneeloch, Yangmu Li, Qiang Li and John M. Tranquada; BNL, United States)

The discovery of 3D topological insulator materials and topological superconductor open up a new research field in the condensed matter physics. In order to search for the topological superconductor, we have grown a large number of the single crystals of Pb-system (Pb-Sn-In-Te) topological superconductor. We have measured the physical properties on these single crystals by various techniques. We have studied the effect of crystal growth condition, impurity and composition on the bulk electrical conductivity of these single crystals. We try to find out which composition and crystal growth condition is the best for the ideal topological superconductor. We have got the bulk topological superconductor with $T_c$ ~5 K.

2:15 PM QT04.08.04

Absence of Nematic Instability in The Kagome Metal CsV$_3$Sb$_5$ (Zhaoyu Liu$^1$, Yue Shi$^1$, Qianni Jiang$^1$, Elliott M. Rosenberg$^1$, Jonathan DeStefano$^1$, Jinjin Liu$^2$, Chaowei Hu$^1$, Yuzhou Liu$^2$; $^1$University of Houston, United States; $^2$University of North Texas, United States)

The discovery of 3D topological insulator materials and topological superconductor open up a new research field in the condensed matter physics. In order to search for the topological superconductor, we have grown a large number of the single crystals of Pb-system (Pb-Sn-In-Te) topological superconductor. We have measured the physical properties on these single crystals by various techniques. We have studied the effect of crystal growth condition, impurity and composition on the bulk electrical conductivity of these single crystals. We try to find out which composition and crystal growth condition is the best for the ideal topological superconductor. We have got the bulk topological superconductor with $T_c$ ~5 K.
Focused Electron and Ion Beam Induced Deposition (FEBID and FIBID, respectively) are direct-write resist-free nanolithography techniques enabling the growth of high-resolution nano- and micro-structures. They rely on a gas precursor that is injected into the area of interest and decomposed by a focused electron or ion beam. Using the WOCOx precursor and Ga+ or He+ FIBID [1], we grow superconducting in-plane nanowires with high lateral resolution [2], as well as three-dimensional superconducting nanostructures [3]. In this contribution, we will present recent results on the fabrication of Josephson junctions and nanoSQUIDs based on FIBID- and FEBID-grown W-C deposits. First, results of W-C nanoSQUIDs patterned as two large pads connected by two short nanowires will be shown. In these devices, the critical current oscillates as a function of the externally-applied magnetic field, which results in a large output voltage to magnetic flux change (1.3 mV per magnetic flux quantum) [4]. Interestingly, these nanoSQUIDs can be implemented on a cantilever for application in scanning-SQUID technology [5]. Other experiments in which Josephson Junctions (JJs) are created with alternate geometries and also with FEBID will be shown here. In summary, FEBID and FIBID represent techniques that can be exploited for the direct-write fabrication of superconducting devices for application in quantum technologies [6].


4:00 PM QT04.09.03 Josephson Diode Effect in Chiral Carbon Nanotubes Joseph J. Cuozzo1, Michael Sizemore2, Francois Leonard1 and Enrico Rossi2, 1Sandia National Laboratories, United States; 2William & Mary, United States

Within superconducting electronics, the Josephson diode effect (JDE) has attracted interest in recent years. Josephson diodes are characterized by an asymmetry in positive and negative switching currents of a Josephson junction (JJ) and could potentially find utility in a growing number of applications at cryogenic temperatures in the Quantum Information Sciences. Despite extensive theoretical and experimental work investigating the JDE, little attention has been paid to nanotube devices where non-reciprocity can be introduced in chiral structures. In this talk, we will present analytic and numerical results on the JDE in chiral carbon nanotubes (CNT). We find that chiral nanotubes in JJs can exhibit diode efficiencies far exceeding those of superconducting chiral nanotubes when an external magnetic field is applied along the nanotube. Furthermore, our numerical simulations show the Josephson diode polarity can be tuned by electrostatically gating CNTs in a Josephson junction. We will discuss the microscopic details that give rise to large diode efficiencies and gate-tunability in chiral CNT JJs.

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under Award DE-SC0022245. The work at Sandia is supported by a LDRD project. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

4:15 PM QT04.09.04 Fabrication of Superconducting Devices on Diamond Maniith Bose1,2 and Christopher I. Pakos2, 1The University of Melbourne, Australia; 2La Trobe University, Australia

Recent advancements in Chemical Vapour Deposition (CVD) based synthetic diamond growth have opened new avenues for the development of electronic devices capitalising on diamond's exceptional properties, including its high critical field (Hc) and transition temperature (Tc). Achieving superconductivity in lab-grown diamond with high boron concentrations is well-documented in bulk diamond, but limited research focuses on superconducting devices in diamond. The focus of this study was on developing innovative methodologies to engineer micro and nano-scale superconducting diamond devices using thin films of boron-doped nanocrystalline diamond (BNCD) and single crystalline diamond (BSCD). We employ electron beam lithography (EBL) and reactive ion etching (RIE) to engineer highly overdamped and non-hysteretic sub-micron bridges with varying dimensions on superconducting diamond films and low temperature magnetotransport measurements were conducted. A novel fabrication methodology involving neon-ion milling was developed to further define Dayem bridge junctions that demonstrated Josephson effects. The first NCD diamond nano-SQUID was created using these nanobridges as weak links, with a 50 nm loop size.

The nano-SQUID showed a very low flux noise Φ0noise = 0.14 μΦ0/Hz at 1 kHz, and concurrent spin sensitivity of 11 spins/√Hz, comparable to that of the lowest noise nano-SQUIDs reported so far in established materials such as niobium. The successful fabrication methodologies on BNCD films were further translated to locally grown BSCD films and superconducting bridges were demonstrated for the first time. In this presentation, we will discuss our results on BNCD nano-SQUIDs and outline our current efforts in developing devices on BSCD films and their corresponding transport measurement results.

4:30 PM QT04.09.05 Towards Atomic Precision in Superconducting Qubits: Mechanisms of Ta Oxidation and Strategies for Oxidation Suppression Peter V. Sushko1,2, Chenyu Zhou1, Junsk Kim3,
Superconductivity in Nanowire Devices Formed by Al-Si Exchange

Jeffrey C. McCallum1, Brett Johnson2, Manjith Bose3, Michael Stubber4, Daniel Creedon5, Sergey Rubanov5, Vincent Mourik6, Jared Cole2 and Alex Hamilton7; 1The University of Melbourne, Australia; 2RMIT University, Australia; 3Melbourne Centre for Nanofabrication, Australia; 4CSIRO Manufacturing, Australia; 5University of Melbourne, Australia; 6Julich Research Institute, Germany; 7University of New South Wales, Australia

Development of devices that contain both superconducting and semiconducting components on a single chip is an important area of investigation for emerging quantum technologies. We have investigated superconductivity in nanowire devices fabricated using the Al-Si exchange process in silicon-on-insulator wafers. Aluminum from deposited contact electrodes undergoes an Al-Si exchange with the silicon substrate, leading to the formation of a 2D superconducting layer. The phase-transformed material is conformal with the predefined device patterns. In magnetono-transfer measurements, nanowire structures formed using this fabrication process exhibit periodic features in the differential resistance and in the critical current that result from fluxoid quantization. The re trapping current also exhibits oscillations. The devices can be operated in temperature/magnetic-field regimes where some components of the device are in the superconducting state while others are in a resistive state. Under these conditions the magnetono-transport data exhibit more complex features which may provide insight into how these mixed-state devices could be further developed for uses in magnetometry and other quantum technologies. The details of the Al-Si exchange process also suggest that it could allow a range of new nanoscale superconducting-semiconducting device structures to be formed. In this presentation, our exploration of these superconducting nanowire devices and their promise for quantum technologies development will be discussed.

SYMPOSIUM QT05

Advances in Detection Methods for Emergent Phases in Quantum Materials

April 23 - May 8, 2024

Symposium Organizers
Jessica Boland, University of Manchester
SESSION QT05.01 Advances in Detection Methods for Emergent Phases in Quantum Materials I
Session Chairs: Shelly Michele Conroy and Yang Zhang

Tuesday Afternoon, April 23, 2024
Room 446, Level 4, Summit

1:30 PM *QT05.01.01
‘Seeing’ Physical Properties of 2D Materials on Nanoscale Gizia Kazakov2,1,; National Physical Laboratory, United Kingdom; 2The University of Manchester, United Kingdom

We present a unique opportunity of ‘seeing’ physical (and chemical) properties of 2D materials and heterostructures on (sub)nanoscale. Using a combination of advances functional scanning probe microscopy (SPM) techniques, we perform a detailed local study of electrical, electronic, optoelectronic, and thermal properties. These studies are complemented by development of scanning gate microscopy techniques, where the gate can be a local source of electric/magnetic field, heat or near-field. We thus combine functional imaging with an active control and manipulation of the device properties. We demonstrate that advanced functional SPM techniques are a very powerful tool to obtain detailed information on the unique sample properties (such as the effect of non-uniformity, defects, degree of molecular absorption, etc.), which are not assessable by more traditional methods. We also demonstrate the accuracy of the measurements, which allows us to eliminate the common artefacts, which are not usually taken into account in many other approaches. The present work facilitates development of realistic 2D materials devices and their faster and reliable implementation.

We also aim to showcase the measurement capability associated with the quantum material nanoprobe facilities for the research and applications of materials for quantum technologies, at scales ranging from several micrometers down to individual atoms.


2:00 PM *QT05.01.02
The Interplay of Topology and Symmetry in Non-Symmorphic Square-Net Tellurides Probed by Scanning Tunnelling Microscopy Sarah Burke; University of British Columbia, Canada

The non-symmorphic square-net materials have been of interest due to their symmetry enforced band crossings giving rise to Dirac nodal loops and both topologically trivial and non-trivial surface states. Crystals of the P4/nmm space group feature a plane of atoms in a square net (e.g. the Si plane in the ZrSiX family or Sn plane in RESnX family) with a 2-atom unit cell due to the surrounding lattice. This doubling of the square net unit cell, along with glide plane symmetry, enforces a degeneracy at the edge of the Brillouin zone driving a crossing of different orbital symmetry that prevent hybridization. These features give rise to wide-bandwidth linear crossings which revolve around the Brillouin zone enclosing regions of distinct topology.

I will describe our recent work on two of these materials: ZrSiTe which exhibits a topologically non-trivial surface state, and LaSbTe which has a doping-dependent structural distortion that gaps portions of the nodal loop. Using Scanning Tunnelling Microscopy and Spectroscopy (STM/STS), we have investigated the surface structure and electronic states through quasiparticle interference (QPI) measurements. In ZrSiTe, the large area between two nodal loops hosts a topologically non-trivial “drumhead” surface state, previously observed up to EF by ARPES1.

However, the presence of spin-orbit coupling in this system gaps the nodal lines, raising the question of what happens to the drumhead state. Using QPI we observed strong signatures of the drumhead state below and above EF, confirming this topologically protected state persists, owing to the small energy scale of spin-orbit coupling relative to the large band width of the nodal lines2. We find that the drumhead state disperses over an energy range of ~600meV and is split, but not gapped by the presence of spin-orbit coupling.

Unlike the mild perturbation of spin-orbit coupling, changes in symmetry (perhaps obviously) break the symmetry-enforced protection of the nodal-lines giving the potential for much larger gap openings. While Si square net is held together by strong interaction with Zr, the square nets with rare-earths off plane are prone to distortion from the heavily nested Fermi surface. Indeed, stoichiometric LaSbTe forms in an orthorhombic phase featuring a buckled square-net with zig-zag chains, with a gap opening in the nodal-lines in Γ-S direction. Here we have investigated the surface structure and electronic states of twinned o-LaSiTe. The zig-zag rows of the Sb lattice can be seen in STM images, and a soft-gap of ~300meV can be observed consistent with DFT calculations for the distorted structure. Twin-boundaries show the two perpendicular orientations with domain “walls” several unit cells wide that appear tetragonal. Highly directional QPI is seen around Sb-lattice defect sites and is consistent with scattering from the remaining pockets of the nodal loops appearing in the tetragonal phase. I will also discuss the potential for doping to traverse this phase diagram and topological implications of these structural changes.

1 L. Mühler, et al. PRX 10, 011026 (2020)
2 B. Stuart, et al. PRB 105, L121111 (2022)

2:30 PM BREAK

3:00 PM *QT05.01.03
Multiscale Characterization of Quantum Materials Donald M. Evans; University of Warwick, United Kingdom

Quantum materials, defined by their unique electronic properties, are central to current scientific and technological research. Their distinct conductivity and complex phase behaviour present an intriguing puzzle with both opportunities and challenges. Central to this exploration is the interplay between microstructures, compositional changes, and the resulting electronic properties. Adopting a multiscale approach provides essential insights into the impacts of these atomic-scale changes on the material’s functional properties. In this presentation, we utilize the topological superconductor Fe(SCe,Te) to showcase the importance of applying advanced multiscale characterization techniques. Initial bulk characterization confirmed the quality of our material system, indicating high-quality homogeneous single crystals. However, local real-space mapping of the enhanced conductivity of the superconducting phase, via low temperature conductive atomic force microscopy (cAFM), revealed unexpected spatial inhomogeneities. Specifically, across five orders of real space imaging, we see that the majority of the crystal is relatively insulating, with only localized regions of heightened conductivity. To confirm and substantiate these observations, we use atom probe tomography (APT) and energy dispersive x-rays (EDX) to discern that the different regions have distinct chemical compositions. This highlights the vital role of multiscale characterization in quantum materials, illustrating their true complexities that may elude classical characterization techniques. Such approaches are essential for refining our methods and advancing quantum material research.
3:30 PM QT05.01.04
Revealing Emergent Magnetic Charge in an Antiferromagnet with Diamond Quantum Magnetometry
Anthony Tan, Harim Jani, Michael Hogen, Lucio Stefan, Claudio Castelnovo, Daniel Braund, Alexandra Geim, Annika Mechнич, Matthew Feuer, Helena Knowles, Ariando Ariando, Paolo Radaelli and Mete Atature
1University of Cambridge, United Kingdom; 2University of Oxford, United Kingdom; 3National University of Singapore, Singapore

Whirling topological textures play a key role in exotic phases of magnetic materials and offer promise for logic and memory applications. In antiferromagnets, these textures exhibit enhanced stability and faster dynamics with respect to ferromagnetic counterparts, but they are also difficult to study due to their vanishing net magnetic moment [1]. One technique that meets the demand of highly sensitive vectorial magnetic field sensing with negligible backaction is diamond quantum magnetometry. Here, we show that the archetypal antiferromagnet, hematite, hosts a rich tapestry of monopolar, dipolar and quadrupolar emergent magnetic charge distributions [2]. The direct readout of the previously inaccessible vorticity of an antiferromagnetic spin texture [1] provides the crucial connection to its magnetic charge through a duality relation. Our work defines a novel paradigmatic class of magnetic systems to explore two-dimensional monopolar physics, and highlights the transformative role that diamond quantum magnetometry could play in exploring emergent phenomena in quantum materials.

References:

3:45 PM QT05.01.05
Exploiting The Coherence of Synchrotron X-Rays to Study The Dynamics of Quantum Matter
Sophie Morley; Lawrence Berkeley National Laboratory, United States

A challenging aspect of designing functional materials is to understand the impact of a wide range of characteristic spatial and temporal scales on stabilizing novel quantum phases. Commonly used mean field approaches often provide reasonable estimates for static properties at macroscopic length scales, however, it does not provide the requisite fundamental insight into the important processes governing deviations from these averages. Such fluctuations are critically important. Soft x-rays are a powerful element-specific probe to study such mesoscopic charge and spin textures. The coherence available at current and newly upgraded light sources will enhance our tools to give significantly more detailed information of otherwise difficult to probe quantum states. We select the coherent part of the x-ray beam to produce an interference pattern known as speckle. Here I will discuss how we use that speckle to look inside, and better understand, the transitions of orbital order, amorphous noncollinear magnets and metal-to-insulator materials.

4:15 PM QT05.01.06
Optimisation of CVD Diamond for Applications in Room-Temperature Masers
Dan M Arner, Wern Ng, Yongqiang Wen, Philip Diggle and Neil McN. Alford; Imperial College London, United Kingdom

Masers are the microwave analogue of lasers and can be operated as oscillators and amplifiers with quantum-limited noise performance. Despite their exceptionally low noise, conventional masers have historically been limited to niche applications in radio astronomy and deep-space communications due to their requirement for ultrahigh vacuums and cryogenic temperatures.

Recently masers capable of operating continuously at room temperature have been demonstrated using ensembles of nitrogen-vacancy (NV) centres in diamond, opening a route to the widespread use of masers across a range of new applications in telecommunications, medical imaging and quantum sensing.

In order to realise these broad applications it will be necessary to build miniaturised, portable diamond masers that can be readily integrated into existing standards but to date this has been limited by the highly homogeneous magnetic fields required for diamond masers to maintain coherence. Here we discuss strategies for releasing the field-homogeneity requirement by optimising the material parameters of CVD-grown NV-diamond and present results benchmarking the performance of diamond masers using diamond gain media in which the concentrations of 13C nuclei and nitrogen-vacancy spins are varied. We conclude by discussing recent progress in the development of miniaturised diamond masers.

4:30 PM QT05.01.07
A Quantum Coherent Spin in a Two-Dimensional Material at Room Temperature
Hannah Stern, Carmm M. Gilaridou, Qiushi Gu, Simone E. Barker, Oliver F. Powell, Xiaoli Deng, Stephanie A. Fraser, Louis Follet, Chi Li, Andrew Ramsay, Hark Hoe Tan, Igor Aharonovich and Mete Atature; 1The University of Manchester, United Kingdom; 2University of Cambridge, United Kingdom; 3Hitachi Cambridge Laboratory, Hitachi Europe Ltd, United Kingdom; 4University of Technology Sydney, Australia; 5The Australian National University, Australia

Quantum networks and sensing require solid-state spin-photon interfaces that combine single photon generation and long-lived spin coherence with scalable device integration, ideally at ambient conditions. Despite rapid progress reported across several candidate systems, those possessing quantum coherent single spins at room temperature remain extremely rare. In this talk, I will show new results of quantum coherent control under ambient conditions of a single-photon emitting defect spin in a two-dimensional material, hexagonal boron nitride. I show that the carbon-related defect has a spin-triplet electronic ground-state manifold and that the spin coherence is governed predominantly by coupling to only a few proximal nuclei and is prolonged by decoupling protocols. These results allow for a room-temperature spin qubit coupled to a multi-qubit quantum register or quantum sensor with nanoscale sample proximity.

SESSION QT05.02 Advances in Detection Methods for Emergent Phases in Quantum Materials II
Session Chairs: Shelly Michele Conroy and Jessica Wade
Wednesday Morning, April 24, 2024
Room 446, Level 4, Summit

8:30 AM QT05.02.01
Nanoscop Advanced Materials Engineering for Quantum Technologies
Ravi Acharya, Maddison Coke, Mason Adshead, Kexue Li, Barat Achmim, Rongsheng Cai, Baset Gholizadeh, Janet Jacobs, Jessica L. Boland, Sarah J. Haigh, Katie Moore, David Jamieson and Richard J. Curry; 1Photon Science Institute, United Kingdom; 2The University of Melbourne, Australia; 3The University of Manchester, United Kingdom

The ability to engineer the electrical, optical and magnetic properties of advanced materials on the nanoscale is of increasing importance to the development of future quantum technologies. One approach to achieving this is through impurity doping, with increased control over the spatial resolution and isotopic purity enabled by the development of dedicated tools. To achieve this goal a new capability (the ‘Platform for Nanoscale Advanced Materials Engineering, P-NAME’, Facility) has been developed and applied specifically to the engineering of materials for quantum technology. We demonstrate how the combined utilisation of novel ion source and mass selection technology enables the direct-write creation of bespoke materials utilising ultra-high ion doses (>1E19 ions/cm2) down to single-ion doping. The validation of such capability requires the utilisation of advanced detection and characterisation techniques. We draw upon the combined use of electrical, photonic, mass spectroscopy and electron microscopy methods in order to enable this. Together this allows us to demonstrate the delivery of ultra-enriched 7Li as a platform for quantum technology device fabrication, and also for the doping of single-ion impurity centres within solid-state systems. Of particular interest is the development of methods to reliably detect single-ion doping events. This is a key enabling step to the inherent limitation that is otherwise imposed by Possionian statistics. Progress within this area remains a key challenge if scaling to deliver qubit arrays of the order of 10⁶ is to be achieved in order to deliver full error corrected quantum computation.

9:00 AM QT05.02.02
Magneto-transport for Dirac Semimetal Phase of Topological Insulator SnTe
Satoshi Sasaki and Joshua T. Grettton; University of Leeds, United Kingdom

Antimony Telluride (Sb₂Te₃) makes up the second generation of Topological Insulator (TI) materials with other layered chalcogenides Bi₂Se₃ and Bi₂Te₃. The TI phase in these materials arises from a spin-orbit induced band crossing of opposite parity orbitals at the Γ point of the Brillouin Zone, resulting in a single topologically protected Dirac cone projected to all surfaces. Another set of surface states have been identified in Sb₂Te₃; intrinsic Rashba spin-orbit split surface bands extending from 300 to 750 meV below the valence band edge exist within a partial valence band gap. Also, a strong linear character to the bulk valence band dispersion has been established in Angle Resolved Photo-Emission Spectroscopy (ARPES) experiments, where accidental
band crossing points\textsuperscript{2,3,6,7} imply a Dirac energy spectrum and so Dirac semimetal phase.\textsuperscript{8,9} $\text{Sb}_2\text{Te}_3$ is usually heavily hole doped due to a combination of Te vacancies and $\text{Sb}_2\text{Te}_3$ anti-site defects,\textsuperscript{10,11} with $p \approx 10^{20}$ cm$^{-3}$ the typical carrier density for nominally stoichiometric samples.\textsuperscript{12,13} The intrinsic doping effects in this material class are typically difficult to overcome, however they should also place the chemical potential close to the Dirac-like spectrum of bulk bands,\textsuperscript{2,3,12} meaning these could contribute to the transport without significant tuning of the carrier density.

So far no studies of the electronic transport looking for indications of these states has been carried out. To better understand the material system and probe for these contributions, $\text{Sb}_2\text{Te}_3$ single crystals have been grown using a modified Bridgman method with excess Te in the melt, and the magnetotransport of (001) oriented single crystal $\text{Sb}_2\text{Te}_3$ with p-type carrier densities in the range 2.4 - $10^{19}$ cm$^{-3}$ is studied up to 8 T. It is found that the semiclassical magnetotransport is described by a two-carrier band model, finding contributions from majority hole and minority electron bands, and clear Shubnikov de Haas Oscillations (SDHO) are resolved at 1.5 K across the carrier density range. The conduction of different frequency SDHO cause novel beating envelopes for samples with reduced carrier densities and non-trivial Berry phases are extracted for carrier densities in the range 4.1 - $7.9 \times 10^{19}$ cm$^{-3}$. Detailed consideration of the SDHO points away from either the Rashba or Dirac surface bands causing these, and instead the region of multiple pockets of linearly dispersive Dirac-like bulk band crossing points in the upper valence band is found responsible. This work therefore confirms a bulk Dirac semimetal phase in the well-known TI $\text{Sb}_2\text{Te}_3$.

References:

9:30 AM BREAK

10:00 AM *QT05.02.03

Intrinsic Magnetism in Infinite-Layer Nickelate Superconductors Jennifer Fowlie; Stanford University, United States

Nickel and copper are nominally similar so the search for superconductivity in nickelates is a story as old as the quest to understand the high temperature superconductivity of the cuprates. In this talk, I will introduce the recent discovery of superconductivity in infinite-layer nickelates\textsuperscript{1} and the ever-growing family of nickelate superconductors. I will touch on some of the materials challenges involved before summarizing the key physics we have learned so far. In particular I will focus on results from low-energy muon spin rotation\textsuperscript{2} that reveals local magnetism in these materials that 1) onsets at rather high temperature, 2) is independent of the rare earth 4f electrons, 3) appears to be robust to doping and 4) is antiferromagnetic and possibly short-range-ordered in nature and 5) coexists with superconductivity at low temperatures. Finally, I will come back to the comparison between nickelates and cuprates and discuss how the disparities in the magnetic properties may be understood.

References:

10:30 AM *QT05.02.04

Microstructural Effects of Topotactic Reduction in Nickelate Single Crystals Y. Eren Suyolcu, Yu-Mi Wu, Pascal Puphal, Hangoo Lee, Masahiko Isobe, Bernhard Keimer, Matthias Hepting and Peter A. van Aken; Max Planck Institute for Solid State Research, Germany

Rare-earth nickel oxides, known for their intricate interplay between structure and properties, serve as a pivotal foundation for the exploration of novel quantum phases and advanced applications. Recent topotactıve transformations of perovskite nickelates have enabled precise control over oxygen vacancies, thereby harnessing the consequential coupling effects in these materials. Gaining in-depth insights into the atomic-scale lattice and electrical structure during topotactic reduction is imperative for unraveling the potential of these phenomena. In this study, we employ atomic-resolution scanning transmission electron microscopy (STEM) imaging and electron energy-loss spectroscopy (EELS) to examine two distinct nickelate single crystal variants, namely $R_1\text{Ca}_2\text{NiO}_4\text{S}_2$ (where $R$ represents either La or Pr). These single crystals are synthesized through topotactic reduction of the perovskite phase, employing CaH$_2$ as a reducing agent. The presentation will provide a comprehensive analysis of the oxygen vacancies, hole doping into the material, and the influence of cation structure.

We primarily focus on $R_1\text{Ca}_2\text{NiO}_4\text{S}_2$ single crystals, revealing an oxygen-deficient phase with $\delta \approx 0.25$ occurring during topotactic reduction. A novel arrangement of oxygen vacancies within the brownmillerite structure, previously only observed in reduced rare-earth nickelates, Precise quantification of polyhedral tilting and bond angles shows a significant amount of internal strain drives wave-like variations in polyhedral tilting and rotations to accommodate the local lattice structure\textsuperscript{1}. Subsequently, we studied $\text{La}_1\text{Ca}_2\text{NiO}_4\text{S}_2$ single crystals subjected to topotactic reduction, resulting in the formation of an infinite-layer phase with a composition of $\delta \approx 1$ \textsuperscript{2}. Additionally, we unraveled the microstructural effects of topotactic reduction on the unoptimized $\text{La}_2\text{NiO}_3\text{S}_2$ single crystals\textsuperscript{3}. Our attention is devoted to a precise examination of the detailed lattice and chemical structures of these crystals, where our measurements of Ni$^{2+}$-O bonding conditions and electronic structures affirm the existence of the infinite-layer structure following the reduction process. The removal of apical oxygen atoms forming NO$_3$ planes within the infinite-layer phase results in metallic behavior reminiscent of weakly doped thin films. These discoveries establish a critical connection between the observable characteristics of nickelates and their underlying microscopic origins, paving the way for further exploration of nickelates with distinct crystal structures achievable only through topotactic reduction.\textsuperscript{4}

References:
3. Yu-Mi Wu et al., unpublished.
4. This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No. 823717 – ESTEEM3.

11:00 AM QT05.02.05

Visualizing Thermal Vibrations and Phonon Mode Softening in Real Space Harikrishnan K. P.; Stanford University, United States

Lattice vibrations lie at the very heart of exotic phases in quantum materials, either directly as in the case of phonon mode softening that drives the polarization in ferroelectrics or indirectly as in the phonon mediated interaction that creates Cooper pairs in superconductors. Typical methods for characterizing phonons like infrared or Raman spectroscopy and neutron scattering provide only partially averaged measurements. Although vibrational electron energy spectroscopy offers high spatial resolution, the measurements are often restricted to few well defined models. In this talk, we demonstrate the capability of electron ptychography\textsuperscript{2,5} as a novel detection tool to directly visualize lattice vibrations in real space.

We illustrate the capability of the technique to directly visualize the thermal ellipsoid of metal atoms that are intercalated in the van-der Waals gap of layered materials. The in-plane vibrational modes of the intercalants have a larger amplitude in comparison to the quenched out-of-plane mode\textsuperscript{6} and is reflected in the anisotropic thermal blur of the intercalant columns. We also show how ptychography enables us to study lattice distortions associated with a spatially localized phonon mode that is on the verge of softening in barium hexaferrite, a candidate material for quantum paraelectricity and room temperature multiferroicity.\textsuperscript{4} By analysing the potential landscape associated with this near-sof phonon mode in three dimensions, we detect the presence of nanometer-scale polar regions\textsuperscript{7} from short-range ordering in the material.
**References**

2. Z. Chen et al., Science 372, 826–831 (2021)
5. H. K. P. et al., Microscopy and Microanalysis, 28(S1), 476–478 (2022)

11:15 AM QT05.02.06

**Characterizing Coupled Order Parameters Across Successive Phase Transitions at Atomic Resolution in SmBaMnO$_6$**

Noah Schnitzer$^1$, Yorick Birkholzer$^1$, Anna S. Park$^1$, Evan Krysko$^1$, Jacob Steele$^1$, Shigeki Yamada$^2$, Taka-hisa Arima$^3$, Ismail El Baggari$^4$, Berit Goodge$^5$, Darrell G. Schlom$^1,^1$, David Muller$^1,^1$ and Lena Kourkoutis$^1,^1$; 1Cornell University, United States; 2Yokohama City University, Japan; 3The University of Tokyo, Japan; 4Rowland Institute at Harvard, United States; 5Max-Plank Institute for Chemical Physics of Solids, Germany; 6Leibniz-Institut für Kristallzüchtung, Germany

Rich phase diagrams and highly tunable ground states arising from strong coupling between electronic, magnetic, and lattice degrees of freedom make complex oxides an ideal playground for exploring connections between material structure and exotic strongly correlated properties. The A-site ordered double-perovskite manganite SmBaMn$_6$O$_9$ is a paradigmatic example: a complex set of structural distortions host a charge and orbital ordered (COO) polar antiferromagnetic ground state [1,2]. With increasing temperature, the material undergoes a series of structural, magnetic, and COO transitions governed by competing order parameters [3]. Coupling of these order parameters to the lattice generates intricate structural distortions and offers a tuning knob to control and stabilize new phases such as an anticipated ferromagnetic metallic phase under biaxial compressive strain [4].

To characterize these distortions, we measure SmBaMn$_6$O$_9$ in bulk and epitaxial thin films at atomic resolution with *in situ* scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). Studying the ground states and successive phase transitions in both the strain-free single crystal and epitaxial thin films under a series of strain states allows the role of the lattice in stabilizing electronic and magnetic order to be systematically investigated. Cryogenic STEM reveals the polar COO distortion defining the ground state structure as well as the low temperature phase transitions which reshape the COO and extinguish the polar and antiferromagnetic order. Characterization at higher temperatures can in turn clarify the structural mechanisms at play as the system undergoes an insulator-metal transition into a charge ordered phase.

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**SESSION QT05.03: Advances in Detection Methods for Emergent Phases in Quantum Materials III**

**Wednesday Afternoon, April 24, 2024**

**Room 446, Level 4, Summit**

1:30 PM *QT05.03.01*

**Brownian Electric Bubble Quasiparticles**

Jorge Iniguez$^{1,2}$; 1Luxembourg Institute of Science and Technology, Luxembourg; 2University of Luxembourg, Luxembourg

In this talk I will describe our theoretical predictions on the possibility to stabilize a new kind of quasiparticle in ferroelectric nanostructures, by suitably controlling the elastic and electric boundary conditions. These novel particles are electric bubbles (e-bubbles) that present a non-trivial topology at low temperatures (skyrmion-like) and become spontaneously mobile upon moderate heating (Brownian diffusion). I will present the typical time scales for the e-bubble dynamics and discuss the basic inter-bubble interactions -- as predicted from our atomistic (second-principles) simulations. I will also show how the e-bubbles' diffusion speed and lifetime can be tuned by controlling the temperature and the defining features of the ferroelectric nanomaterials (thickness, epitaxial strain they are subject to). I will conclude by giving an outlook of the field; in particular, I will comment on the possible use of these objects in Unconventional Computing applications.

*Work done in collaboration with Hugo Aramberry and Natalya Fedorova (Luxembourg Institute of Science and Technology). Work funded by the Luxembourg National Research Fund through Grant C21/MS15799044/FERROYDYNAMICS.*

2:00 PM *QT05.03.02*

**Ultrafast Diffraction Microscopy for Revealing Emerging Phases and Their Dynamics**

Haidan Wen, Argonne National Laboratory, United States

Light-matter interaction has been an effective approach for producing emergent phases in quantum materials. However, these phases and associated dynamics often arise on nanometer scales and evolve on ultrafast time scales, making them challenging to capture. Combined with ultrafast laser excitation, x-ray and electron diffraction microscopes have become an essential tool for studying nanoscale structural evolution. In this talk, I will demonstrate the application of laser-pumped x-ray and electron diffraction microscopy comparatively. In the first example, ultrafast x-ray diffraction imaging reveals ultrafast nanoscale phase transition in FeRh film and ferroelectric domain reconfiguration in BiFeO$_3$. In the second example, ultrafast electron microscopy reveals acoustic harmonic modes in FePS$_3$ mediated by defects. The strengths and limitations of x-ray and electron diffraction microscopy will be discussed. The exciting outlook of these techniques in the dawn of next-generation x-ray facilities will be presented.

*These works are primarily supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, under award no. DE-AC02-06CH11357 and DE-SC-0012509.*

2:30 PM BREAK

3:30 PM *QT05.03.03*

**Characterizing Disorder in High Entropy Oxides at Every Length Scale**

Alannah Hallas, The University of British Columbia, Canada

The field of high entropy oxides (HEOs) flips traditional materials science paradigms on their head by seeking to understand what properties arise in the presence of profound configurational disorder. This disorder, which emerges as the result of multiple elements sharing a single crystalline lattice appears to imbue some HEOs with functional properties that far surpass their conventional analogs. However, there are significant questions surrounding the actual degree of configurational disorder, its role in stabilizing the HEO phase, and its effect on other physical properties. Grasping the true extent of the elemental disorder in HEOs requires advanced characterization across orders of magnitude in length scales - from the atomic scale to the average structure, preferably with elemental sensitivity.

In my talk, I will discuss my group's efforts towards addressing these questions using x-ray and neutron methods. Our measurements extend from the nanoscale (x-ray absorption and extended x-ray absorption fine structure, both of which are sensitive to the immediate environment at each metal site) to the microscopic (scanning electron microscopy and x-ray fluorescence microscopy) to the average (bulk diffraction). We find that the true configurational disorder is greatly influenced by synthesis method and that significant kinetic and thermodynamic control is needed to ensure the most random elemental distributions. The most profound differences between samples are, surprisingly, observed at intermediate length scales, in the mesoscopic regime.
Here, we explore the topological phase transitions in epitaxial perovskite oxide heterostructures, for example in systems of (PbTiO3)/(SrTiO3) and (BiFeO3)/(TbScO3), using a combination of theory (DFT) calculations will help elucidate the exact mechanism of this atomic-scale manipulation.

One region of the nanodiamond; and 2. redistribute the N throughout the nanodiamond. This is a significant step toward single-defect manipulation in nanodiamond, and density functional theory (DFT) calculations will help elucidate the exact mechanism of this atomic-scale manipulation.

2. This work is supported by JST ERATO grant number JPMJER2202 and the JSPS KAKENHI (grant number 20H05659).

 SESSION QT05.04: Poster Session
Session Chairs: Jessica Boland, Shelly Michele Conroy and Ismail El Baggari
Wednesday Afternoon, April 24, 2024
Flex Hall C, Level 2, Summit

5:00 PM QT05.04.01
STEM-EELS/EDS Identification and Manipulation of Color Centers in Nanodiamond Bethany M. Hudak1 and Rhonda Stroud2; 1U.S. Naval Research Laboratory, United States; 2Arizona State University, United States

Single-photon-emitting color centers in nanodiamonds are studied extensively for their application in quantum materials. In addition to strong single-photon photoluminescence from the color centers, diamond has many advantages such as chemical inertness, mechanical hardness, and zero nuclear spin. Nitrogen-vacancy (NV) centers in nanodiamonds are a potential architecture for single-atom quantum systems. However, unambiguous identification of a single NV center in a nanodiamond is challenging. Computational work has predicted that the NV center produces a peak at 282.4 eV near the carbon K-edge in electron energy loss spectroscopy (EELS). Here, we perform simultaneous EELS and energy dispersive x-ray spectroscopy (EDS) spectrum imaging in an aberration-corrected scanning transmission electron microscope (STEM) to identify single NV centers by identifying pixels that contain both the EELS 282.4 eV peak and the EDS nitrogen signal at 0.39 keV.

Atomic-scale identification of NV centers is an important first step toward single-atom quantum device fabrication. We further demonstrate that the focused probe of the STEM can be used to reposition N and NV centers in the diamonds. By scanning the electron beam over a single nanodiamond for an extended period of time, we demonstrate the ability to: 1. corral N atoms into one region of the nanodiamond; and 2. redistribute the N throughout the nanodiamond. This is a significant step toward single-defect manipulation in nanodiamond, and density functional theory (DFT) calculations will help elucidate the exact mechanism of this atomic-scale manipulation.

 SESSION QT05.05: Advances in Detection Methods for Emergent Phases in Quantum Materials IV
Session Chairs: Shelly Michele Conroy and Ismail El Baggari
Thursday Morning, April 25, 2024
Room 446, Level 4, Summit

8:30 AM QT05.05.01
Capturing Excitons and Phonons in Quantum Materials Sandhya Susarla: Arizona State University, United States

The interplay of spin, lattice, orbital and charge degrees of freedom controls most of the emergent properties in quantum materials. The detection of these parameters at the atomic scale can unravel novel structure-property relationships that could be used to create interesting device architectures. The recent developments of direct electron detectors in analytical scanning transmission electron microscope (STEM) have made the detection of subtle electronic and structural features in quantum materials possible. In this talk, I will enlighten the contribution of our group towards measuring subtle features in quantum materials from 1) unravelling light-matter interactions in the twisted moiré materials, to 2) exploring vibrational properties across ferroelectric and multiferroic domain walls. I will end my talk with the current and future challenges that we need to address to unravel atomic scale structure-property relationship in quantum materials.

9:00 AM QT05.05.02
Emergent Excitons in Two-Dimensional Organic-Inorganic Van der Waals Heterostructures Jeffrey B. Neaton1,2,3; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States; 3Kavli Energy NanoScience Institute, United States

The ability to synthesize new classes of chemically-diverse two-dimensional materials attractive for optoelectronic applications has driven the development of new theory, computational methods, and intuition for predicting the nature of their excitons and how they may be tuned. Here, we describe the recent synthesis and measurements of an emerging class of van der Waals heterostructures, namely a bilayer consisting of atomically-thin monolayers of non-covalently bonded molecular monomomers interfaced with a transition metal dichalcogenide (TMD) monolayer. Specifically, we consider different recently-synthesized monolayers of perylene-derivative monomers, whose relative orientation can be tuned via choice of functional group, on MoSe2 and WS2 monolayers. We use state-of-the-art first-principles calculations – based on density functional theory and the ab initio GW-Bethe-Salpeter equation approach – to reveal the nature of the
Monochromated electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) is a technique that has achieved the ability to combine ultrahigh energy and spatial resolution simultaneously. As a result, a new wave of experiments on ultralow energy excitations, such as phonons, phonon-polaritons, molecular vibrations, shallow electronic structure, and infrared optical excitations have achieved exciting results in the STEM.

Here, I will show recent work at ORNL on the monochromated EELS of quantum materials with an emphasis on the emergence electronic structure and quasi-particles generated from coupling between layers in quantum dot networks and oxide superlattices. I will also focus on recent efforts at ORNL to incorporate cryogenic cooling alongside monochromated EELS in the analysis of quantum materials and some of the challenges and progress that has been made on the spectroscopy of low-dimensional quantum materials at liquid nitrogen temperatures.

Control of material processes at the level of atoms and electrons is a 'grand challenge' of materials design. With the rise of quantum materials and increasing security, resource scarcity, and sustainability considerations, the need for alternative methods of manufacturing at the atomic scale is paramount. Direct visualization of atomic-scale mechanisms allows precise tailoring of nanostructures from the bottom up. In situ transmission electron microscopy (TEM) is powerful in achieving this goal due to its high spatial and temporal resolution, obtaining atomic-scale movies while the sample undergoes functional changes, for example during nucleation, phase transformation, or current-biasing. Such direct observation of atomic motion can uncover kinetic models of nucleation and growth, as well as allow direct comparison with ab-initio or molecular dynamics simulations.

Here, I will explore the atomic-scale structure and in situ growth of an emerging class of van der Waals bonded materials termed 'mixed dimensional' heterostructures, which consist of two-dimensional (2D) + nD (where n = 0, 1, 3) materials adhered primarily through non-covalent interactions. The weak quasi-van der Waals bonding in certain 2D/3D heterostructures (exemplified by Au/MS2) results in reproducible moiré patterns that modify the electronic structure at the interface. In contrast, more strongly bound heterostructures, such as Ti3Gr, exhibit ordered arrays of dislocation networks that are strongly modulated by the 2D material layer number and compliance. We introduce a criterion for dislocation formation in such suspended systems and tailor the thin non-dislocated structures towards ultra-thin heterostructure stacks, of application in quantum sensors. We demonstrate the feasibility of forming epitaxial and single crystalline metal/2D/3D heterostructures using suspended 2D materials, with implications for next-generation Josephson junctions. Lastly, we explore the nucleation and growth of lower symmetry structures, such as 1D nanowires and nanoribbons, examining the influence of symmetry on nanostructure morphology. Such understanding of growth kinetics allows versatile design of heterostructures for next generation nanoscale devices and showcases the powerful role of in situ TEM in unraveling the intricacies of quantum materials at the atomic scale.

In EELS Compton scattering the incident electron beam undergoes an inelastic collision with individual electrons in the solid. The Compton signal appears as a broad peak in an EELS spectrum of lower symmetry structures, such as 1D nanowires and nanoribbons, examining the influence of symmetry on nanostructure morphology. Such understanding of growth kinetics allows versatile design of heterostructures for next generation nanoscale devices and showcases the powerful role of in situ TEM in unraveling the intricacies of quantum materials at the atomic scale.

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layer region. The inter-layer charge accumulates between overlapping W atoms, thereby screening the ‘wrong’ bonds generated by the twist angle. The charge accumulation is also accompanied by a local dilation of the inter-layer spacing. Time permitting I will also present other examples of EELS Compton scattering that are of interest.


SESSION QT05.06: Advances in Detection Methods for Emergent Phases in Quantum Materials V
Session Chairs: Shelly Michele Conroy, Juan Carlos Idrobo and Suk Hyun Sung
Thursday Afternoon, April 25, 2024
Room 446, Level 4, Summit

1:30 PM *QT05.06.01
Attractively Stable Cryogenic In Situ TEM Biaising Holder with Accurate Temperature Control Yevheniy Pivak, DENSolutions, Netherlands
Cryo scanning transmission electron microscopy (STEM) becomes an indispensable tool to study phase transitions in various quantum materials [1-3] at the atomic scale. Detailed characterization of the structural and electronic properties of these samples across phase transitions necessitates the need of the double tilt capability of the sample holder, atomic image stability and a continuous temperature control of the specimen. The latter is achieved through using microelectromechanical systems (MEMS)-based heating and biasing chips [4] in combination with a cryo TEM sample holder. To accurately control the structural and electronic properties of the samples during the experiment, the chips need to be calibrated to correlate the resistance of the microheater with the temperature of the sample. Since not all heater materials possess a linear resistance-temperature response and the high temperature coefficient of temperature resistance might not be valid for negative temperatures, a dedicated calibration of chips on cooling is required. While the calibration above the room temperature is nowadays done routinely by different methods [5, 6], it’s not so common in cryogenic conditions. In this talk we will present a novel method of sub-zero chip calibration based on Raman spectroscopy. The temperature calibration performed in a wide temperature range is used as the calibration factor for the R-Τ correlation at cryo conditions. The resulting calibration factor was used to continuously control the temperature of Au-Pd nanoparticles -175°C to +800°C while keeping the holder cooled. It was found that the atomically stable imaging at -175°C is maintained till the highest temperature of +800°C though the stabilization time increases as the difference between the holder and the sample temperature increases. Similar in situ cooling experiments with continuously varied temperature but in a smaller temperature range have been performed using ferroelectric FIB lamellae. With the help of electron diffraction and TEM imaging, we were able to follow all, known and unknown phase transitions, in these samples.


2:00 PM *QT05.06.02
Spatially Structuring The Surface Energy of Monolayer Graphene through Selective Heterointerface Engineering Zakaria Al Balushi1,2; 1University of California, Berkeley, United States; 2Lawrence Berkeley National Laboratory, United States
Selective bottom-up chemical synthesis of low dimensional quantum materials with high spatial resolution has long been a goal of crystal growers. The challenge, however, lies in the spatial modification of the surface energy landscape of a substrate, a crucial factor that promotes the diffusion and accumulation of adatoms and/or molecules along the surface energy gradient, consequently facilitating nucleation in regions of reduced surface energy. Herein, we demonstrate the achievement of a highly controllable surface energy landscape of monolayer graphene on diamond like carbon (DLC) substrate through a heterointerface containing trapped gallium in a uniquely designed spatial structure. The process involves three steps: (i) spatial-selectively Ga+ implantation into DLC substrate to create “hill” features with a step height of 4 nm; (ii) polymer-free transfer of monolayer graphene on top of Ga+–implanted DLC; (iii) in-situ high-vacuum annealing process above 300°C for gallium precipitation on the graphene-DLC heterointerface with low energy electron microscope (LEEM). During the annealing process, both gallium precipitation and gallium-catalyzed reconstruction of the DLC structure contribute to a shift in the local surface work function of graphene, resulting in a decrease in the surface energy of graphene compared to that of pristine graphene. At 300°C, the surface work function difference between graphene residing on the “hill” features and unmodulated region is -142 meV, corresponding to a surface energy difference between the modulated graphene region and unmodulated region of -0.23 mN/m. However, at 500°C, it is 240 meV with a of -14.5 mN/m. Notably, this difference remains consistent even upon cooling down to 300°C due to the irreversibility of gallium precipitation. In summary, a surface energy landscape of graphene with a high level of complexity can be realized by carefully tuning annealing conditions and the spatial arrangement of “hill” features, facilitating the selective area growth of materials in various nanofabrication processes.

2:30 PM *QT05.06.03
Emerging Properties of Chiral Functional Materials for Next-Generation Technologies Jessica Wade and Kim E. Jell; Imperial College London, United Kingdom
The use of organic semiconductors as low-cost, lightweight, easy-to-process active layers in optoelectronic devices has attracted considerable research and technological interest for over thirty years. The functional properties of chiral organic semiconductors, including the absorption and emission of circularly polarised light or the transport of spin-polarised electrons, are highly anisotropic. As a result, the orientation of chiral molecules impacts the functionality and efficiency of chiral devices. We have developed a strategy to control the orientation of helicenes, prototypical chiral small molecules. Our approach forces the helicenes to adopt a face-on orientation and self-assemble into upright supramolecular columns oriented with their helical axis perpendicular to the substrate, or an edge-on orientation with parallel-lying supramolecular columns, which can independently switch on and switch off low- and high-energy chiroptical responses. Our templating methodologies provide a simple way to engineer orientational control and, by association, anisotropic functional properties of chiral molecular systems for a range of emerging technologies. In this talk I will speak about our efforts to control and characterise the orientation, order and supramolecular assembly of chiral small molecules and polymers, and the impact that has on the functional properties of chiral thin films and devices.

3:00 PM BREAK

3:30 PM QT05.06.04
Probing In-Situ Twistable Moiré Quantum Emitters with Near-Field Scanning Optical Microscopy Arnab Manna, Shiang-Bin Chiu, Laurel E. Anderson, Jiaqi Cai, Xiaodong Xu and Arthur Barnard; University of Washington, United States
Transition metal dichalcogenide (TMD) Moiré superlattices are formed when two layers of TMD materials are stacked with a slight twist angle. This creates a periodic potential that can trap electrons and holes to form an array of optically active single emitters and other exotic quantum states. Compared to other solid-state emitters, Moiré emitters exist in a planar crystal and do not rely on crystal defects, giving the advantage of scalability, electrical tunability, optimized photon extraction efficiency, and ease of integration with nano-photonic structures to realize single-photon nonlinear optical effects. The twist angle in TMD Moiré superlattices critically determines the properties of the superlattice potential and thereby the optical properties of the emitters. But twisted devices are generally fabricated with a fixed angle that cannot be modified once the device has been made. In addition, the Moiré unit cell is very small, making it difficult to address single emitters with free-space optics. In this work, we propose and develop a new platform for reliable creation and read-out of Moiré emitters. This platform combines two capabilities: 1) a “Twistronics” apparatus that can bring two vDW layers into direct contact and rotate them relative to each other which allows for precise in-situ control of the twist angle between the layers, and 2) a near-field scanning optical probe that can focus and collect light from a subwavelength scale spot, making it possible to address single photon emitters in moiré superlattices. We discuss the merits and challenges of the design and report our progress in using it to study the optical properties of TMD heterobilayers. We believe that our proposed platform will be a powerful tool for exploring the correlated physics of moiré superlattices and for developing new quantum technologies based on these materials.

3:45 PM QT05.06.05
Thermoelectric Probing of Flat Bands in Twisted Bilayer Tungsten Diselenide Churing Cai, Yajie Huang, Devika Mehta and Li Shi; The University of Texas at Austin, United States

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Due to the relatively strong electron coulombic interaction compared to the small kinetic energy of the flat bands, twisted bilayer graphene moiré system exhibits strongly correlated behaviors including superconducting, insulating, and topological states at different band fillings. Compared to twisted bilayer graphene, transition metal dichalcogenides (TMDs) moiré system with a large range of twisted angles can produce very flat bands and strong correlations based on tight-binding calculation. Transport measurements of twisted bilayer tungsten diselenide (WSe2) reveal insulating and superconducting states at half-filling of the first moiré valence band. With a twisted angle less than 3° in this system, the topmost valence band appears at the Gamma-valley, with narrow bandwidths and strong correlation. Here, we employ thermoelectric measurement as a unique probe of the flat band structures and interactions in twisted bilayer WSe2 of different twisting angles. As a measure of the average entropy per charge, the Seebeck coefficient is highly sensitive to the asymmetry of the electron density of states near the chemical potential and is expected to switch sign when the chemical potential is moved across a flat band. For a sample with a twisted angle near 3°, the measured Seebeck coefficient shows pronounced modulation as the hole concentration is varied by a gate voltage. The observed dependences of the measured Seebeck coefficient on the band filling and temperature provide detailed insight into both the flat band features such as the bandwidth, as well as electron-electron and electron-phonon interactions that cause a deviation of the Seebeck coefficient from the semiclassical Mott relation.

**Non-Collinear Mn3N3In Antiferromagnets**

Lesley F. Cohen; Imperial College, United Kingdom

Antiferromagnets (AFM) hold interest because of their potential for application in high density, high speed spintronic devices, as an active layer and also as a component in superconducting S/FM/S Josephson junctions. Frustrated non-collinear antiferromagnets offer additional attractive functional properties due to their magnetic space group symmetry. Stimulated by these predictions we embarked on a growth program of non collinear antiferromagnetic antiperovskite Mn3N3In films on various perovskite substrates by pulsed laser deposition. We have used observation of the anomalous Hall effect [1] to piece together the experimental phase diagram of magnetic order with biaxial strain [2]. Theory predicts that compressively strained films should support a high temperature collinear ferrimagnetic phase [3]. We use polar MÖKE spectroscopy which in combination with DFT calculations sheds light on the origin of the magneto-optical signal as the material evolves from antiferromagnetic to ferrimagnetic phase [4]. Employing a laser scanning technique to create an out-of-plane temperature gradient we can also use the anomalous Nernst effect to provide information about domain structure in our films [5]. Finally, I will review the evidence for piezomagnetism [6,7] predicted to exist in these materials and as time allows, our recent work on the role of piezomagnetism in films grown on highly mismatched substrates.

[5] Identifying the octupole antiferromagnetic domain orientation in Mn3N3In by scanning anomalous Nernst effect microscopy, F. Johnson et al., Appl. Phys. Lett. 120, 232402 (2022)
**SYMPOSIUM QT06**

Quantum Phenomena in Oxide—Synthesis, Characterization and Automation
April 23 - May 9, 2024

**Symposium Organizers**
Lucas Caretta, Brown University
Yu-Tsun Shao, University of Southern California
Sandhya Susarla, Arizona State University
Y. Eren Suyolcu, Max Planck Institute

* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSON QT06.01: Oxide-Based Quantum Materials and Applications
Session Chairs: Sandhya Susarla and Y. Eren Suyolcu
Tuesday Morning, April 23, 2024
Room 447, Level 4, Summit

10:30 AM *QT06.01.01
Engineering Boundary Conditions to Stabilize Improper Ferroelectricity in Hexagonal LuFeO3 Films Down to the Monolayer Limit Darrell G. Schlom,1,2,3, 1Cornell University, United States; 2Kavli Institute at Cornell for Nanoscale Science, United States; 3Leibniz-Institut für Kristallzüchtung, Germany

Ultrathin ferroelectric films with out-of-plane polarization and high Curie temperatures are key to miniaturizing electronic devices, including low-power non-volatile memories. Most ferroelectrics employed in devices are proper ferroelectrics, where spontaneous polarization is the primary order parameter. Unfortunately, the Curie temperature of proper ferroelectrics is drastically reduced as the ferroelectric becomes thin; nearly all proper ferroelectrics need to be thicker than several unit cells. The absence of an ultrathin limit has been predicted, but not verified for improper ferroelectrics. These are ferroelectrics where the polarization emerges secondary to the primary order parameter, such as a structural distortion. The prime issue in thin films of improper ferroelectrics has been that they clamp to substrates that lack a structural distortion; such clamping thwarts the needed structural distortion and thus ferroelectricity. In this talk I will describe the use of an insulating substrate covered by a conducting electrode and followed by a monolayer transition layer that are not improper ferroelectrics themselves, but that do possess a structural distortion akin to that of the improper ferroelectric deposited upon them by molecule-beam epitaxy. The result is ferroelectricity with an undiminished Curie temperature in a formula-unit-thick (0.5-unit-cell) improper ferroelectric hexagonal LuFeO$_3$ (h-LuFeO$_3$) film grown on a SrCo$_3$RuO$_4$, bottom electrode with a carefully engineered monolayer transition layer. Our results* demonstrate the absence of a critical thickness for improper ferroelectricity and provide a methodology for creating ultrathin improper ferroelectrics by stabilizing its primary order parameter.

* This work was performed in collaboration with the following coauthors: Yilin Evan Li, Rachel A. Steinhardt, Megan E. Holtz, Kunchikrishnan Premakumari Harikrishnan, Rustem Ozgur, Zhuyun Xiao, Evan Krysko, Adriana LaVopa, Petruccio Barrozo da Silva, Charles M. Brooks, Mario Briit zam, Hai Li, Tanay A. Gosavi, Cha-ching Lin, Dmitri E. Nikonov, Ian A. Young, Dmitri A. Tenne, Rob N. Candler, Padraic Shafer, Elke Arenholz, Julia A. Mundy, Craig J. Fennie, Ramamoorthy Ramesh, David A. Muller, Robert J. Cava, and Christo Gussechek.

11:00 AM *QT06.01.02
Epitaxy enables emergent phenomena Rama moorthy Ramesh; Rice University, United States

The past decade has witnessed dramatic progress related to various aspects of emergent topological polar textures in oxide nanostructures displaying vortices, skyrmions, merons, hopfions, dipolar waves, or labyrinthine domains, among others. For a long time, these nontrivial structures (the electric counterparts of the exotic spin textures) were not expected due to the high energy cost associated with the dipolar anisotropy: the smooth and continuous evolution of the local polarization to produce topologically protected structures would result in a large elastic energy penalty. However, it was discovered that the delicate balance and intricate interplay between the electric, elastic, and gradient energies can be altered in low-dimensional forms of ferroelectric oxide nanostructures. These can be tuned to create and manipulate order parameters in ways once considered impossible, thanks to a fruitful, positive feedback between theory and experiment: advances in materials synthesis and preparation (with a control at the atomic scale) and characterization have come together with great progress in theoretical modeling of ferroelectrics at larger length and timescales. The new emergent states of matter join together with exotic functional properties (such as chirality, negative capacitance, and coexistence of phases) that, along with their small size and ultrafast dynamical response, make them potential candidates in multifunctional devices. Finally, some open questions and challenges for the future are presented, underlining the interesting future that is anticipated in this field.

SESSON QT06.02: Novel Synthesis for Complex Oxides
Session Chairs: Sandhya Susarla and Y. Eren Suyolcu
Tuesday Afternoon, April 23, 2024
Room 447, Level 4, Summit

1:30 PM *QT06.02.01
Unlocking the Promise and Simplicity of Atomically Precise Synthesis for 4d- and 5d Metal Oxides through Hybrid MBE Bharat Jalan; University of Minnesota, United States

The ability to achieve atomically precise material synthesis has marked a profound advancement in the field of materials science. Yet, it is often the degree of ease and precision in the synthesis process that paves the way for groundbreaking application and discovery. Consider an element of periodic table that is hard to oxidize and also difficult to evaporate, how do we create an atomically precise thin films of such metals, metal oxides or their heterostructures? This has been a central question in the synthesis science for many decades. In this talk, I will present my group’s effort to address this question. We have recently shown that both the low vapor pressure and difficulty in oxidizing a “stubborn” element can be addressed by using a solid metal-organic compound with significantly higher vapor pressure, and with the added benefits of being in a pre-oxidized oxidation state along with excellent thermal and air stability. Using this approach, we show, for the first time, the synthesis of Pt, RuO$_2$, SrRuO$_3$, and superconducting Sr$_3$Ru$_2$O$_7$ films with the same ease and control as afforded by III-V MBE. Finally, I will present a detailed MBE growth study of SrRuO$_3$ films combined with structural and transport characterizations emphasizing the role of structural inhomogeneity on anomalous hump-like magnetotransport, which has long been interpreted as a signature of Skyrmions formation.
Transition metal complex oxides exhibit a host of intriguing properties for new technologies that can be tuned by the choice of ions from the 3d, 4d, and 5d blocks of the periodic table. This combination of properties, including superconductivity, ferromagnetism, and ferroelectricity, in a single class of materials offers rich opportunities for engineering of unusual combinations of behavior through the design of multi-layer thin films. Such heterostructures can exhibit topological phenomena due to interfacial coupling between distinct phases. Our work employs hybrid metal-organic MBE and in situ X-ray photoelectron spectroscopy (XPS) to explore oxide films that exhibit strong spin-orbit coupling and interfacial charge transfer. We have demonstrated the growth of hard-to-grow materials including SrNbO3, SrRhO3, and SrRhO3 using metal-organic precursors and examined how interfacial phenomena can be tuned via charge transfer.

In this talk, I will discuss our work on SrRhO3 heterostructures grown using an Ir(acac)3 solid-source metal-organic precursor. We have synthesized epitaxial films under different conditions and strain compositions and examined the role that these play on the electronic transport and carrier dynamics. We show that the metallicity can be tuned via increasing compressive strain and employ time-domain THz spectroscopy to examine the origins of this behavior. Additionally, we have examined ways to tune the Fermi level in SrRhO3 using SrNbO3 as an n-type interfacial donor and SrCoO3 as a ferromagnetic p-type interfacial acceptor. I will discuss how these interfaces change the transport behavior in SrRhO3 through charge transfer using in situ XPS and ex situ X-ray absorption spectroscopy and scanning transmission electron microscopy. These new synthesis capabilities open routes to tuning of electronic structure in iridate films, which have been predicted to exhibit superconductivity in low-dimensional systems.

References

3:30 PM QT06.02.03
Thermal Laser Epitaxy for Ultraclean Heterostructures Hans Boshcker1, Felix Hensling2, Lena Majer2, Brendan D. Faeth2, Jochen Mannhart2 and Wolfgang Braun1,2, 1Epiray GmbH, Germany; 2Max Planck Institute for Solid State Research, Germany
We have developed a new thin-film deposition technique that is especially suited to the growth of an extremely wide range of heterostructures with atomic precision. Thermal laser epitaxy (TLE) uses chemical elements as sources, which are evaporated with continuous-wave lasers [1]. The lasers’ virtually arbitrary power density allows for the evaporation of practically all elements of the periodic table in the same setup [2]. Furthermore, a wide range of elements has been grown in oxygen environments up to pressures as high as 10^-2 mbar, yielding films of binary oxides [4,5]. In addition, extremely clean oxide surfaces can be prepared with the use of a CO2 laser substrate heater that enables temperatures up to 2000 °C [5]. Here, I will introduce the advantages of TLE for epitaxy and focus in detail on the epitaxy of ultraclean oxide heterostructures.

References
Independence of Antiferrodistortive and Ferroelectric Transition in Strained SrTiO₃ Revealed by STEM

We present a novel route to fabricating nanocrystalline oxide structures of exceptional quality utilizing freestanding oxide membranes. The thermally induced self-assembly of nanocrystalline structures is driven by dewetting oxide membranes once they are lifted off and transferred onto sapphire substrates. Upon annealing at temperatures below the melting point of the membranes, they self-assemble systematically into a variety of nanostructures such as nanovoids, nanowires, and nanocrystals. The orientation of the nanostructures is exactly provided by the crystal lattice of the transferred membrane. The microstructure of the nanocrystals exhibits exceptional quality, characterized by a pristine crystal structure and uniform stoichiometry, and their alignment exceeds the capabilities of lithography and ion-milling techniques. These findings illustrate the nanofabrication opportunities created by dewetting complex oxides. Furthermore, the physics underlying the self-assembly process in the membranes can potentially enhance our understanding of interface diffusion, which is important to epitaxial thin film growth.

Spatially Reconfigurable Antiferromagnetic states in Topologically-Rich Freestanding Nanomembranes

Antiferromagnets hosting real-space topological textures are promising platforms to model fundamental ultrafast phenomena and explore spintronics. However, to date, they have only been fabricated epitaxially on specific symmetry-matched substrates, to preserve their intrinsic magneto-crystalline order [1,2]. This curtails their integration with dissimilar supports, markedly restricting the scope of fundamental and applied investigations. Here, we circumvent this limitation by designing detachable crystalline antiferromagnetic nanomembranes of α-Fe₂O₃, that can be transferred onto other desirable supports after growth [3]. First, we show that flat nanomembranes host a spin reorientation transition and rich topological phenomenology via transmission-based antiferromagnetic vector-mapping. Second, we exploit the extreme flexibility of oxide membranes to demonstrate reconfiguration of antiferromagnetic states across three-dimensional ‘folds’ resulting from flexure-induced strains. Finally, we combine these developments using an in-situ strain manipulator to realize the first demonstration of non-thermal Kibble-Zurek-like generation of topological textures at room temperature. Integration of such freestanding antiferromagnetic layers with flat/curved nanostructures could enable spin texture designs via magnetoelectric/geometric-effects in the quasi-static and dynamical regimes, opening new explorations into curvilinear antiferromagnetism and unconventional computing.

Quantum Sensing with Rydberg Excitons

Rydberg excitons are promising quasi-particles for quantum sensing applications due to their extended wavefunctions and strong dipolar interaction strengths at higher quantum states. Electromagnetic excitations surrounding the excitons can be accurately quantified and measured when pump-probe processes are performed on them. The transitions between high-lying Rydberg states are in the microwave to terahertz frequency range, thus the excitons can absorb resonant or nearly resonant electromagnetic fields and eventually get excited into a higher state. This will lead to characteristic photon emission when the excited state spontaneously decays to the ground state. Exciton-based sensors are stable and immune to manufacturing variations, aging, and calibration issues since atoms of the same isotopic species are the same everywhere. To enable Rydberg sensing, a suitable material platform capable of hosting highly excited Rydberg excitons is crucial. Until now, cuprous oxide (Cu₂O) is the only known semiconductor in which Rydberg excitons having principal quantum numbers as high as n = 25 have been observed. This is because of its high binding energy and symmetric lattice structure, which allow it to support many Rydberg exciton states without succumbing to thermal ionization. However, reaching a defect-free condition in naturally occurring bulk cuprous oxide remains a challenge, necessitating a more controlled manufacturing technique to produce high-purity, customized synthetic cuprous oxide. Thin-film cuprous oxide samples with thicknesses less than the blockade radius are especially appealing because they make the Rydberg blockade utilizable for nonlinear behavior in semiconductors.

SESSION QT06.04: Advanced Electron Microscopy for Oxide Quantum Materials

Independent of Antiferrodistortive and Ferroelectric Transition in Strained SrTiO₃ Revealed by STEM

Doped SrTiO₃ is a prominent example of an unconventional superconductor that cannot be described by the BCS-Eliasberg paradigm. One of the main open questions is how superconductivity is connected to two other order parameters in this material, namely an antiferrodistortive instability and a ferroelectric instability. Recently, we have revealed the presence of static polar distortions in the paraelectric phase of SrTiO₃, and have discussed their role in the superconducting transition. Some studies have suggested that the antiferrodistortive distortion plays no role in the superconductivity, while others speculate that antiferrodistortive domain walls may enhance superconductivity. In this study, we use scanning transmission electron microscopy (STEM) to unveil the antiferrodistortive and ferroelectric distortion in the compressively strained, doped SrTiO₃ films. We identified the antiferrodistortive phase in real space by mapping out oxygen atoms using annular bright field (ABF) STEM. The dopant effects on the antiferrodistortive and ferroelectric phase are further elucidated by applying a free energy model with near density functional theory-level accuracy. The antiferrodistortive phase exhibits a single-domain structure, as expected due to the compressive in-plane strain. Using maps of the Ti column positions, we simultaneously measured the local polar domains. We find that unlike the local polar ferroelectric phase, which is suppressed by dopants, antiferrodistortive order persists in the presence of dopants. We show that the two transitions are largely independent of each other and the antiferrodistortive phase plays no role in the superconductivity.

Cryogenic Electron Microscopy of Electronic Order in Oxides

In correlated oxides, quantum-mechanical effects and strong electron-electron interactions give rise to superb electronic properties and a vast potential for future technologies. In these materials, electrons may self-organize into new spatial patterns that break the symmetry of the underlying crystal. This electron ordered states display a rich interplay between distinct degrees of freedom and may induce novel functionalities through the breaking of additional crystal symmetries. I will show vivid atomic-scale visualizations of electronic order enabled by the development of cryogenic capabilities (near 100 K) for scanning transmission electron microscopy. These measurements are combined with advanced analysis tools to reveal picoscale atomic displacements governing electronic transitions, the nature and symmetry of electronic order at the local scale, and nanoscale fluctuations that underlie macroscopic properties. Despite these advances, a persistent challenge in the field of cryogenic transmission electron microscopy is the lack of stable liquid-helium-cooled sample conditions. I will discuss recent developments that provide access to ultra-low temperatures, as low as 20 Kelvin, while maintaining atomic-resolution imaging performance, paving the way for broader explorations of ultra-low temperature...
phenomena in oxide and beyond.

9:00 AM *QT06.04.03
Applications of High Spatial and Energy Resolution EELS in Functional Oxides for Thermoelectric Applications  
Demie Kepaptsoglou1,2, Shihao Wang3, Feridoun Azough3, Robert Freer1 and Quentin Ramasse1,  
1SuperSTEM, United Kingdom; 2University of York, United Kingdom; 3The University of Manchester, United Kingdom

Recent advances in instrumentation, such as the introduction of advanced, high-resolution monochromators have allowed for new exciting experiments in the electron microscope. Spectroscopic signatures of optical and acoustical phonons, excitons and defect gap states are now accessible with an atom size probe and in tandem with high precision imaging. Here, we present recent results on the phonon and electronic structure of thermoelectric (TE) materials systems for heat recovery applications, using advanced electron microscopy. 

tobe expanded...

9:30 AM *QT06.04.04
Probing the Magnetic Cations in Multiferroic Magnetoelastic Thin Films  
Shelly Michele Conroy1, Geri Topore2, Demie Kepaptsoglou2, Quentin Ramasse2 and Sinead M. Griffin3,  
1Imperial College London, United Kingdom; 2University of York, United Kingdom; 3Lawrence Berkeley National Laboratory, United States

Magneetoelastic multiferroic materials show considerable potential for use in low-power computer memory and storage devices due to their coupled ferromagnetism and ferroelectricity, meaning that one could use an electric field to induce ferromagnetic domain switching. The opposite is also true, whereby a magnetic field can also cause ferroelectric domain switching. One such multiferroic material system is Aurivillius-phase Bi$_{5}$Ti$_{x}$Fe$_{y}$Mn$_{z}$O$_{18}$ (B6TFMO) thin films, where this coupling has been shown to exist in a single phase at room temperature. A large contribution to the room-temperature ferromagnetic ordering is the preferential partitioning of the magnetic cations (Mn and Fe) towards the center of the perovskite layers. Furthermore, even more complex polar topologies such as vortices around antiphase boundaries have been observed using atomic-scale scanning transmission electron microscopy (STEM) and polarization mapping. Understanding the mechanisms behind the cation segregation in the crystal structure and around crystallographic defects is of great importance if one aims to exploit the multiferroic ordering in these thin films for the manufacture of low-power, multi-state memory devices.

While atomic-scale STEM alongside techniques like Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive X-Ray (EDX) spectroscopy have been invaluable characterization tools in analysing this material system, they only provide a 2D-projected view for what really are 3D features, especially in the case of complex topologies such as polar vortices. Hence, Atom Probe Tomography (APT) will be used due to its unique 3D chemical and structural analysis capabilities and a correlated workflow will be presented. For the same sample, structural information and specimen shape measurements from STEM will be correlated with APT analysis, as well as aid in the correct choice of atom probe reconstruction parameters. This combined dataset will provide invaluable insight about the mechanisms behind the fascinating room-temperature multiferroicity in these thin film material systems.

With the aim of better understanding the cation segregation mechanisms, we will show a controlled experimental method whereby magnetic Mn cations are implanted on Bi$_{5}$Ti$_{3}$Fe$_{2}$O$_{18}$ and their segregation will be observed before and after annealing, and compared to B6TFMO in which Mn was incorporated during growth from chemical solution deposition.

10:00 AM BREAK

SESSION QT06.05: Machine Learning and Theory for Quantum Materials  
Session Chair: Y. Eren Soyokca  
Wednesday Morning, April 24, 2024  
Room 447, Level 4, Summit

10:45 AM *QT06.05.01
Machine-Guided Understanding of Functional Oxides in Extremes  
Steven R. Spurgeon1,2; 1Pacific Northwest National Laboratory, United States; 2University of Washington, United States

Directing the evolution of functional oxides in extreme environments is a longstanding challenge that requires new approaches to precision synthesis, characterization, and analytics. Our current inability to acquire, interpret, and act on multi-modal signatures greatly limits our control of materials for emerging applications, including quantum computing and energy storage. There is presently a transformative opportunity to harness artificial intelligence (AI) and domain-specific machine reasoning to guide the evolution of functional oxides more richly than ever before. Here I will describe our new framework for AI-guided experimentation, analytics, and modeling to explore oxides in extremes. This framework is transforming the study of fast-evolving phenomena, allowing us to discover latent defect signatures and determine key design parameters to control materials performance.

11:15 AM QT06.05.03
Irreducible Phonon Interactions and Phonon-Strain Couplings in SrTiO$_3$  
Shenwei Wu1, Mark A. Mathis1, Enda Xiao2 and Chris A. Marianetti1; 1Columbia University, United States; 2National Institute for Materials Science, Japan

While strontium titanate (SrTiO$_3$) has undergone extensive first-principles analysis, there remains a need for a systematic study of the irreducible phonon interactions to gain a comprehensive understanding of the vibrational Hamiltonian within a given first-principles method. Here we accurately compute cubic, quartic, and selected sextic irreducible phonon interactions, employing both the lone and bundled irreducible derivative approaches. Furthermore, the leading order irreducible strain phonon couplings are computed, yielding a detailed Taylor series of the Born-Oppenheimer potential in terms of displacements and strains. Particular focus is placed on the R-point antiferrodistortive (AFD) soft mode and the R$_{1u}$ manifold. We demonstrate that the three-fold AFD manifold has a potential that is nearly spherical, while the linear strain coupling mildly favors the experimentally observed tetragonal distortion. The full anharmonic Hamiltonian is solved within the Hartree-Fock approximation for phonons, and the resulting observables are compared to previous similar calculations and experimental data.

11:30 AM *QT06.05.04
Precise Calculations of Strong Electronic Interactions and Transport in Oxides  
Marco Bernardi; California Institute of Technology, United States

Combining density functional theory with many-body techniques is enabling rapid advances in first-principles calculations of electron dynamics in materials. Yet, oxides remain challenging because of their intricate structure and electronic interactions. In this talk, I will present new methods to model electronic interactions and transport from first principles, emphasizing their relevance to complex oxides. I will show calculations of electron interactions and transport in transition metal oxides with strong electron-lattice coupling, pronounced polaron effects, strong electron correlations, and their combinations. These results advance microscopic understanding of structure-property relationships in insulating and metallic oxides.

The talk will conclude with a discussion of PERTURBO, an open source code developed in my group providing quantitative tools to study electron interactions and dynamics in conventional and quantum materials. The recent addition of data-driven methods to compress electronic interactions and significantly speed-up their computation will be highlighted.

SESSION QT06.06: Advanced Metrology for Oxide Quantum Materials  
Session Chair: Yu-Tsun Shao  
Wednesday Afternoon, April 24, 2024  
Room 447, Level 4, Summit

1:30 PM *QT06.06.01
Defect-Property Relations at Charged Interfaces in Ferroic Oxides  
Dennis Meier; Norwegian University of Science and Technology, Norway
Oxide materials exhibit a broad range of tunable phenomena, including magnetism, multiferroicity, and superconductivity. Oxide interfaces are particularly intriguing, giving a new dimension to property engineering of functional materials. The low local symmetry at the interfaces, combined with their sensitivity to electrostatics and strain, leads to unusual physical effects, offering amazing opportunities for fundamental and applied research.

In my talk, I will discuss the unique electronic properties that arise at natural and artificially designed charged interfaces in ferroelectric and multiferroic oxides. To give an overview and demonstrate how structural, electric, and compositional degrees of freedom at such interfaces control the material’s behavior, I will present three examples: (i) ferroelectric domain walls in BiFeO$_3$, (ii) grain boundaries in ferroelectric ErMnO$_3$ polycrystals, and (iii) epitaxial heterointerfaces in multiferroic (LuFeO$_3$)$_y$(LaFeO$_3$)$_{1-y}$ superlattices. To characterize the different types of interfaces, we perform correlated microscopy measurements, combining scanning probe microscopy, electron microscopy, and atom probe tomography. The imaging experiments provide new insight into the atomic-scale structure and chemical composition at charged oxide interfaces that charge the key role polar discontinuities and point defects play for their emergent physical properties.

2:00 PM *QT06.06.02
Spin Structures and Spin Transport in Oxidic Heterostructures Mathias Klauke; University of Mainz, Germany

Magnetic oxidic insulators are exciting as they exhibit low damping and can thus be potentially used for low power GreenIT devices. Recently topological spin structures have been observed in these systems [1] and spin-orbit torques and in particular orbital torques can be used to efficiently manipulate these [2]. The low damping also lends itself to magnonic spin transport for instance in antiferromagnetic oxides. For the spin transport, spin currents are generated by heating as resulting from the spin Seebeck effect and by spin-flop pumping measurements and we find in vertical transport short (few nm) spin diffusion lengths [3,4].

For hematite, however, we find in a non-local geometry that spin transport of tens of micrometers is possible [5,6]. We detect a first harmonic signal, related to the spin conductance, that exhibits a maximum at a spin-flop reorientation, while the second harmonic signal, related to the Spin Seebeck conductance, is linear in the amplitude of the applied magnetic field [5]. The first signal is dependent on the direction of the Néel vector and the second one depends on the induced magnetic moment due to the field. We identify the domain structure as the limiting factor for the spin transport [6]. We also achieved transport in the easy plane phase [7], which allows us to obtain long distance spin transport in hematite even at room temperature [7]. Beyond hematite, we recently identified representatives of the broad class of orthoferrites, such as YFeO$_3$ and others to exhibit long distance spin transport, which additionally is highly anisotropic [8].

References:

2:30 PM BREAK

SESSION QT06.07: Quantum Phenomena in Oxide Thin Films and Interfaces
Session Chair: Sandhya Susarla
Wednesday Afternoon, April 24, 2024
Room 447, Level 4, Summit

3:30 PM QT06.07.01
Boosting the Edelstein Effect of Two-Dimensional Electron Gases by Ferromagnetic Exchange Gabriel Lazrak$^1$, Annika Johansson$^{2,3}$, Börge Göbel$^{2,3}$, Ingрид Mertig$^{2,3}$, Agnès Barthelemy$^1$ and Manuel Bipes$^1$; $^1$Unité Mixte de Physique, CNRS / Thales, Université Paris Saclay, France; $^2$Max Planck Institute of Microstructure Physics, Germany; $^3$Martin Luther University Halle-Wittenberg, Germany

Strontium titanate (SrTiO$_3$) two-dimensional electron gases (2DEGs) have broken spatial inversion symmetry and possess a finite Rashba spin-orbit coupling [1], which endows the electronic bands with unique spin textures and couples the spin of mobile electrons to their momentum. This enables the interconversion of charge and spin currents through the direct and inverse Edelstein effects (EE/IEE), with record efficiencies at low temperature [2,3].

In this work, we show that making these 2DEGs ferromagnetic enhances the conversion efficiency by nearly one order of magnitude. Starting from the experimental band structure of non-magnetic SrTiO$_3$ 2DEGs [4], we mimic magnetic exchange coupling by introducing an out-of-plane Zeeman term in a tight-binding model. We then calculate the band structure and spin textures for increasing internal magnetic fields and compute the Edelstein effect using a semiclassical Boltzmann approach [5]. We find that the conversion efficiency first increases strongly with increasing magnetic field, then shows a maximum and finally decreases.

This field dependence is caused by the competition of the exchange coupling with the effective Rashba interaction. While enhancing the splitting of band pairs amplifies the Edelstein effect, weakening the in-plane Rashba-type spin texture reduces it. Experimentally, we are studying the 2DEG at the interface between SrTiO$_3$ and the ferromagnetic oxide EuO, to imprint ferromagnetism in the gas.

References:

3:45 PM *QT06.07.02
Multipolar Ordering in CaIrO$_3$ Thin Films Regina Dittmann$^1$, Marjana Lezaic$^2$, Alexandros Sarantopoulos$^1$ and David Gustin$^2$; $^1$PGI-7, Germany; $^2$Forschungszentrum Jülich GmbH, Germany

5d-transition metal oxides, where correlations and spin-orbit coupling play at the same energy scale, create a great playground in search for high-$T_C$ and unconventional superconductivity, spin liquids and novel magnetic ordering phenomena. The metastable perovskite phase of CaIrO$_3$ was previously grown in thin-film form and characterized as semimetallic by ab-initio calculations (Yang et al., J. Phys. Condens. Matter (2010) ), although the optical conductivity spectra were inconclusive in this respect, leaving open the possibility of a small-gap insulating state. We performed first-principles calculations which yield a small insulating gap, despite a large spatial extent of Ir 5d wavefunctions. Ordering of higher-order magnetic multipoles is shown to go hand-in-hand with the gap formation.

In order to verify our calculations we have grown CaIrO$_3$ thin films on SrTiO$_3$ by pulsed laser deposition. Due to the high volatility of IrO$_3$ significant off-stoichiometry is observed despite a high crystalline quality and the formation of a stable perovskite structure. In order to obtain stoichiometric CaIrO$_3$ thin films, we had to adjust the growth kinetics while reducing the oxygen partial pressure to prevent the formation of volatile IrO$_3$. We will discuss the electrical and magnetic properties of our films in the framework of the presence of multipolar ordering, gap formation and possible structural defects.

4:15 PM QT06.07.03

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Epitaxial Synthesis of Oxide Dirac Semimetal CaNbO$_3$ Thin Films Yunkyu Park, Seoung-Hun Kang, Hua Zhou, Jong Mok Ok, Hwangsun Kim, Shan Lin, Andrew R. Lupini, Mina Yoon$^1$, Satoshi Okamoto$^1$ and Ho Nyung Lee$^1$; 1Oak Ridge National Laboratory, United States; 2Argonne National Laboratory, United States; 3Pusan National University, Korea (the Republic of)

Dirac/Weyl semimetals exhibit massless behaviors, leading to high carrier mobility and exotic quantum transport phenomena. Until now, only a limited number of studies have been conducted to explore Dirac/Weyl semimetals in oxide system, because the observation of a topological band structure to enable quantum transport is rare in oxide materials. Here, we report epitaxial synthesis of high-quality CaNbO$_3$ thin films by pulsed laser deposition on various substrates and their structural and physical properties. While bulk CaNbO$_3$ is orthorhombic, thin films revealed a delicate change of the structure depending on the growth conditions, including the type of substrates, thickness, and strain. Both tetragonal and orthorhombic phases with different octahedral symmetries were observed through X-ray Bragg rod measurements. Epitaxial strain is found to effectively manipulate oxygen octahedral symmetry from $a/b/c$ to $a' b'/c'$ or $a/b' c'$ along with structural phase transition from tetragonal phase to orthorhombic phase. Furthermore, high-mobility transport was achieved on CaNbO$_3$ films along with a large linear magnetoresistance (LMR), which is one of the representative signatures of a Dirac semimetal.

4:30 PM QT06.07.04
Directional Anomalous Skin Effect in ReO$_3$ Timothy Branch$^1$,1, Graham Baker$^2$, Mohamed Oudah$^3,3$, James Day$^{1,1}$, Alannah Hallas$^{1,1}$ and Douglas A. Bonn$^1,1$; 1The University of British Columbia, Canada; 2Max Planck Institute for the Chemical Physics of Solids, Germany

Rhenium oxide (ReO$_3$) is the most highly conducting oxide material due to its extraordinarily low residual resistivity.[1] Due to this property it has a remarkably long low-temperature electronic mean free path, similar to that seen in the ultrapure delafossites. Recent observations from broadband microwave spectroscopy have revealed a new directional anomalous skin effect (ASE) in the quasi-2D delafossite material palladium cobaltate (PdCoO$_2$)[2]. This effect has also been found in ReO$_3$. The anisotropic ASE response in these materials is influenced by the alignment of surface currents, the electromagnetic wavevector, and the facets on their Fermi surfaces. For PdCoO$_2$, recent nonlocal Boltzmann transport models for anisotropic metals accurately describe its behaviour, which falls between the ballistic and hydrodynamic electronic transport regimes.[3,4]

However, the directional ASE in ReO$_3$ has more complexity due to its three-dimensional electronic structure and multiple Fermi surface sheets. In this study, we provide microwave spectroscopy results for high-purity single-crystal samples of ReO$_3$ at low temperatures. These results demonstrate the unique anisotropy that arises for surface currents flowing in different directions with respect to the Fermi surface facets. Our findings confirm the directional ASE in ReO$_3$, and we interpret these results using nonlocal skin effect transport models.


4:45 PM QT06.07.05
Unusual Quantum Oscillations and Indications of Non-Trivial Electronic States in a Quass Two-Dimensional Electron System at Intricate Oxide Interfaces Manish Dumen$^1$ and Km Rubi$^2$; 1INST Mohali, India; 2Los Alamos National Laboratory, United States

Two-dimensional electron systems (2DES) built from perovskite transition metal oxides are potential prospects for the next generation of spintronics and quantum computing due to the simultaneous occurrence of electric-field driven superconductivity and spin-orbit interaction. To enhance technological applications, it is necessary to fully comprehend the electronic bands and confirm the anticipated electronic states in these 2DES by experimentation. Here, using thorough studies of Shubnikov-de Haas oscillations in two distinct systems, EuOKTaO$_3$ (EuOKTO) and LaAlO$_3$/SrTiO$_3$ (LaO/STO), we give new insights into the electronic states of the 2DES at oxide interfaces. We performed transport tests in high magnetic fields up to 60 T and low temperatures down to 100 mK in order to precisely resolve these oscillations. We saw a progressive increase in oscillations for 2D confined electrons at both contacts. We saw a progressive increase in oscillation frequency and cyclotron mass with the magnetic field for 2D confined electrons at both interfaces. We analyze these fascinating results by taking into account the possibility of non-trivial electronic bands, for which both linear and parabolic dispersion relations are included in the $\epsilon$-$k$ dispersion. The unconventional oscillations presented in this study not only establish a new paradigm for quantum oscillations in 2DES based on perovskite transition metal oxides, where the oscillations frequency exhibits quadratic dependence on the magnetic field, but also provide experimental evidence for topological-like electronic states in KTO-2DES and STO-2DES.

SESSION QT06.08: Poster Session: Oxide-Based Quantum Materials
Session Chairs: Sandhya Susara and Y. Eren Suyolcu
Wednesday Afternoon, April 24, 2024
Flex Hall C, Level 2, Summit

5:00 PM QT06.08.01
Isotopic Purification of TiO$_2$ Obtained by Surface-Enhanced Interstitial Injection Heonjae Jeong, Jan I. Suni, Raylin Chen, Xiao Su and Edmund Seebauer; University of Illinois, United States

Use of isotopically pure semiconductors is important in the fabrication of devices for quantum computing, as spinning nuclei require isolation from environmental perturbation by isotopically pure layers having nonspins of zero. Raw materials of sufficiently high isotopic purity are expensive and difficult to obtain, so a post-synthesis method for removing isotopic impurities would be valuable. Through isotopic self-diffusion measurements of oxygen in rutile TiO$_2$, single crystals immersed in water near room temperature, we demonstrate fractionation of $^{18}$O by a factor of three below natural abundance in a near-surface region up to 10 nm wide. Application of electrochemical biases increases the width of this region by a factor up to five. The submerged surface injects O interstitials that displace lattice $^{18}$O deeper into the solid due to the statistics of interstitial-mediated diffusion combined with steep chemical gradients of interstitials. The steep gradients arise because lowered chemical coordination at clean metal oxide surfaces facilitates the creation of interstitial atoms with energy barriers near or below roughly 1 eV.$^2$ The atomic configurations for interstitial injection resemble those for site hopping in the bulk, with barriers only slightly higher. The modest hopping barriers of interstitials. The steep gradients arise because lowered chemical coordination at clean metal oxide surfaces facilitates the creation of interstitial atoms from adsorbed atoms with energy barriers near or below roughly 1 eV. The atomic configurations for interstitial injection resemble those for site hopping in the bulk, with barriers only slightly higher. The modest hopping barriers of interstitials.

References

5:00 PM QT06.08.03
Single Crystal Growth and Properties of BaFe$_2$O$_4$ using The Floating Zone Technique Orrin Clarke-Delgado$^1$, Kevin Allen$^1$, Leroy Salary$^1$, Sunil Karna$^2$ and Doyle Temple$^1$; 1Norfolk State University, United States; 2Prairie View A&M University, United States

Materials with topological spin textures are in demand for applications like memory storage and quantum computing. The AB2O$_4$ family of crystals has a spinel structure and has been
generally requires thousands of wake-up cycles to produce the ferroelectricity which is a practical issue while integrating into nanoelectronics. The solution processed La doped hafnia thick films are extensively studied due to their potential in nanoelectronics.

Our study presents the effect of dopant and electrode on achieving robust ferroelectricity in hafnia thick films prepared by solution deposition method. Defect based systems like hafnia are stabilised by means of various parameters like dopants, temperature, electrodes, oxygen vacancies etc. Achieving ferroelectricity in Hafnia below 5nm and above 30 nm is quite challenging here we explore the efficacy of unconventionally ferroelectric Hafnia systems which are promising candidates for nanoelectronics due to their CMOS compatibility, robust ferroelectricity at this issue, as they can provide large, continuous power output and fast thermal cycling.

Cryogenic operation of devices is one of the essential requirements in the field of quantum technologies. Electrocaloric (EC) materials are promising as silent solid-state alternates to coolers at low cost.

Magnetic measurements were conducted with a Quantum Design Dynacool PPMMS. The BFGO sample shows an upturn in the magnetic susceptibility near 50 K, evidence of magnetic ordering. The M-H hysteresis curve was observed at a temperature of 2 K, indicating that the sample is ferromagnetic. To understand the underlying physics and intrinsic behavior of BFGO, a single crystal is needed. Therefore, single crystals of BaFeGaO4 are being grown using the floating zone technique to control the spinel phase structure and characterize its morphology, thermal, magnetic, and electronic properties. Results of single crystal growth will be presented.

An experimental technique known as Conversion Electron Mössbauer Spectroscopy (CEMS) is built in our laboratory to study the surface properties of thin films prepared by Molecular Beam Epitaxial method (MBE). Pure Fe (30% enriched with 57Fe) deposited on MgO substrate of 100 nm thickness is used to calibrate the CEMS system. The Zeeman spectrum and its intensity ratios of the spectral lines are analyzed in relation to the single crystal orientation. X-ray data of the thin film is correlated with this single crystal orientation and the easy axis of magnetization is determined. Comparison to the conventional transmission geometry is made for a polycrystalline sample of natural Fe absorber. The theory behind the magnetic dipole transition and the origin of the intensity Mössbauer lines are explained. Lorentzian line functions are used to obtain the least-squares fit of the experimental data.

This work is supported by the NSF PREM – Emergent Interface Materials, Grant 2122147.

SESSION QT06.09: Unconventional Superconductivity in Nickelates
Session Chairs: Yu-Tsun Shao and Y. Eren Suyolcu
Thursday Morning, April 25, 2024
Room 447, Level 4, Summit

8:15 AM QT06.09.01
Absence of Hydrogen in Highly Crystalline Superconducting Infinite Layer Nickelates
Martin Gonzalez1,2, Kyyhu Lee3,1, Yijun Yu3,2, Wooin Kim3,2, Jennifer Fowlie3,2, Anton Levlev4 and Harold Y. Hwang3,1,1 Stanford, United States; 2SLAC National Accelerator Laboratory, United States; 3Stanford University, United States; 4Oak Ridge National Laboratory, United States

Infinite-layer nickelates are promising candidates for studying unconventional superconductivity because of their electronic and structural comparison with the cuprates [1]. Superconductivity in the nickelates was first realized in strontium-doped neodymium nickelate (Nd,Sr)NiO2, which has since sparked a plethora of studies investigating Ni-based compounds [2-3]. The synthesis of infinite-layer nickelate thin films (BNiO2, R = lanthanide), is a two-step process: first involving the growth of the perovskite precursor phase followed by the deintercalation of apical site oxygen atoms via topotactic reduction [4,5]. The topotactic structural transition is commonly achieved using calcium hydride (CaH2) as a reducing agent [6,7]. It remains debated, however, whether the use of calcium hydride results in the insertion of hydrogen into the infinite layer structure [8-10]. To determine whether hydrogen is present in the infinite layer nickelates, we performed secondary ion mass spectroscopy (SIMS) measurements on optimally doped (Nd,Sr)NiO2 thin films to quantify the hydrogen content resulting from calcium hydride reduction. We find that hydrogen does not play a critical role for superconductivity in nickelates, and that the presence of hydrogen is a result of poor crystallinity in non-optimally synthesized thin films.

References

8:30 AM QT06.09.02
Advances and Challenges in The Single-Crystal Synthesis of Infinite-Layer and Ruddlesden-Popper Phase Nickelates
Mathias Horting; Max Planck Institute for Solid State Research, Germany

Unconventional superconductivity remains a key focus in condensed matter research, traditionally centered on material classes such as cuprates, iron pnictides, and heavy fermion compounds. Recently, rare-earth nickel oxides have emerged as a new class with potential for unconventional superconducting behavior. Within this nickelate family, two types of structures have drawn particular interest. The first type comprises nickelates with the infinite-layer crystal structure, such as Nd6O15NiO2, showing superconducting transition temperatures (Tc) up to 20 K. The second type encompasses Ruddlesden-Popper phase nickelates, such as La3Ni2O7, which under hydrostatic pressure manifest a remarkably high Tc of 80 K. Despite these promising...
observations, the possibly distinct mechanisms driving the superconductivity in these two types of nickelates are not yet fully understood.

To address this, further investigations employing advanced spectroscopic methods are warranted, which are capable of probing the complex interplay between electronic, magnetic, and lattice degrees of freedom typically found in unconventional superconductors. Accordingly, a tailored sample synthesis is desirable to meet the specific requirements of each spectroscopic technique, such as large sample masses for neutron scattering and cleavable single crystals for surface sensitive techniques.

Yet, both nickelate families present unique challenges in material synthesis that have previously hindered the application of certain spectroscopic methods. For infinite-layer nickelates, synthesis can only be realized via a topotactic reduction of the parent perovskite phase. This process is invasive for the sample surface and has previously been executed primarily on thin films and polycrystalline powders. In this talk, we will discuss our advances in the topotactic reduction of single-crystalline samples [1,2]. Furthermore, we have performed resonant inelastic x-ray scattering (RIXS) experiments on these crystals, providing unprecedented insights into spin excitations and charge ordering of the bulk phase [3]. The topotactic infinite-layer nickelates are also suitable for future experiments using neutron or surfaces sensitive spectroscopies.

In the case of La$_2$NiO$_4$$_5$, sizable single crystals can be readily grown using the optical floating zone method and do not necessitate topotactic treatment. However, we recently observed that these crystals exhibit multiple crystallographic phases and a pronounced sensitivity to oxygen stoichiometry, affecting their physical properties. We will delineate how a close feedback loop between advanced characterization methods and iterative adjustments of growth parameters facilitates control over the material's phases, thereby enabling the realization of single crystals optimized for subsequent spectroscopic studies.


9:00 AM *QT06.09.03

Probing The Electronic Dispersion of Superconducting Nickelates

Gael Grissomanche 1,2, Grace A. Pan 3, Harrison Labollita 4, Dan Ferenc Segedin 3, Qi Song 3, Hanjong Paik 3, Charles M. Brooks 3, Antia Botana 3, Julia Mundy 3 and Brad Rashshaw 2; 1École Polytechnique, France; 2Cornell University, United States; 3Harvard University, United States; 4Arizona State University, United States

The origin of unconventional superconductivity in the cuprates remains a mystery partly due to the complex interplay of several competing states and relatively strong disorder. Superconducting nickelates are a new family of materials [1,2] that also combine strongly correlated magnetism with unconventional superconductivity. While comparisons with the superconducting cuprates are natural, very little is known about the metallic state of the nickelates, making these comparisons difficult.

To investigate the electronic structure of the nickelates, we measured the Seebeck coefficient $S$ of a superconducting 5-layer nickelate Nd$_6$Ni$_5$O$_{12}$ ($n$ = 5 nickelate), whose resistivity is predominantly linear—indicative of strange metal physics—as well as a more-overdoped, non-superconducting, 3-layer nickelate Nd$_n$Ni$_3$O$_6$ ($n$ = 3 nickelate) for comparison. We find that both the $n$ = 5 and $n$ = 3 nickelate share a similar temperature-independent, negative $S/T$, but dramatically differs from the positive Seebeck effect measured on cuprates at similar doping [3].

To interpret our measurements, we used Boltzmann transport theory to show that the electronic dispersion obtained from first-principles calculations accounts for both the magnitude and sign of the temperature-independent Seebeck coefficient in the nickelates. This demonstrates that the electronic structure obtained from first-principles calculations is a good starting point for calculating the transport properties of superconducting nickelates, and suggests that, despite indications of strong electronic correlations, there are well-defined quasiparticles in the strange metallic state of this family of materials.

Finally, we explain the differences in the Seebeck coefficient between nickelates and cuprates as originating in strong dissimilarities in impurity concentrations. Beyond establishing a baseline understanding of how the electronic structure relates to transport coefficients in the superconducting nickelates, this work [4] demonstrates the power of the semi-classical approach to quantitatively describe transport measurements in strongly correlated electron systems, even in the strange-metallic state.

References


9:30 AM QT06.09.04

Topotactic Reduction: From Brownmillerite to Infinite-Layer Strontium Ferrite

Aarushi Khandelwal 1,2, Wooin Kim 3 and Harold Y. Hwang 1,2; 1Stanford University, United States; 2SLAC National Accelerator Laboratory, United States; 3Pusan National University, Korea (the Republic of)

Isostructural to high-temperature superconducting cuprates, other infinite-layer materials like nickelates, cobaltates, and ferrites have attracted significant interest in recent years. A popular route to synthesizing these infinite layers in thin films is growing perovskite or brownmillerite films and removing oxygen through topotactic reduction [1]. In strontium ferrite, there has been substantial work dedicated to understanding both the as-grown brownmillerite phase, which is notable for high ionic conductivity and interesting magnetic structure [2,3], as well as the reduced infinite layer phase, which is an antiferromagnetic Mott insulator studied for its correlated electronic, magnetic, thermal, and optical properties [4-8]. However, relatively little is known about the mechanism of the reduction process, which can depend on the orientation of oxygen vacancy channels in the brownmillerite films [4,9].

In this work, we grow epitaxially-strained brownmillerite SrFeO$_2$$_3$ thin films on various substrates using pulsed laser deposition and reduce them to the infinite layer phase, SrFeO$_2$, through low-temperature topotactic reduction using CaH$_2$ reducing agent. During this reduction, we track the evolution of structure and topography, probing the spatial distribution of the brownmillerite and infinite-layer phases as a function of reduction time and strain. We also study the strain dependence of the final infinite layer phase. This work sheds light on the oxygen diffusion pathways relevant to the topotactic reduction process to enable further refinement and control of the transformation between the phases.

References


9:45 AM BREAK

SESSION QT06.10: Advances in Complex Oxides

Session Chair: Sandhya Susarla

Thursday Morning, April 25, 2024

Room 447, Level 4, Summit

10:15 AM *QT06.10.01

Emerging Phase Transitions in Lead-Free Antiferroelectric Thin Films

Ruijuan Xu; North Carolina State University, United States
Transition metal oxypnictides are known to exhibit a range of exotic phenomena. For example, high temperature superconductivity in LnFeAsO$_{1-x}$F$_x$ and colossal magnetoresistance in LnMnO$_3$ are well-known phenomena. The magnetic structure at $T_{II}$ can be described using the Berezinskii-Kosterlitz-Thouless (BKT) model.

For TbMnO$_3$, the spin-freezing model fits with the parameters $H_0 = 599.79$ G and a slightly better fit with $R^2 = 0.999$; however, we note that for orthorhombic DyMnO$_3$ the spin freezing model gives a better fit with parameters $H_0 = 30.32$ G.

The superinsulating transition can be tuned by increasing $x$ in CeMnO$_3$. Variable temperature synchrotron and neutron diffraction studies confirm that there is no change in the crystal or magnetic structure at $T_R$. Results from AC transport and Hall measurements suggest this transition could be the first observation of many-body localization (MBL) in the solid state. The most significant characteristic of MBL systems is that below a transition temperature they become perfect insulators, exhibiting zero electronic conductivity. The MBL phase also acts as a quantum memory and can be used to protect quantum memory allowing the tantalising possibility of performing topological quantum computation at finite temperatures.

Emerging thin-film technology, and its electronic applications rise in parallel with the advances in their atomic-scale synthesis and characterization. Oxide based heterostructures are one key reason for these advancements. Oxide heterostructures can exhibit robust superconductivity with limited contacts.

As one of the prominent lead-free antiferroelectric alternatives, NaNbO$_3$ has received considerable research attention owing to its significant potential in energy storage applications. It is also used in the LCD industry. In this presentation, I will discuss the nature of the phase transitions in these systems and the implications for their use in energy storage applications.

In this presentation, I will discuss the nature of the phase transitions in these systems and the implications for their use in energy storage applications. Finally, I will discuss the potential for using these systems in energy storage applications and the challenges that need to be overcome to realize their potential.

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In this presentation, I will discuss the nature of the phase transitions in these systems and the implications for their use in energy storage applications. Finally, I will discuss the potential for using these systems in energy storage applications and the challenges that need to be overcome to realize their potential.
\[ \Delta H_0 = 1477.6 \text{ (G)} \]. A = 3069.9 \text{ (G)}, T_N = 70 \text{ K}, \ T_P = 189.69 \text{ and the goodness of the fit factor } R^2 = 0.997. \text{ The parameters for the BKT fit are } \Delta H_0 = 185.26 \text{ (G)}, m = -4.88, T_{BKT} = 16 \text{ K } \Delta H_0 = 3263.4 \text{ (G) and a slightly poorer fit with } R^2 = 0.994. \text{ We discuss the implications of the subtle differences in the spin dynamics as reflected in these numbers.}


**SYMPOSIUM QT07**

**3D Topological Semimetals—From Fundamentals to Applications**

**April 23 - April 25, 2024**

**Symposium Organizers**
Rafal Kurleto, University of Colorado Boulder
Stephan Lany, National Renewable Energy Laboratory
Stephanie Law, The Pennsylvania State University
Hsin Lin, Academia Sinica

* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

**SESSION QT07.01: Fundamentals, Theory and Modeling I**

**Session Chairs: Stephan Lany and Stephanie Law**

**Tuesday Morning, April 23, 2024**

**Room 448, Level 4, Summit**

**10:30 AM *QT07.05.01**

**Chirality and Topology** Claudia Felser, Max Planck Institute, Germany

Chirality is a very active field of research in organic chemistry, closely linked to the concept of symmetry. Topology, a well-established concept in mathematics, has nowadays become essential to describe condensed matter [1,2]. At its core are chiral electron states on the bulk, surfaces and edges of the condensed matter systems, in which spin and momentum of the electrons are locked parallel or anti-parallel to each other. Magnetic and non-magnetic Weyl semimetals, for example, exhibit chiral bulk states that have enabled the realization of predictions from high energy and astrophysics involving the chiral quantum number, such as the chiral anomaly, the mixed axial-gravitational anomaly and axions [3-5]. Chiral topological crystals exhibit excellent chiral surface states [6,7] and different orbital angular momentum for the enantiomers, which can be advantageous in catalysis. The potential for connecting chirality as a quantum number to other chiral phenomena across different areas of science, including the asymmetry of matter and antimatter and the homochirality of life, brings topological materials to the fore [8].

References:

**11:00 AM QT07.01.02**

**Redox-Coupled Structural Distortions in the Quasi-1-Dimensional Au2M2-xP2 System** Scott B. Lee1, Joseph Stiles1, Fang Yuan1, Fatmagül Katmer1, Stephanie Dulovic1, Tieyan Chang2,3, Yu-sheng Chen2,3 and Leslie Schoop1; 1Princeton University, United States; 2Advanced Photon Source, United States; 3The University of Chicago, United States

Symmetry and Fermi-level filling are two variables that lie at the foundation in investigating topological materials. For example, in the GaSe\textsubscript{2} system, the Ga:Se ratio governs the electron-filling of the band structure, producing a tunable system of structural distortions in its square-net layer. At specific ratios, these distortions retain certain symmetry-protected bands, such as a Dirac node on the Fermi surface, and gap out topologically trivial bands at the Fermi surface. One interest now is to investigate tunable topological structural motifs beyond a square-net of atoms. A one-dimensional (1D) chain of atoms realizes analogous symmetry protected Dirac nodes as the square net. The first part of my presentation expands on previously reported Au\textsubscript{2}M\textsubscript{2-x}P\textsubscript{2} (M=Hg, Tl, Pb, and now Bi), which contains a 1D chain of M atoms. Surprisingly, this structure type stabilizes across a difference of four electrons per chain atom, while the Bi analogue also contains a monoclinic polymorph that retains the linear chain of Bi atoms. The second part of my presentation demonstrates the importance of chemical workup in solid state compounds. X-ray and electron diffraction characterizations indicate crystals of the Au\textsubscript{2}M\textsubscript{2} system undergoes a redox-mediated structural distortion whose resulting symmetry and size of supercell depends on the identity of M. Further characterization and computations suggest modulated coordination environments as a possible driving force for the distortions. Finally, electronic transport between the modulated and unmodulated compounds are compared. As a result of these insights, nearly isolated 1D chains can be further probed in differing chemical
Probing The Low-Resistivity in Sub-5 nm Thin Nanocrystalline NbP and TaP Semimetals

Asir Intisar Khan

QT07.02.03
2:15 PM


intrinsic

United States; 2University of Colorado, Boulder, United States; 3King's College London, United Kingdom

Cd3As2 is a three-dimensional Dirac semimetal with sustained scientific interest. Intrinsic point defects, however, induce excess electron carriers that elevate the Fermi level EF away from the Dirac point and limit accessibility to its topological features. By combining density functional theory (DFT) calculations of defect formation energies and quasiparticle self-consistent GW (QSGW) electronic structure calculations, we demonstrate an innate concentration dependence of defect formation energies, and we find that Cd interstitials are the primary source of this self-doping. We extrapolate formation energies to arbitrary electron concentrations, and we utilize a thermodynamic defect equilibria model to study how extrinsic electron accepting dopants (e.g. Si, Ge, Sn) and particular growth conditions can tune EF closer to the Dirac point. Separately, Zn3As2 is a trivial semiconductor with a direct band gap of 1.0 eV that typically forms with intrinsic p-type doping, so the (Cd,Zn)As2 alloy system is expected to undergo both a topological phase transition and a net doping crossover. Using Monte Carlo simulations, we determined representative alloy structures, which can serve as the basis for predicting electronic structure and defect properties of the alloy.

11:30 AM *QT07.01.04

Chiral Topological Semimetals: Next-Generation Quantum Materials at The Intersection of Topology, Correlations and Magnetism

Niels Schröter, Max Planck Institute of Microstructure Physics, Germany

The term chirality is derived from the Greek word for ‘hand’ (kheir) and generally describes objects that are distinct from their own mirror image. It is long known that chirality plays a crucial role in nature, providing powerful functionality to chiral molecules in living organisms. Our goal is now to extend this concept from the molecular to the solid state to discover new chirality-enabled functionalities in crystals that could form the basis for new technologies. One particular focus of our activities are chiral topological semimetals, a new class of quantum materials at the intersection of structure and electronic chirality. We discovered the first example of this material class a few years ago (1) and have since demonstrated that they host new fermionic quasiparticles without analogue in high-energy physics, which carry large and controllable topological charges (2).

In this talk, I will present new results that go beyond these initial works and demonstrate that these materials realize an isotropic parallel spin-momentum locking that can be considered the natural counterpart of Rashba spin-orbit coupling (3). Moreover, I will also present fingerprints of parallel locking of the linear momentum to the orbital angular momentum. Finally, I will discuss magnetic chiral topological semimetals and the effect of spin-dependent correlations on the quasiparticle lifetimes of bulk and chiral surface states.


Here we uncover an unconventional (compared to metals) reduction of electrical resistivity with decreasing film thickness of thin nanocrystalline NbP and TaP semimetals. Our electrical measurements suggest surface-channel dominated transport with decreasing film thicknesses in these nanocrystalline semimetals.

NbP and TaP thin films are sputtered on both sapphire and MgO substrates at 400 °C, a process compatible with back-end-of-the-line semiconductor fabrication. High-angle annular dark-field (HAADF) scanning transmission electron microscope (STEM) imaging reveals nano-crystallinity of the ultrathin NbP films with short-range ordering at the NbP surface, irrespective of the film thickness. A thin seed layer of Nb (or Ta) is used to reduce lattice mismatch between the substrate and spattered NbP (or TaP) thin films, which also helps promote the local short-range order within the NbP films. The compositional homogeneity of the NbP thin films is further confirmed by energy-dispersive X-ray analysis.

The electrical resistivity of NbP and TaP shows a decreasing trend with decreasing film thicknesses (from ~80 nm down to ~1.2 nm) measured across a temperature range from 5 K up to room temperature. The sub-5 nm thin TaP and NbP films show significantly lower resistivity (e.g., ~12 µΩ-cm for 1 nm thin TaP and ~34 µΩ-cm for ~1.5 nm NbP, at room temperature) compared to their bulk single-crystal counterparts, as well as topological insulators and most metals at similar thicknesses [1,2,5,6].

Temperature-dependent measurements of our thin NbP films show increased conductivity with decreasing temperature. In contrast, bulk thick NbP (~80 nm) shows an opposite trend indicating impurity- or disorder-limited transport [5]. Based on a two-channel (surface and bulk) model of the experimental transport data, we deduce that with decreasing film thickness, the surface-to-bulk conductance ratio increases. We simultaneously find that the surface conductance increases with decreasing temperature, consistent with metallic behavior [5, 6]. Hall measurements show a decreasing trend of carrier density with decreasing thickness, and thus the estimated mobility increases for thinner films (e.g., ~7.4 cm²/Vs for ~4.3 nm NbP vs. ~0.2 cm²/Vs for bulk NbP). This also allows us to estimate a high surface-area-normalized carrier density of ~10²⁶ cm⁻², and a 2D surface mobility of ~12 cm²/Vs. As film thickness decreases, the surface mobility contribution becomes more pronounced, leading to an increased conductivity in ultrathin NbP.

In summary, we uncovered surface-state-dominated conduction in ultrathin nanocrystalline NbP and TaP films. This leads to an exceptional decrease in the resistivity with decreasing film thickness in such semimetals, promising for next-generation nanoelectronics. This work was supported in part by the Stanford SystemX Alliance.

References:

2:30 PM *QT07.02.04
Light-Field-Driven Non-Ohmic Current and Keldysh Crossover in a Weyl Semimetal Shin-ichi Kimura1,2, Osaka University, Japan; 2Institute for Molecular Science, Japan

In recent years, coherent electrons driven by light fields have attracted significant interest in exploring novel material phases and functionalities. However, observing coherent light-field-driven electron dynamics in solids is challenging because the electrons are scattered within several femtoseconds in ordinary materials, and the coherence between light and electrons is disturbed. However, when we use Weyl semimetals, the electron scattering becomes relatively long (several hundred femtoseconds - several picoseconds), owing to the suppression of the back-scattering process. This study presents the light-field-driven dynamics by the THz pulse to Weyl semimetal Co₃Sn₂S₂, where the intense THz pulse of a monocyte electric field nonlinearly generates direct current (DC) via coherent acceleration without scattering and non-adiabatic excitation (Landau-Zener Transition). In other words, the non-Ohmic current appears in the Weyl semimetal.

We uncover surface-state-dominated conduction in ultrathin nanocrystalline NbP and TaP films, leading to an exceptional decrease in the resistivity with decreasing film thickness in such semimetals, promising for next-generation nanoelectronics. This work was supported in part by the Stanford SystemX Alliance.

References:

3:00 PM BREAK

SESSION QT07.03: Interfaces and Surfaces
Session Chairs: Stephan Lany and Hsin Lin
Tuesday Afternoon, April 23, 2024
Room 448, Level 4, Summit

3:30 PM *QT07.03.01 Quantum transport and spintronics in topological semimetal heterostructures Nitin Samarth: The Pennsylvania State University, United States

We provide an overview of the synthesis and study of epitaxially grown topological semimetal heterostructures, focusing on Dirac semimetals (Cd₃As₂, ZrTe₂) and Weyl semimetals (TaAs, NbAs). Studies of the integer quantum Hall effect in high mobility films of Cd₃As₂ provide new insights into the effects of quantum confinement on the g-factor of Dirac states [1]. By interfacing Cd₃As₂ and TaAs with a ferromagnetic metal (Ni₀₃Sn₀₃), we probe efficient spin-charge conversion at room temperature, in agreement with first principles calculations of the spin hall conductivity [2,3]. We also observe surprising effects of an interfacial oxide on the magnitude and sign of the spin-charge conversion efficiency. Finally, we discuss the spin-charge conversion and spin orbit torque in ZrTe₂/CrTe₂ heterostructures wherein a Dirac semimetal is interfaced with a 2D ferromagnet [4].

This work is sponsored in part by SMART, a funded center of nCORE, a Semiconductor Research Corporation (SRC) program sponsored by NIST, the Institute for Quantum Matter under DOE EFRC grant DE-SC0019331, and the Penn State Two-Dimensional Crystal Consortium-Materials Innovation Platform (2DCC-MIP) under NSF Grant No. DMR-2039351.

Acknowledgments

4. Y. Ou et al., "ZrTe₂/CrTe₂: an epitaxial van der Waals platform for spintronics," Nature Communications 13, 2972 (2022).

4:00 PM QT07.03.02 Magnetic Field-Effect Transistors based on The Topological Semimetal NbP Lorenzo Rocchioni1, Federico Baldini1, Heinz Schmid1, Mathieu Luisier2, Vicky Süss2, Claudia Felser2, Bernd Gottsmann1 and Cezar Zota1; 1IBM Research-Zurich, Switzerland; 2ETH Zürich, Switzerland; 3Max Planck Institute for Solid State Research, Germany

In the ever-evolving landscape of electronics and semiconductor technology, the quest for faster and more efficient transistors has driven researchers to explore unconventional materials and device architectures. Topological semimetals, like Weyl semimetals (WSMs), are promising candidates for redefining transistor technology in this context. Their unique transport properties, such as linear electronic bands, chiral fermions, and topologically protected surface states, can enable innovative device architectures, potentially outperforming standard complementary metal-oxide-semiconductor (CMOS) technology. Linear energy dispersion, in particular, yields low carrier mass and ultra-high mobility, which translates to the extreme magnetoresistance, up to 10⁶ %, exhibited by these materials, such as Cd₃As₂, NbP, and WPS, and many others.

In this work, we demonstrate a new type of transistor that operates through a magnetoresistive coupling between a WSM and a superconductor. The active material is a topological WSM, NbP, whose resistivity is modulated via a magnetic field generated by the nearby superconductor. By using magnetic fields as a control quantity, the performance of the realized device is not reliant on ultra-thin channels, as is the case for semiconductor electric-field devices. More importantly, this type of device allows to modulate the resistivity of a semi-metallic channel material with extremely low resistivity, and high carrier density (up to 10⁹ cm⁻³), which is also not possible in a traditional semiconductor field-effect transistor.

A full characterization of the NbP crystalite, performed with an externally generated magnetic field (up to 9 T), reveals very high values of MR, consistent with the ones reported in the literature. The fit of quantum oscillation data according to the Lifshitz–Kosevich formula allows the extraction of the main transport-related quantities, such as electron mobility, carrier density, and effective mass. The superconductive gate is made of NbN, and it is implemented to eliminate the contribution of self-heating, caused by the power dissipated in the gate electrode, to the resistivity modulation. The SC transition of the NbN gate occurs in a temperature range of 13.1 to 13.4 K, above the operating point of the device (5 K).
The device characterization was done superposing the locally generated field with an external field offset which is able to shift the operating point of the device towards a region where the MR coupling, dp/dB, is maximized. Furthermore, we were able to accurately reproduce the resistivity variation of the external magnetic field with the local magnetic gate using point-wise measurements. Due to the exceptionally large electron mobility of this material, which reaches over $10^6$ cm$^2$/Vs, and the strong magnetoresistive coupling, we showed that the realized magnetic Weyl transistor operates with very high transconductance gain at nanowatt levels of power dissipation. Transconductance gain, together with overall low parasitic RC delay indicates the potential for improvements over standard cryogenic amplifiers technologies.

We foresee qubit readout signal amplification as a highly attractive area of application for this device due to the increasing need for low-power cryogenic amplifiers, operating at power budgets that will continue to shrink as quantum computers advance. Moreover, our device presents a generalized scheme to control the transport properties of Weyl semimetals, many of which are sensitive to magnetic fields. Overall, the obtained results indicate a promising path forward for integrated Weyl semimetal electronics that can leverage the often extreme transport properties of such materials.

References:

4:15 PM *QT07.03:03 Quantum Metric Nonlinear Hall Effect in a Topological Antiferromagnetic Heterostructure*

Anju Gao1, Ted Liu1, Barun Ghosh2, Thais Trevisani2, Yugo Onishi3, Chunhui Du6, Liang Fu4, Ni Ni5, Peter Orth3, Qiong Ma7 and Suyang Xu4

1Harvard University, United States; 2Northeastern University, United States; 3Iowa State University, United States; 4Massachusetts Institute of Technology, United States; 5University of California, Los Angeles, United States; 6University of California, San Diego, United States; 7Boston College, United States; 8National Cheng Kung University, Taiwan; 9Tata Institute of Fundamental Research, India; 10National Institute for Materials Science, Japan; 11Academia Sinica, Taiwan

Quantum geometry - the geometry of electron Bloch wavefunctions - is central to modern condensed matter physics. Due to the quantum nature, quantum geometry has two parts, the real part quantum metric and the imaginary part Berry curvature. Berry curvature has led to countless breakthroughs, ranging from the quantum Hall effect in 2DEGs to the anomalous Hall effect (AHE) in ferromagnets. In contrast, the quantum metric has rarely been explored. In this talk, I will report a new nonlinear Hall effect induced by quantum metric dipole by interfacing even-layered MoB2Te4 with black phosphorus. This nonlinear Hall effect switches direction upon reversing the AFM spins. It exhibits distinct scaling demonstrating the non-dissipative nature. Like the AHE brought Berry curvature under the spotlight, our results open the door to discovering quantum metric responses. Moreover, our data suggests that the AFM can harvest wireless electromagnetic energy, enabling applications that bridges nonlinear electronics with AFM spintronics.

A. Gao et al. Quantum metric nonlinear Hall effect in a topological antiferromagnetic heterostructure. Science 381, 181 (2023)
10:45 AM *QT07.06.01
Insights into The Role of Disorder in Topological Semimetals Kirstin M. Alberi 1, National Renewable Energy Laboratory, United States

As a result of their bandstructures, three-dimensional topological semimetals (TSMs) exhibit phenomena that are of potential interest for device applications, including ultra-high electron mobility, broadband optical absorption, linear magnetoresistance and the chiral anomaly. These behaviors have largely been studied in bulk crystals, but thin films will be required for devices. Given that disorder, in the form of defects, impurities and interfaces, will inevitably be present in thin films, it is important to understand the role they play on the behavior of TSMs. In this talk, I will discuss our use of epitaxy to intentionally vary specific forms of disorder and thereby generate new insights into property-disorder relationships. Our studies, mostly performed in Cd$_3$As$_2$ grown by molecular beam epitaxy, suggest that point defects modestly affect electron mobility but can substantially influence magnetoresistance. Impurities also offer important control knobs for controlling the Fermi level, either as extrinsic dopants or through indirect influence on the balance of point defects. Finally, I will discuss challenges and outstanding questions that the TSM field must address to effectively implement these materials into device applications.

11:15 AM *QT07.06.03
Properties of Topological Semimetal Cd$_3$As$_2$ Thin Films as a Function of Growth Optimization and Buffer Choice Thomas G. Farinha 1,2, Edwin Supple 3, Gregory M. Stephen 2, Nicholas A. Blumenstein 2, Adam L. Friedman 2, Brian Gorman 4 and Christopher J. Richardson 1,2. 1The University of Maryland, United States; 2Laboratory for Physical Sciences, United States; 3Colorado School of Mines, United States

The Dirac semimetal Cd$_3$As$_2$ is a high mobility, 3D topological semimetal with potential for exploration of quantum phenomena and future information science devices. However, the dependence of its topological properties on growth and heterostructure design is not well explored. Such parameters include growth temperature, dislocation density, and biaxial strain owing to lattice mismatch. The growth of Cd$_3$As$_2$ on different abrupt metamorphic buffer layers is therefore completed via molecular beam epitaxy. The aforementioned growth variables are considered for their effect on the final electronic and physical quality and characteristics of the thin film Cd$_3$As$_2$. Cd$_3$As$_2$ is grown on relaxed AlInSb, GaInSb, and InAsSb layers with engineered lattice constants at temperatures ranging from 50 to 130 °C. X-ray diffraction and transmission electron microscopy are used to evaluate the buffer layer maximizing and threading dislocation density. Van der Pauw measurements are conducted to determine carrier mobility and density according to the experimental variables. With the objective of maximizing electron mobility, films are grown over a range of variables including layer thickness and annealing times.

11:30 AM *QT07.06.04
Unique Electromagnetic Responses of Unconventional Topological Semimetals Junyeong Ahn 1 and Barun Ghosh 2. 1Harvard University, United States; 2Northeastern University, United States

Elucidating the physical manifestations of nontrivial band topology in materials is of great interest in quantum materials science. Recent advances in the classification of topological band cross have led to the discovery of various new kinds of low-energy excitations. Yet, the unique physical properties that qualitatively distinguish them from Weyl and Dirac fermions or conventional metals are rarely known. In this talk, we present our theoretical discovery of unique electromagnetic response properties in unconventional topological point-node semimetals [1,2]. First, we reveal the pattern of the divergent nonlinear responses as the chemical potential approaches the energy of an overtilted (i.e. the so-called type-II) nodal point, with the leading divergence determined by the dispersion and dimensionality [1]. Then, we show that chiral multifold nodal points feature the unique circular dichroism that is absent for Weyl or Dirac fermions [2]. Our finding demonstrates that new types of excitations indeed possess new responses, motivating further exploration of other unconventional fermions whose unique response properties are elusive.

This work was supported by the Center for Advancement of Topological Semimetals (CATS), an Energy Frontier Research Center funded by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences, through the Ames Laboratory under contract No. DE-AC02-07CH11358.


SESSION QT07.07: Transport
Session Chairs: Kirstin Alberi and Stephan Lany
Wednesday Afternoon, April 24, 2024
Room 448, Level 4, Summit

1:30 PM *QT07.07.01
Lattice-Geometry Driven Hybrid Nodal Fermions in Topological Semimetals Bahadur Singh 1 and Sougata Mardanya 2. 1Tata Institute of Fundamental Research Mumbai, India; 2Howard University, United States

Successful classification of topological electronic states based on the crystalline lattice symmetries led to the identification of many topological materials through high-throughput first-principles modeling. Such symmetry-to-topology characterizations, however, ignore the effects of various crystallographic or nanoscopic motifs and their associated wavefunction properties even though they are essential for describing the numbers, energy-momentum relations, and geometries of the nontrivial states. Here, we discuss how spatial arrangements of atoms dictate the nature of energy dispersions of topological states in materials [1]. Specifically, we focus on anisotropic lattice materials and demonstrate that the lattice geometry-driven effective mass anisotropies dictate the hybrid nodal-line states by considering transition metal tetraphosphides MP4 (M = Transition metal) as exemplary materials. We also discuss a general theory of incorporating orientation-dependent carrier effective masses as experimental fingerprints for determining energy dispersion in topological materials.


2:00 PM *QT07.07.02
Structural Goldilocks Effect in The Ultra-Pure Topological Semimetal PtSn$_4$ Samikshya Sahu 1,2, Dong Chen 1,2, Niclas Heinsdorf 1,2, Mohamed Oudah 1, Douglas A. Bonn 1,1, Sarah Burke 1,3,4 and Alannah Hallas 1,1. 1University of British Columbia, Canada; 2Max Planck Institute for Solid State Research, Germany; 3The University of British Columbia, Canada

The Residual Resistivity Ratio (RRR) serves as a pivotal metric to gauge sample quality for metals, where RRR is the ratio of the resistivity at room temperature (~ 300 K) to the resistivity at base temperature (~ 0 K). For common metals like Au or Cu, transport behavior at 0 K primarily reflects the inherent defects and disorders within the material. Whereas at room temperature, the electronic transport is substantially influenced by other factors, such as phonons. Therefore, a sample with a high RRR can be valued as possessing fewer intrinsic defects and less disorder. However, such pristine materials are tough to come by and often require a lot of effort to optimize the crystal growth technique to make defect-free samples.

PtSn$_4$ is a rare exception, and shows ultra-low resistivity around 2 K and remarkable RRR values exceeding 1000. One of the other dominating electronic properties of this material is its ultrahigh magnetoresistance (XMR), which onsets at 30 K. Magnetoresistance (MR) is the resistance that develops in a material as a response to the application of the magnetic field. PtSn$_4$ is
Experimental Observation of Nonreciprocal Reflection in a Magnetic Weyl Semimetal at Zero Applied Field

QT07.08.01
3:30 PM

Weyl nodes. This unique topological effect paves the way for the realization of practical Berrytronic devices.

The cyclotronic resonance frequency, the nonreciprocal response of magnetic Weyl semimetals is believed to be governed by the nontrivial Berry curvature that exists between recombinant electron and hole-like Fermi surfaces characterized by anisotropic carrier scattering likely due to the lack of Lorentz invariance.

We report a transport study on PtSn4, which displays multiple Dirac type-II nodes in its electronic dispersion. PtSn4 is characterized by low residual resistivities and high mobilities, which are consistent with Dirac-like quasiparticles. For an applied magnetic field ($\mu_0 H$) having a non-zero component along the electric current, we find a large, positive, and linear in $\mu_0 H$ longitudinal magnetoresistivity (LMR). The sign of the LMR and its linear dependence deviate from the behavior reported for the chiral-anomaly-driven LMR in Weyl semimetals. Interestingly, such anomalous LMR is consistent with predictions for the role of the anomaly in type-II Weyl semimetals. In contrast, the transverse or conventional magnetoresistivity (CMR for electric fields $E$) is large and positive, increasing by $10^3 - 10^4 \%$ as a function of $\mu_0 H$ while following an anomalous, angle-dependent power law $\rho_{xx} (\mu_0 H)^n$ with $n(0) \lesssim 1$. The order of magnitude of the CMR, and its anomalous power-law, is explained in terms of uncompensated electron and hole-like Fermi surfaces characterized by anisotropic carrier scattering likely due to the lack of Lorentz invariance.

References

Topological Semimetals in Heavy Fermion Compounds
Silke Buehler-Paschen; Vienna University of Technology (TU Wien), Austria

Gapless electronic topology driven by strong correlations is an emerging field of great interest, with heavy fermion compounds at its forefront. I will introduce the first such materials class, Weyl-Kondo semimetals [1-3], and report on the giant signatures of topology observed in Ce5Bi3Pd4 [1,3] and the genuine topology control that can be achieved by magnetic field tuning [4,5]. I will also discuss design strategies for further correlation-driven topological phases, and discuss several realizations [6,7].

This work was supported by the Austrian Science Fund (FWF-I4047, I5868-FOR5249-QUAUST, SFB F 86, Q-M&S), the European Union’s Horizon 2020 Research and Innovation Programme (824109, EMP), and the European Research Council (ERC Advanced Grant 101055088, CorMeTop).


RARE-EARTHR-BASED RSBTE MATERIALS, WHICH ARE ISOSTRUCTURAL TO THE NODAL-LINE SEMIMETALLIC ZrSiS, ARE GATHERING RESEARCH ATTENTION BECAUSE OF THE POSSIBLE ELEMENTS OF ELECTRONIC CORRELATIONS AND MAGNETISM. THE EFFECTIVE ELECTRONIC STRUCTURE OF THE R3RSBHETE FAMILY OF MATERIALS IS DENSELY POPULATED, WHICH CAN LEAD TO THE OCCURRENCE OF PHASE TRANSITIONS, CRITICAL SUPERCURRENT DENSITIES FOR CURRENT FLOWING IN OPPOSITE DIRECTIONS WITHIN THE MATERIAL, AND THE PREDICTION OF MEV-SCALE QUANTUM SENSING.

SESSION QT07.09: van der Waals and 2D Materials
Session Chairs: Stephanie Law and Hsin Lin
Thursday Morning, April 25, 2024
Room 408, Level 4, Summit

10:00 AM *QT07.10.01
The Josephson Diode Effect in Junctions formed from 2D Van der Waals Metals
Stuart S. Parkin; Max Planck Institute of Microstructure Physics, Germany

Recently, we have discovered a non-reciprocal Josephson diode effect in several Josephson junctions, both lateral and vertical, formed from conventional superconducting oxides (Nb, NbSe2) and non-superconducting oxides (MoTe2, MoOx, and MoO3) separated by a 2D van der Waals Dirac semi-metal, NiTe2 [1]. We discuss a variety of other 2D materials that show a Josephson diode effect including WTe2 [2], as well as the observation of a coherent Josephson effect, and we focus on the results of our recent studies on the superconducting interlayer coupling in van der Waals Dirac materials. These junctions are promising candidates for ultra-sensitive quantum sensors at cryogenic temperatures.


10:30 AM QT07.10.02
Engineering Van der Waals Heterostructures of Layered Dirac Materials for meV-Scale Quantum Sensing
Elizabeth Peterson and Jian-Xin Zhu; Los Alamos National Laboratory, United States

Quantum sensing of meV-scale scattering and absorption of impinging particles with electrons in solid state detectors has important applications not only of interest for fundamental physics, such as the detection of astronomical phenomena and light dark matter, but also for quantum information, such as single photon detectors for quantum key distribution. Current sensing and detection schemes often use single-phase detectors, such as superconductors or narrow gap semiconductors. These detector targets face challenges in differentiating between signals that come from impinging particles of interest and those from inherent quasiparticles, such as phonons and magnons, requiring operation at extreme cryogenic temperatures.

Heterostructures of layered Dirac materials offer a novel pathway to selective detection of impinging particles that can operate at more realistic temperature scales for scalable quantum sensing technology. In our scheme, by engineering interfacial orbital hybridization in van der Waals heterostructures of Dirac materials, interlayer charge transfer is promoted only for pre-selected types of impinging particles based on their dispersion relations (i.e., specific quantum mechanically allowed combinations of energy and momentum transfer). Here we present first-principles density functional theory calculations on exemplar heterostructures of the layered Dirac materials ZrTe5 and HfTe5 as a proof-of-principle of this novel quantum sensing scheme. As massive Dirac materials with narrow band gaps and strain-sensitive band structures, ZrTe5 and HfTe5 are ideal testbeds for detection of meV-scale absorption and scattering events. We demonstrate that the electronic structure of these heterostructures exhibits a promising distribution of regions of single-layer and hybridized interlayer orbital character necessary for selectable interlayer charge transfer. We examine the effects of strain and layer number for tunable hybridization in the electronic structure and the type of impinging particle that may be detected. We suggest that by exploiting hybridization in heterostructures of Dirac materials, it is possible to construct “dispersion filters” for next-generation quantum sensors.
Exceptional Electronic Transport and Quantum Oscillations in Thin Bismuth Crystal Grown inside Van der Waals Materials

Amy Wu1, Laisi Chen1, Naol Tulu1, Joshua Wang1, Adrian Juans2, Kenji Watanabe1, Takashi Taniguchi2, Michael T. Pettes3, Marshall Campbell1,4, Chaitanya Gadre1, Yinong Zhou1, Hangman Chen2, Penghui Cao1, Luis Jauregui1, Raqian Wu1, Xiaoxing Pan1,1,1 and Javier Sanchez-Yamagishi1
1University of California, Irvine, United States; 2California State University Long Beach, United States; 3National Institute for Materials Science, Japan; 4Los Alamos National Laboratory, United States.

Most materials are challenging to produce as uniform and thin crystals with large grain size. Varying the thickness of a material alters its electronic behaviors and enables new devices. We have developed a new synthesis technique to grow crystals in a nanoscale mold defined by atomically-flat van der Waals (vdW) materials. We heat and compress bismuth in a vdW-mold made of hexagonal boron nitride (hBN), resulting in controlled thickness such as ultraflat 10 nm to 100 nm thick bismuth. The vdW-molded bismuth at different thickness all shows exceptional electronic transport, enabling the observation of Shubnikov–de Haas quantum oscillations originating from the (111) surface state Landau levels, which have eluded previous studies. Our vdW-mold growth technique establishes a platform for electronic studies and control of bismuth’s Rashba surface states and topological boundary modes. Other than molding bismuth, we have also successfully molded tin and gold. Beyond confining in thickness, we also molded bismuth into vdW-molds with predefined shapes. This vdW-molding approach provides a low-cost way to synthesize ultrathin crystals and directly integrate them into a vdW heterostructure.

We thank Teodor Todorov, Jean Jordan-Sweet, Lerato Takana and Yuri Suzuki for the technical support in materials characterization. We thank Pavlo Sukhachov, Arun Bansil, Tay-Rong Kerns1, Franco Stellari1, Nathan Marchack1, Vesna Stanic1, Utkarsh Bajpai3, Ion Garate4, Gengchiau Liang5, Yi-Hsin Tu6, Shang-Wei Lien6, Ravishankar Sundararaman7, Sushant Kumar7,3, Prineha Narang; Princeton University, United States.

10:45 AM QT07.10.03

Symmetric State Topological Heavy Fermion Metal in Twisted Bilayer Graphene

Bogdan A. Bernevig and Prineha Narang; Princeton University, United States.

We show that the noninteger filling low temperature state of twisted bilayer graphene is a symmetric metal which exhibits a kondo resonance. This fermi liquid state can then become susceptible to pairing, as it efficiently screens the coulomb interaction.

11:00 AM QT07.10.04

Applications of Topological Semimetals for Post-Cu Interconnects

Ching-Tzu Chen
1, Hsin Lin2, Christian Lavoie1, Nicholas Lanzillo3, Guy M. Cohen1, Oki Gunawan1, John Bruley1, Peter Kerns1, Franco Stellari1, Nathan Marchack1, Vesna Stanic1, Utkarsh Bajpai3, Ion Garate4, Gengchiau Liang5, Yi-Hsin Tu6, Shang-Wei Lien6, Ravishankar Sundararaman7, Sushant Kumar7,3, Prineha Narang; Princeton University, United States.

Conventional diodes are characterized by an asymmetry in positive and negative switching currents and could potentially find utility in the second half of the talk, we will report detailed experimental studies of CoSi. We present first-principles-based electrical transport calculations of a Si-CMOS compatible topological semimetal CoSi and a prototypical Weyl semimetal NbAs. We will summarize the simulation results of pristine films and films with point defects, line defects, or grain-boundaries. We will also report the contact resistance scaling between a topological semimetal and a conventional liner material.

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Ion Diffusion and Morphology of PEDOT:PSS. Insight from Molecular Dynamics Simulations

Jior Zozoulenko, Tahereh Sedghamiz, Mohsen Modarresi and Aleksandar Mehandzhiyski; Linköping University, Sweden

Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is one of the most important mixed electron-ion conducting polymers, where the efficiency of the ion transport is crucial for many of its applications. Despite of the impressive experimental progress in determination of the ionic mobilities in PEDOT:PSS, the fundamentals of ion transport in this material remain poorly understood and the theoretical insight of the ion diffusion on the microscopical level is completely missing.

In the present paper, Martini 3 coarse grained molecular dynamics (MD) model for PEDOT:PSS is developed and applied to calculate the ion diffusion coefficients and ion distribution in the film.1 A prerequisite to study the ion diffusion in PEDOT:PSS is to build its adequate morphological model properly describing its two-phase morphology as well as water intake and ion exchange. Using the coarse-grained calculations we developed this model by mimicking experimental process of film formation by drying the emulsion of PEDOT:PSS particles.2 We demonstrate that PEDOT:PSS film is an essentially three component system, consisting of positively charged PEDOT chains, PSS chains with mostly deprotonated sulfonate groups, and protonated PSS chains.3 PEDOT-rich regions are predominantly composed of PEDOT and deprotonated PSS chains, whereas PSS-rich regions are composed of protonated PSS chains. Our calculations unravel how PEDOT-rich and PSS-rich regions are formed from the solution phase during drying process. We show that when the dry polymer film is immersed in water its swells by nearly 60%, and we demonstrate that the origin of swelling is related to deprotonation of the sulfonate groups in the PSS-rich regions. It is mostly PSS-rich regions that swell while the PEDOT-rich regions remain rather unchanged.

Using the obtained morphology we calculated the ion diffusion coefficients for Na⁺ ions and we found that they are practically the same in the PEDOT-rich and PSS-rich regions and do not show sensitivity to the oxidation level. We compare the calculated diffusion coefficients with available experimental results. Based on this comparison, and based on the MD morphology simulation of PEDOT:PSS revealing the formation of pores inside the film, we revised a commonly accepted granular morphological model of PEDOT:PSS. Namely, we argue that PEDOT:PSS films, in addition to PEDOT-rich and PSS-rich regions, must contain a network of pores, where the ion diffusion takes place.

We believe that our results demonstrate the power of the MD simulations for organic mixed electron-ion conductors providing the essential insight into polymer morphology and ion diffusion that is difficult to obtain by other means.

References:

Organic Electrochemical Transistor Materials for Bio-Interfacing Electronics

Ting Lei; Peking University, China

Organic electrochemical transistors (OECTs) are one of the most promising options for bio-interfacing electronics, as they have high transconductance, low operation voltage (<0.8 V), good biocompatibility, and intrinsic compatibility with ion-related biological events. Compared to the abundant high-performance p-type OECT materials, n-type and ambipolar OECT materials are rare, and more importantly, their performances lag far behind, which largely limits the development of OECT-based logic circuits and amplifiers for bio-interfacing electronics. To address this issue, we designed and synthesized a series of n-type and ambipolar materials and proposed a design strategy, namely "doped state engineering", which has greatly improved the performance and response speed of both n-type and ambipolar OECT materials. Based on these materials, we have realized high-performance logic circuits and amplifiers that exhibit high voltage gains, suitable for in vivo biosignal capture and amplification.

Next-Generation Design Strategies for Organic Mixed Conductor Technologies

Alexandra F. Paterson; The University of Kentucky, United States

Organic mixed ionic-electronic conductors (OMIECs) and organic electrochemical transistors (OECTs) have enormous potential to impact everyday life and society – from low-cost biotechnologies in a widespread healthcare internet of things, to versatile neuromorphic computing technologies operating at the bio-hybrid interface. While significant research progress has
Dopant-Induced Morphology Changes and Their Impact on Thermoelectricity in Polymers
Oliver Fenwick
Queen Mary University of London, United Kingdom

Conducting polymers have attracted interest as thermoelectric materials because of their processability, light weight, flexibility, low toxicity and cost. In terms of performance, it is their intrinsically low lattice thermal conductivity (typically 0.2 – 0.5 Wm$^{-1}$K$^{-1}$) which is of particular interest to the thermoelectric community. However, can we assume that the thermal conductivity is always low in these systems? Doping these systems is required to obtain useful electrical conductivities, but causes significant morphological changes in order to incorporate the large molecular dopants and further structural adjustments occur to accommodate the polaronic charge carriers. How do these morphological changes impact the thermal conductivity of polymers? How does this impact zT?

This presentation aims to shed some light on these questions, by investigating the cases of four polymers, poly(3-hexyl thiophene) [P3HT], poly(3,4-ethylenedioxythiophene) [PEDOT], poly[(6,9-dihydro-6,9-dioxbisbenzimidazo[2,1-b]indenazol [mm]phenanthroline-2,12-diy] [BBB] and poly[1-oxy-7,10-benz[de]-imidazo[4,5,6]-benzimidazo[2,1-a]isoquinoline-3,4:10,11-tetrayl]-10-carbonyl] [BBB]. We measure in-plane thermal conductivity of different P3HT morphologies produced by spin-coating, drop coating and aligned by mechanical rubbing. We also compare doped and undoped analogues of these films. We do find an effect of morphology on thermal conductivity in aligned polymer films that we can link to structural changes. However, by far the biggest effect on lattice thermal conductivity comes from electrical doping, which induces a subtle change to the morphology but a significant increase in thermal conductivity. We find thermal conductivity states in the range of 0.2 to 1 Wm$^{-1}$K$^{-1}$.[1] In PEDOT, we de-dope the polymer to improve the Seebeck coefficient, but also aim to maintain or improve charge transport. We observe significant morphological changes in this process which we link to the macroscopic observables.

In the case of BBB and BBL we investigate the effect of ladderisation on polymers (BBB being a ladder-type polymer and BBL it’s non-ladder type analogue). Ladder-type polymers should be more planar and more rigid than non-ladder types. Correspondingly, we find that the thermal conductivity in the ladder-type polymer can be 3 times that in the non-ladder-type analogue. When doped the lattice thermal conductivity increases to remarkably large values > 2 Wm$^{-1}$K$^{-1}$.

In spite of tremendous progress in molecular design, engineering and processing, only few small molecule organic semiconductors (OSCs) have reached charge carrier mobilities ($\mu$) higher than 10 cm$^2$/Vs, typically with single-crystal devices. However, $\mu$ is a material property and not a molecular one. It is thus of paramount importance to take supramolecular order into consideration at all length scales. As recently evidenced, the best OSCs tend to self-organize into large plate-like single-crystals exhibiting a layer-by-layer herringbone packing motif. Moreover, thermal lattice fluctuations cause temporal variations of transfer integrals ($J$) and impose a transient localization of charges leading to reduced macroscopic $\mu$ in these weakly bonded van der Waals solids. We will present recent progress achieved in our group in terms of molecular design and understanding of the impact of thermal energetic disorder: design by theory, crystal engineering, quantum-chemical calculations and evaluation of transport properties in electronic devices.

References:

4:00 PM SB02.03.02
Polymeric Organic Crystals of P(NDI2O-T2): Impact of Microstructure on the Charge Transport Properties
Chamkara D. Karunasena1, Hong Li2, Casey Davis2, Megan R. Brown3, Joel H. Bombille1, Vaeceleav Coropceanu1, Chad Risko3, Michael Toney2 and Jean-Luc Bredas1;1 The University of Arizona, United States;2 University of Colorado Boulder, United States;3 University of Kentucky, United States

The electronic charge transport characteristics of organic semiconductors (OSCs) are intricately linked to their solid-state morphology. Deciphering the complex interplay of these OSC polymer properties with the supramolecular organizations in their (semi)crystalline state is of importance in the pursuit of high-performance materials for next-generation optoelectronic technologies. However, currently available in-situ experimental characterization techniques offer limited nano-scale insight, making it challenging to comprehensively describe the microstructure of fabricated films in terms of crystallinity and polymer conformations and orientations, and thus to rationalize the relationship of structure with associated electronic properties. In this study, we present an in-depth characterization of the supramolecular crystal organization and its impact on the electronic charge transport properties of polymeric crystalline forms of the n-type hydro-carbon polymer P(NDI2O-T2); this material can have low energetic disorder and high electron mobility, making it well-suited for a wide range of electronic device applications. Based on available experimental data from X-ray scattering techniques and infra-red spectroscopy, we derive the crystal unit-cell structures of the three reported polymeric forms at the atomistic scale, through a meticulously parameterized classical molecular dynamics force field in conjunction with periodic density functional theory (DFT) calculations. Furthermore, we extend our simulations to investigate the diverse morphological aspects of the semicrystalline structure following thermal treatment and account for the factors governing the polymeric interconversion and selectivity. We sample the nano- to microstructure of the simulated thin films and quantify charge carrier transport through density functional theory calculations. These results serve as the foundation to establish critical and fundamental correlations between crystalline transport properties and the nano- and microstructure of the polymer, as well as the associated disorder. This, in turn, allows the determination of the dominant transport microscopic parameters and provides insight into how these parameters can be tuned through precise processing techniques.

4:15 PM SB02.03.03
Synthesis and Functionalization of New Chromophores for Organic Electronics & Photonics
John Anthony, Tanner Smith, Karl Thorley and Dean Windemuller; University of Kentucky, United States

High-performance organic electronic and photonic devices require optimization of both the core chromophore and the chromophores’ interactions in the solid state. Recently, we have explored the synthesis and implementation of larger chromophores - either linked trimeric systems or very long (> 8) fused-ring aromatic compounds to enhance both photonic properties and improve intermolecular contacts. Along with these new chromophores, we have developed new functionalization strategies to allow solution processing and to impart some control over the solid-state order of the cores. By this process, we have made a series of remarkably stable large aromatic systems with absorption well into the near-infrared. By tuning electronic coupling within chromophores, we have developed new singlet fission chromophores that yield quintet states exclusively. By tuning the functional groups on other systems, we have found approaches using C-H...H interactions to dramatically reduce disorder, and are studying the impact on charge transport. Due to their increased rigidity, we expect these larger polycyclic systems to demonstrate significant improvements in mobility. Thorough studies of decomposition mechanisms for these higher fused aromatic compounds have elucidated new reaction pathways, along with approaches to minimize reactions with oxygen or dimerization, yielding materials with unprecedented stability.

4:30 PM SB02.03.04
Exploiting Charge Transfer States in Molecular and Organic Electronics
Oana D. Jurchescu; Wake Forest University, United States

The growing demand for smaller, faster, and more versatile electronics has led to a surge of interest in new device concepts. One promising approach is to exploit charge-transfer (CT) state that forms at the interface between charge donor and acceptor molecules. However, establishing reliable relationships between donor/acceptor molecular structures, the resulting CT, and physical properties is challenging. In this talk, the implications of the hybrid electronic states will be discussed by examining two model systems: a monolayer of co-assembled molecules with strong electron donor and acceptor termini, and a polymorphic system based on a donor/acceptor charge transfer salt in the form of single crystals with varying donor-acceptor overlap. In the molecular rectifiers based on self-assembled molecules, the charge transfer state is responsible for the observed increase in the rectification ratio, despite the reduction caused in the film degree of order. These high-performance molecular diodes have been employed in circuits to effectively rectify an AC signal. In the single crystals, we correlate the solid-state packing with the degree of charge transfer and the resulting electrical properties. We also probe the sub-gap, trap states, through the measurement of field-effect transistors, an analysis which has so far seen little application in ambipolar devices. Our results provide evidence that small differences in donor/acceptor overlap can induce significant changes in electronic coupling and electrical properties of organic devices and highlight the potential of charge transfer states as a disruptive approach to engineering organic electronics.
adjusting the synthetic procedure and use of surfactants, we achieve an impressive conductivity of up to 66 S/cm (with an average of 48 ± 18 S/cm), ranking among the highest for n-type polymers processed using green solvents. The new n-type polymer also exhibits outstanding stability, maintaining 89% of its initial conductivity after 146 days of storage in air. Our synthesis approach, along with the novel polymer it yields, promises significant advancements in the field of electronic polymers.

5:00 PM SB02.04.02
Spin Transport Modeling in The Small Tetraheme Cytochrome William Livernois and Anant Anantram; University of Washington, United States

Multi-heme cytochromes have attracted attention due to their conductive properties [1] and, more recently, their spin-selective properties [2]. The small tetraheme cytochrome (STC), a c-type cytochrome found in S. oneidensis, has been demonstrated experimentally to act as a spin filter [3], with the potential to be used in nano-scale spintronic devices. Building upon a spin-dependent transport model previously applied to related biornaterials and cytochromes [4], we investigated decoherent transport through the cytochrome and electron hopping between heme groups. This model incorporated spin-orbit coupling and a generalized spin model to explore non-collinear effects. Preliminary findings indicate that collinear effects, arising from electron exchange and spin state, predominantly influence the transport pathway while spin-orbit effects only cause minor shifts in orbital energies. Notably, the peptide backbone functions primarily as a structural scaffold facilitating heme-to-heme electron transport, rather than directly contributing to electron conduction. We also examined the impact of solvation within our model and identified its role in modulating the coupling between heme sites and the overall conductivity of the cytochrome.

The research was supported by National Science Foundation NSF Grant Number 2317843, NSF Future of Manufacturing Grant No. 229131, and the NDSEG fellowship.

References:

5:00 PM SB02.04.03
Exploring DNA-Carbon Nanotube Interfacial Transitions and Interaction Olaiyan M. Alolaiyan1,2 and M. P. Anantram1; 1University of Washington, United States; 2King Abdulaziz City for Science and Technology, Saudi Arabia

In the rapidly changing world of combined scientific studies, two standout materials are drawing attention: DNA and carbon nanotubes (CNTs). DNA, known for its central role in carrying genetic information, is a wonder of nature's design. On the other hand, CNTs, recognized for their strength and electrical properties, represent the best of modern material advancements. Studying the interaction between DNA and carbon nanotubes (CNTs) presents a series of tangible challenges. One of the main obstacles is that the inherent differences in their chemical properties make direct interactions between them non-trivial. In addressing the challenges of understanding the intricate interactions between DNA and CNTs, our approach leverages the power of Molecular Dynamics (MD) simulations. MD simulations offer a dynamic and detailed perspective, allowing us to scrutinize the behavior of our DNA-CNT system. To initiate our study, we began by modeling the direct interaction between DNA and CNTs without forming any covalent bonds. This step was pivotal, setting the groundwork before introducing the linker and further constructing the comprehensive DNA-Linker-CNT system. The introduction of a linker in the system, studied under MD, can provide insights into creating stable bonds that bridge DNA and CNTs, ensuring their effective interaction without compromising their individual properties.

In our comprehensive study on the DNA-Linker-CNT system, we utilize a systematic methodology to elucidate the behavior and stability of the structure complex. Each component of the system was carefully constructed: the DNA, in its B-form comprises a 12-basepair double-stranded sequence denoted as (3G3C3G3C). The linker, a 10-atom amino linker, served as the bridge in our system. The CNT has a chirality of (6,6) and is 10 primitive cells long. Crucially, to ensure accurate simulations, we employed specific force fields: the Amber force field bscl for DNA, and GAFF (Genetic Amber Force Field) for the linker and CNT. By having the individual components, our next step was to bring them together into a cohesive environment. This involved forming bonds between the DNA, linker, and CNT, followed by the application of force fields – with specific force fields parameters calculated for the linker and CNT. To simulate a realistic biological environment, we introduced a water solvent using the TIP3P model, encapsulating our system in an octahedral geometry with a 15-angstrom buffer. Then we ionized the structure to ensure it was ready for the Molecular Dynamics (MD) simulations.

The MD simulations were significant in revealing the dynamics of our system. Across multiple runs, a consistent observation was the pronounced attraction between the DNA and CNT, with the DNA segment near the CNT's surface, adopting a stable configuration involving the interaction between pi-orbitals on the DNA and CNT. This proximity between the pi-orbitals of the two subsystems, sustained over a significant portion of the simulation, is indicative of potential electron transport opportunities, a phenomenon further corroborated by RMSD analyses which underscored the stability of each component. Our observations so far paint a promising picture for the DNA-Linker-CNT system, hinting at potential channels for electron transport. Complementing our MD studies, we are performing transport calculations which will be presented to further enhance our understanding. These calculations shed light on the electron transfer between the DNA and nanotube systems under a variety of CNT-Linker-DNA-CNT configurations. Together, MD simulations and transport calculations provide a comprehensive and promising approach to unravel the complexities of the DNA-Linker-CNT interactions, paving the way for a deeper understanding of these systems. [We acknowledge NSF FMRG 2328217 and NSF SemisynBio 2027165 grants.]
Spiropyran is a photoswitch that can be used to fabricate light-switchable organic electronic devices. The system is particularly interesting, because the UV light-induced isomerization of the neutral spiropyran (SP) to the zwitterionic merocyanine (MC) can be exploited to reversibly tune OFET characteristics [1-3]. One possible approach to incorporate spiropyran-based photo-switches into organic transistors is to blend them with dielectric polymers to obtain light-responsive gate dielectrics. However, there is no consistent explanation in the literature for how isomerization of the photoswitch alters charge transport of OFETs, and several mechanisms have been proposed. We address this issue by blending spiropyran molecular switches with alkyl side chains of different lengths (i.e., C₁₁, C₁₂, C₁₃ and C₁₄) with poly(methyl methacrylate) (PMMA) and study the reversible switching of these functional blends using UV/Vis absorption spectroscopy, impedance spectroscopy and further electrical characterization in metal-insulator-metal capacitors and OFETs. The UV/Vis absorption data show that all four derivatives isomerize to their respective MC form upon UV irradiation. Thermal annealing induces the reverse reaction from MC to SP. In OFETs, the reversible switching between the SP and MC states translates into pronounced, reversible shifts of the threshold voltage.

Surprisingly, we find that the switching of both capacitor and transistor characteristics strongly depends on the length of the alkyl side chain of the photoswitch. This suggests that the change of the dipole moment (low versus high) and the charge (neutral versus zwitterionic) might be the only cause for the altered device characteristics, but that the side chains must also be considered. This chain length dependent switching is further investigated by bias stress measurements using OFETs and a similar dependence on the chain length is found.

Such a chain length dependent reversal of the switching in light-gated devices has not been reported before. Hence, our results highlight the importance of the chemical design of photocromatic molecules for well-controlled switchable devices.


5:00 PM SB02.04.08
Photoinduced Charge Transfer at Quantum Dot to Dye Interface
Svetlana V. Kilina, North Dakota State University, United States

Recent focus on assemblies of the QDs functionalized by various organic and metal-organic dyes is dictated by their promise to serve as a key element for both solar- to-electrical and solar- to-chemical energy conversion processes. Our simulations of QD/dye composites have led us to predictions of conditions that govern the direction and rates of the charge transfer from the QD to the dye and interpretation of transit-spectroscopy data.

5:00 PM SB02.04.09
Iteratively Synthesized, Atomically Precise Graphene Nanoribbons with Heteroatoms
Steven Koehlerowski, Nicholas Angello, Wesley Wang and Joseph Lyding; University of Illinois at Urbana-Champaign, United States

The semi-metallic electronic structure of graphene has been the major problem in the fabrication and integration of graphene electronic devices. While the thermal, optical, mechanical, and electronic transport properties of graphene vastly outperform silicon, the very low on-off current ratio prevents 2D planar graphene from being used as a controllable channel in field effect transistors (FETs). Graphene nanoribbons (GNRs), laterally confined, 1D structures of graphene exhibit a wide variety of bandgaps while maintaining similar physical properties. For example, GNRs are predicted to have electron mobilities and thermal conductivity over twenty-five times higher than that of Silicon. However, limitations in current GNR synthesis techniques prevent the use of heteroatoms from being incorporated into a length-controlled ribbon. Here, I discuss a solution-based iterative coupling technique capable of synthesizing GNR copolymers and GNRs with heteroatoms. This increase control over GNR synthesis arises from the use of tetramethyl N-vinyl-N-iminodiacetic acid (TIDA) protected haloboronic acid difunctionalized GNR building blocks. By utilizing optimized catch-and-release purification methods and automated machinery, we’ve demonstrated the ability to create user-defined, atomically precise, length controlled GNR copolymers with no human intervention in as little as eight hours. Because TIDA-protected boronic acids can be deprotected under mild, basic conditions, these GNR building blocks can be synthesized with the inclusion of heteroatoms without degradation. GNR building blocks containing Oxygen, Sulfur, and Nitrogen have already been synthesized. The inclusion of these electron-rich species into the graphene lattice alters the electronic band structure and ribbon conductivity, effectively n-type doping the local environment. These synthesized GNRs and GNR copolymers are then exfoliated onto metallic and semi-conducting surfaces in situ in ultra-high vacuum (UHV) using dry-contact transfer. Finally, these on-surface GNRs probed using scanning tunneling microscopy (STM) to better understand their electronic structure, on-surface behavior, and stability. This procedure has the potential to open the floodgates to hundreds of novel GNRs and GNR heterostructures that can be used in post-silicon devices.

5:00 PM SB02.04.10
Active Learning Approaches to Predict Intramolecular Noncovalent Interactions in Organic Semiconductors
Moses Ogbaje1,2, Vijaykumar Karthikeyan3, Kyle Eldridge1, Vinayak Bhat4, Baskan Ganaphathysubramaniam5 and Chad Risko1,2; 1University of Kentucky, United States; 2Center for Applied Energy Research, United States; 3Paul Laurence Dunbar High School, United States; 4Columbia College, United States; 5Iowa State University of Science and Technology, United States

The natures and strengths of intramolecular noncovalent interactions are critical to the formation of organic semiconductors (OSC) from their molecular or polymer-based building blocks. While there are several quantum-chemical approaches available to evaluate intermolecular noncovalent interactions, including symmetry-adapted perturbation theory (SAPT), these methods can be computationally expensive, especially for the types of large building blocks used in OSC. This computational cost limits the ability of machine-enabled searches of the OSC chemical and materials space. Machine learning (ML) models have emerged as powerful tools to provide fast predictions of a variety of molecular and material properties at a fraction of the computational cost when compared to quantum-chemical approaches, though they often require substantially large and labeled datasets, posing challenges when data is scarce or difficult to obtain. Here, we discuss an active learning approach that augments ML models trained to predict intermolecular noncovalent interactions by incorporating a prediction confidence. The active learning scheme is developed to enable the reduction of labeled data requirements by identifying regions in the chemical space where the model exhibits the highest uncertainty. This combined approach demonstrates effective and fast determination of intramolecular noncovalent interactions in OSC.

5:00 PM SB02.04.11
Morphology Control Strategies for Efficient Charge Transport versus Injection in Solution-Processed Organic Electronic Devices
Minsoo Kim, Woong Sik Kang and Dong Hwan Wang; Chung-Ang University, Korea (the Republic of)

**ABSTRACT BODY:**

Organic electronic devices have attracted much attention owing to their advantages such as solution processable, low cost, superior absorption coefficient, flexibility, and so on. By developing of the non-fullerene acceptors (NFAs), organic photovoltaics (OPVs) achieved high power conversion efficiency (PCE) over 19% and organic photodetectors (OPDs) beyond the detectivity of 10¹⁴ Jones. These desirable results are thanks to the various morphology control strategies of organic semiconductor materials, and novel thin film formation process using their. In this study, we suggest the morphology control strategies in terms of various morphology engineering and thin film formation process. Representative methods of controlling the morphology of photovoltaic materials include additive engineering (morphology regulator), and ternary strategies by introducing the guest compounds, those enable efficient charge dynamics by controlling molecular orientation. The morphology of the photovoltaic material which composed of polymer donor PM6 and non-fused ring electron acceptors (NFREAs) TPDC-4F controlled by additive engineering which induce efficient charge transport and photo-induced direction of the donor and acceptor components through volatilization process of the high boiling point of additive. Accordingly, we successfully fabricated efficient OPDs (Detectivity of 1.27 × 10¹³ Jones) with suppressed dark current (3.55 × 10⁻⁹ A cm⁻²) [1]. Moreover, the ternary strategy introducing the high LUMO level guest acceptor (EH-IDTBBr) with PM6:BTP-4F-12 binary blend, can block the injected charge from external efficiently and robust transfer the photo-generated charge carrier, is promising method.
for morphology regulation. The devices with ternary strategy based on optimal ratio of EH-IDTBR showed advanced OPV (PCE of 16.20%), and OPD (Detectivity of 1.31 × 10^13 Jones) performances [2]. In addition, morphology also can be adjusted by thin film lamination process. To achieve a desirable thin film surface morphology with a well-distributed donor (PMe) and acceptor (BTP-4F-12) phase in the vertical structure, we developed a vacuum-free (VF) lamination process, in which the blend films with various thicknesses using the adhesion-optimized PUA mediators are transferred onto the target substrates without the vacuum process. Consequently, the VF-laminated devices achieved improved OPV (PCE of 15.97%) and OPD (D^* of 3.61×10^13 Jones) performances. Additionally, the device prepared using the VF-lamination exhibited improved internal resistance, as well as photoresponsivity response, as observed by optical, electrical, and morphological analyses [3, 4].


5:00 PM SB02.04.12
WITHDRAW (NO REG) 5/20/2024 SB02.04.12 Impact of Dielectric Environment and Counterion Size on Polaron Characteristics in Electrochemically Doped n-Conjugated Polymers
Megan R. Brown1, Joel Bombile1, Jean-Luc Bredas2, Zhitong Chen2, Chamikara Karunasena2, Hong Li2, Erin L. Ratcliff2 and Chad Risko1; 1University of Kentucky, United States; 2The University of Arizona, United States

Electrochemically doped n-conjugated polymers (CP) are central materials in several emerging applications such as semiconductors in optoelectronic devices, active materials in thermoelectric generators, and electrode or binder materials in batteries. In these systems, electronic transport is controlled by the formation of polarons, which act as charge carriers in the CP. As the CP interacts with counterions from an electrolyte source, the charge associated with the polaron is stabilized. While both the counterion and the solvent environment involved in this interaction can impact the optical and charge-carrier properties of CPs, a clear understanding of the governing mechanisms is still lacking. Here we focus on assessing how single-chain polaron properties are impacted by changes in the surrounding dielectric environment and counterion used. We use first-principles calculations based on density functional theory (DFT) and time-dependent density functional theory (TD-DFT) with a tuned range-corrected hybrid functional to determine various polaron characteristics in the model CP N2200 in assorted dielectric environments with and without counterions of varying sizes present. We find that the Coulomb interactions between the polaron and the counterion lead to smaller, more strongly bound polarons as reflected by changes in charge delocalization, bond distortion, and polaron features of the optical absorption spectra. These data provide valuable insight into how such variables impact the charge transport properties of electrochemically doped CPs.

References

5:00 PM SB02.04.13
Expanding The Compatibility of P3HT Hole Transport Layers for Stable NIP Perovskite Solar Cells
David Hardy1, Fang Feng2, and Feng Gao3; Linköping University, Sweden

In order for perovskite solar cells to be commercially competitive, attaining robust environmental stability is of the utmost importance. In a standard nip device stack the material selection for the surface hole transport layer (HTL) is critical, as it will dictate the degree that air and moisture will penetrate into the sensitive perovskite layer. Present high performing devices rely upon passivation layers.

The conjugated polymer poly(3-hexylthiophene) (P3HT) is one such polymer, and has been successfully implemented as an HTL in numerous reported perovskite solar cells, attaining efficiencies up to 24.6% [1]. However, typically these high performances rely upon interfacial perovskite treatments to induce favourable P3HT orientation and packing, and thus introduce restrictions on choice of perovskite chemistry or passivation method, that are not present for Spiro-OMeTAD. While reports that rely on oxidative dopants such as F4TCNQ, to increase the conductivity of P3HT HTL, exhibit lower efficiencies [2]. Therefore, presently P3HT based devices lag behind their Spiro-OMeTAD counterparts, in terms of performance, and versatility.

Recently the novel “ion-modulated radical doping strategy” for Spiro-OMeTAD based HTLs has outlined a doping strategy that relies upon a stable radical (Spiro-2TFSI) to increase conductivity, in conjunction with an ionic modulator (TMBP-TFSI) to improve hopping transport between molecules [3]. Drawing inspiration from the IM-Radical doping strategy, this work aims to develop an analogous co-doping approach, for P3HT (or other low-cost polymers). Oxidising dopants such as charge transfer materials, Lewis acids, photo-initiator salts, and electrophile salts have been screened in order to maximise HTL conductivity, and thus short circuit current, while various ionic modulators have been employed to align material work functions and maximise the open circuit voltage. Through this combined doping approach we aim to develop a low cost P3HT based HTL that can match the performance of established Spiro-OMeTAD based devices and offer improved environmental stability, without imposing material restrictions upon the underlying device stack.

References

5:00 PM SB02.04.14
Measuring Carrier Lifetimes in Organic Solar Cells
Ally Hud1,2, Awwad N. Alotaibi2, Obaid Alqahtani2, James R. Doyle1 and Brian A. Collins2; 1Macalester College, United States; 2Washington State University, United States

Printable and flexible organic solar panels are promising sources of inexpensive, large-scale renewable energy, where panels can be manufactured by printing from polymer inks. There are some limitations to these types of solar cells, however. First, toxic halogenated solvents have historically been necessary to dissolve polymers to make the ink. In addition, organic solar cells typically have high rates of recombination, which limits their efficiency. Here, we use a transient photovoltage (TPV) technique to measure charge lifetimes in cells made from two different organic solvents. The first solvent is toxic, halogenated dichlorobenzene (DCB) which is typically used to make organic solar cells. The other is a less toxic, non-halogenated solvent, carbon disulfide (CS2). By varying the processing methods in this way, we find that cells made from CS2 have longer charge lifetimes and higher efficiencies than those made with DCB. Possible reasons for these differences are explored using semi-analytic and numerical modeling. This work demonstrates that we may be able to decrease the toxicity of organic solar cell manufacturing and simultaneously improve the efficiency of the devices, bringing this powerful method of capturing solar energy to the forefront of sustainable energy solutions.

5:00 PM SB02.04.15
Conductivity Control by Welding of Nanomembrane for Stretchable Electronics
Jeeyoung Kim1,2, Minjeon Kim1,2 and Dae-Hyeong Kim1,2; 1Seoul National University, Korea (the Republic of); 2Institute for Basic Science (IBS), Korea (the Republic of)

Welding is a technology that enhances conductivity by forming junctions of metal nanomaterials within a nanocomposite. Conventional nanocomposites have difficulty forming percolation because conductive nanomaterials are mixed with insulating polymers. Conductivity can be improved only through welding with harsh conditions, making it a challenge to control conductivity through welding. Herein, we introduce welding control technology to enable control over the conductivity of nanomembranes on a wide scale under mild conditions. Welding control is a technique that regulates the interparticle junction diameter of the nanomembrane by controlling the reactivity of the reduction solution, which removes ligands attached to the surface of nanoparticles. Reduction solutions can directly act on the nanoparticles exposed in the form of a monolayer in the nanomembrane. The reactivity of the reduction solution is directly proportional to the degree to which ligands are removed, thus increasing the junction diameter. By adjusting the diameter of these junctions, resistance can be tuned from a few ohms to several thousand ohms. This technology is applicable to various metal nanoparticles, such as Au and Ag, and can simplify circuit design when used for patterning. Hence, it can be used as a universal strategy in stretchable devices.

5:00 PM SB02.04.17
WITHDRAW (NO REG) 5/20/2024 SB02.04.17 Ester Functionalized Di-Pyrrole Containing Chalcogenophene Based Semiconducting Small Molecules for Organic Field Effect Transistor Applications
Ashishet Shrivastava1, Michael C. Biewer2 and Mihaela C. Stefan1; The University of Texas at Dallas, United States

Pyrrole is the most electron-rich molecule among five-membered heterocyclic molecules like furan, thiophene, and selenophene. These five-membered chalcogenophenes are isoelectronic to...
Ultrastructural organization of eumelanin from Sepia officinalis measured by atomic force microscopy.

2. Pullman, A. and B. Pullman, charge carriers (electrons or ions or both). electrical conductivity. Such effects represent opportunities for tailoring charge transport characteristics in Sepia melanin-based devices. We observed that Sepia melanin granules reveal their remarkable high charge carriers, such as calculating the activation energy. confirmed from current-voltage measurement. Also, Temperature-dependent electrical characterizations are helping us shed light on aspects related to hopping transport and de-trapping of

Findings from our ongoing study reveal the influence of structural disorder on charge carrier transport in Sepia melanin, including charge carrier localization and trapping effects as it is of Sepia melanin. Patterns are fabricated by Electron Beam Lithography. We focus our investigations on a nanoscale, inter-digitated planar geometry of patterns (inter-electrodes distance ~200-700 nm) as our goal is to detect signals generated by individual granules eventually leads to melanin nanoparticles ~150-200 nm-sized self-assembled into granules. These nanoparticles result from variety of arrangements of pi-pi stacked molecules [4].

Doping Glycolated Polythiophenes with Lithium Salts
Christine Luscombe

processes. This talk will explore some of the fundamentals of doping of both thin films and bulk materials. The impact of doping on the electrical as well as mechanical properties will be the operation of devices from transistors to solar cells. However, some applications such as thermoelectrics and wearable electronics require bulk materials, which complicates doping

Chemical doping is widely used to modulate the electrical properties of conjugated polymers. Doping of thin films facilitates fundamental spectroscopic studies and, ultimately, is important for the operation of devices from transistors to solar cells. However, some applications such as thermoelectrics and wearable electronics require bulk materials, which complicates doping processes. This talk will explore some of the fundamentals of doping of both thin films and bulk materials. The impact of doping on the electrical as well as mechanical properties will be discussed, and it is shown how doping can be used to tune both the conductivity and stiffness of conjugated polymers. Finally, strategies are explored that permit to decouple the effect of doping on the electrical and mechanical properties.

8:30 AM *SB02.05SB04.02
Doping Glycolated Polythiophenes with Lithium Salts Christine Luscombe; Okinawa Institute of Science and Technology, Japan

Polymer-based mixed ionic/electronic conductors (MIECs) are receiving increased attention, in part due to their utility across a wide range of applications. MIECs show valuable properties, including volumetric capacitance changes, transduction of ionic and electronic signals, and biocompatibility. These properties result in a number of useful features, enabling their use in applications such as batteries and ultracapacitors, (bio)sensors, actuators, and organic electrochemical transistors (OECTs). Homopolymer MIECs originally showed limited ionic mobility due to their highly hydrophobic backbones. There has been a significant improvement in their ionic conductivity by introducing polar groups into the solubilizing side chains; the most popular chemistry for the polar side chains is oligoethylene glycol (oEG). This strategy of introducing oEG has driven significant improvements in MIEC performance in a number of conjugated polymer backbones.

Side chains are known to have a profound influence on the morphology, crystallinity, charge carrier concentration, charge thermal stability and ion/water uptake properties of conjugated polymers. By studying a range of polythiophenes across LiTFSI doping concentrations, we are able to elucidate how variations in the side chain architecture influence the evolution of morphology with increasing levels of LiTFSI doping, highlighting the importance of the architecture of oEG side chains in determining the blended material's morphology and resultant ionic and electronic conductivity. The presentation will focus on how small changes in the side chain structure can affect where the LiTFSI is located and thus the conductivity of the materials.
Organic Photodetectors for Shortwave Infrared Sensing

Thuc-Quyen Nguyen and Hoang Mai Luong; University of California, Santa Barbara, United States

Shortwave infrared (SWIR) has various applications, including night vision, remote sensing, and medical imaging. SWIR organic photodetectors (OPDs) offer advantages such as flexibility, cost-effectiveness, and tunable properties, however, lower sensitivity and limited spectral coverage compared to inorganic counterparts are major drawbacks. We develop a simple yet effective and widely applicable methodology to extend the wavelength detection range of OPD to a longer wavelength, using resonant optical microcavity. We demonstrate a proof-of-concept in PBT-CoTIC-4F blend system, achieving external quantum efficiency (EQE) > 50 % over a broad spectrum (450 – 1100 nm) with a peak specific detectivity (D*) of 1.1 x 10^13 Jones at 1100 nm, while cut-off bandwidth, speed, and linearity are preserved. By employing a novel small-molecule acceptor IR6, a record high EQE = 35 % and D* = 4.1 x 10^12 Jones are obtained at ~ 1150 nm. This work emphasizes the importance of design in optoelectronic devices, presenting a considerably simpler method to expand the photodetection range compared to a traditional approach that involves developing absorbers with narrow optical gaps.

10:00 AM BREAK

SESSION SB02.06: Morphological Control in Organic Semiconductors

Session Chairs: Bob Schroeder and Guillaume Schweicher

Wednesday Morning, April 24, 2024
Room 437, Level 4, Summit

10:30 AM SB02.06.01

Glassy Metallic Character in Amorphous Coordination Polymers of Tetrathiafulvalenetetrathiolate

John S. Anderson1, Jiaze Xie2, Patrick Crossland1 and Chen-Yu Lien1; 1University of Chicago, United States; 2Princeton, United States

New conducting coordination polymers featuring tetrathiafulvalenetetrathiolate (TTFtt) linkers will be presented. These materials possess no long-range order, but are still highly conductive and display signatures of glassy metallic charge transport. Deeper characterization of these charge transport properties including Hall effect measurements will be discussed, as well as new efforts in processing these materials and altering their electronic structures via doping or metal ion exchange.

11:00 AM SB02.06.02

Understanding Polymer-Mediated Thermoelectric Properties in Molecularly Doped Poly(Dodecyl-Quaterthiophene) through Microstructure Gradients

Shrayesh Patel; University of Chicago, United States

Our research delves into the intricate relationship between microstructure changes induced by thermal annealing and the resulting charge transport properties in poly(dodecyl-quadertithiophene) (PQT). Employing targeted characterization techniques, including GIWAXS and ellipsometry, the study unveils the polymorphism and chain orientation within PQT and emphasizes the crucial role of interdigitation of side chains. Through vapor doping with F4TCNQ, the study demonstrates that polymorphs strongly control doping efficiency, thereby significantly influencing charge transport properties. Specifically, the research reveals that the 100 °C annealed sample, characterized by tightly packed side chains, displays low doping efficiency and corresponding low electronic conductivity, whereas the 130 °C annealed sample exhibits markedly improved electronic conductivity from higher doping efficiency. Additionally, the study presents a novel method for fabricating continuously graded (CG) thin films of PQT using controlled thermal annealing, revealing diverse 1D in-plane microstructure gradient profiles modulating electronic conductivity and Seebeck coefficient across a 5 nm distance. Comparing these CG films to their equivalent uniform counterparts, the study showcases their enhanced cooling performance due to the effective redistribution of Joule heating and Peltier cooling effects. These findings underscore the significance of understanding the interplay between local order, polymorphism, and doping efficiency in molecularly doped conjugated polymers. In turn, this work provides valuable insights for the design of semiconducting polymers tailored for precise microstructure and doping levels for organic thermoelectric applications.

11:15 AM SB02.06.03

Operando X-Ray Fluorescence for Direct Ion Composition and Mobility Quantification in Organic Mixed Ionic/Electronic Conductors

Ruheng Wu; Xudong Ji and Jonathan Rivnay; Northwestern University, United States

Organic mixed-ionic-electronic conductors (OMIECs) represent a class of organic materials, mostly conjugated polymers, characterized by their ability to transport both electronic and ionic charges. Understanding the composition and mobility of ions within OMIECs is of paramount importance, as it directly influences the performance and fundamental mechanisms of OMIEC-based devices. Typically, such assessments have relied on indirect methods, often based on assumptions that may not always be accurate. Ex situ X-ray fluorescence (XRF) has been employed to quantify ion composition in OMIECs under different doping states, but potential errors could arise due to the need for sample washing to remove residual electrolyte. Instead, operando XRF emerges as a powerful and direct tool for investigating dynamic ion composition and transport in OMIECs during electrochemical operations. Herein, operando XRF was harnessed to probe ion transport in a model OMIEC material, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS). The findings from this investigation are highly enlightening: the initial electrochemical cycle showed a slow electrowetting and cation-proton exchange. Subsequent cycles demonstrated minimal cation fluctuation, around 5%, implying a rapid, stable response with small, consecutive steps of ion migration. The calculated effective ion mobility displayed thickness-dependent behavior and correlated with the effective interfacial ion transport pathways with higher effective mobile ion density. This decoupling of bulk and interfacial effects on ion mobility enhances our comprehension of ion transport in both conventional and vertical organic electrochemical transistors (OECTs). Furthermore, the correlation between ion mobilities, domain boundaries, and mobile ion density suggests that ions within OMIECs migrate in a highly complex way. These findings promise to advance our understanding of ion transport in OMIECs and related devices, offering valuable insights that can guide molecular design, material processing, and charge/ion migration modeling. Ultimately, this research can contribute to enhanced device performance and faster response times. Importantly, this methodology is not limited to OMIECs; it can be effectively applied to investigate complex ion transport mechanisms in various mixed conductors, spanning diverse fields such as batteries and solar cells, holding the potential to revolutionize the design and optimization of a wide range of technologies.

2:00 PM SB02.07.02

High-Throughput Models of Conjugated Polymers

Alessandro Troisi and Hesam Makki; University of Liverpool, United Kingdom

Structural models of semiconducting polymers are challenging to generate, validate against experiments and interrogate for novel properties and research hypotheses. Despite their importance,
producing a model of reasonable quality requires weeks/months of human and computer time. This situation is totally unsuitable for designing polymers, deriving structure-property relations from large data sets or simply engage with a very dynamic community of synthetic chemists and characterization experts. This lecture explores the recent advances toward high-throughput modelling for polymeric materials and the workflow derived to be deployed over hundreds of different polymers. Methods to extract relevant properties of charge transport will be discussed alongside recent advances in the study of highly doped polymers. As common in our research group, these large scale calculations are used to derive practical generalizations and design rules.

2:30 PM BREAK

3:30 PM SB02.07.03

Machine Learning Guided Prediction of Thermal Properties and Identification of Crystallographic Organic Semiconductors Holly Johnson, Filippo Gusesv, Jordan T. Dull, Yeojoo Seo, Rodney D. Priestley, Oleandr Isayev and Barry P. Rand

Crystalline organic semiconductors feature superb optical properties and enhance exciton diffusion length and charge carrier mobility compared to their amorphous counterparts. Certain organic molecular thin films can be crystallized at large-scale via annealing of initially prepared amorphous layers. These films ideally crystallize as platelets with long-range order on the scale of tens to hundreds of microns, but have also been seen to crystallize as spherulites or to resist crystallization entirely. Molecules that are capable of forming a platelet morphology feature high melting point and crystallization driving force ($\Delta G_c$). Here, we employ machine learning to identify candidate organic materials that were predicted to crystallize into large-area platelets by estimating the aforementioned thermal properties. Six materials identified by the machine learning algorithm were evaluated for their bulk thermal properties using differential scanning calorimetry, and their crystallization behavior via thin film crystallization. Of these six materials, three crystallized as platelets, one crystallized as a spherulite, and two resisted crystallization, displaying a successful application of machine learning in the scope of organic thin film crystallization and reinforcing the principles of melting point and $\Delta G_c$ as metrics that govern the crystallization behavior of organic thin films.

3:45 PM *SB02.07.04

Strategies to Improve the Performance of n-Type Conjugated Polymers Derva Banas, King Abdullah University of Science and Technology, Saudi Arabia

The development of organic semiconductors (OSC) has gained significant attention in the realm of organic electronics (OE). Organic thermoelectrics (OTEs) are of interest owing to their potential for harnessing power from residual waste heat and powering autonomous wearable devices. Although P-type OTEs showed robust thermoelectric performance from an early stage, the development of n-type OTEs has been slower in comparison, owed to limited dopant efficiency and rapid degradation of electronic properties. Here, we present DPP-based n-type conjugated polymers (CPs) for OTEs with three different strategies to enhance their charge transport and TE performance. Our strategies are based on the Hansen solubility parameter (HSP) framework and provide insight to improve charge transport in doped OSCs from morphology control to solvent-host-dopant interaction. First, we utilize HSP to screen thousands of solvents to refine our selection and succeed in controlling the mesoscale morphology of DPP-based n-type CPs films transitioning from nanofilbrils into nanofilbrils. We found that the nanofilbril morphology can simultaneously maintain their electrical properties and enhance its mechanical robustness. Second, we address the limitations of the electrical conductivity ($\sigma$) of n-type CP by employing HSP to assess the suitable solvent that improves miscibility and charge transport. We found that solvent having higher solubility of dopant, and conjugated backbone of the CP can increase $\sigma$ without sacrificing Seebeck coefficient (S). This work emphasizes the effectiveness of HSP-guided solvent selection in hindering $\sigma$-S trade-off and limitations from solution mixing doping. Last, we propose the idea of self-induced anisotropy in n-type OTEs which enhance the thermoelectric power factor (PF) by mitigating the trade-off between $\sigma$ and the S. Utilizing HSP theory, we try to understand the solvent-host-dopant intermolecular interactions and elucidate the origin of self-induced anisotropy. We found that a preferential edge-on orientation would increase the in-plane delocalization length and thus improved the electrical conductivity without hindering the $\sigma$.

SESSION SB02.08: Doping of Organic Semiconductors

8:45 AM SB02.08.02

Ground-State Electron Transfer in All-Polymer Donor: Acceptor Blends enables The Aqueous Processing of Water-Insoluble Conjugated Polymers Tiefei Lin, Johanna Heimonen, Qilian Zhang, Mats Fahlin, Renee Kroon and Simone Fabiano, Linkoping University, Sweden

Conjugated polymers offer a unique blend of solution processability, mechanical flexibility, and semiconducting properties, making them invaluable for diverse applications in industries ranging from displays and energy storage to healthcare. However, conventional processing methods often involve hazardous solvents, posing challenges for broad commercial and sustainable adoption. To address this, we introduce a novel approach based on mutual electrical doping in donor:acceptor polymer blends, which facilitates the dispersion of water-insoluble conjugated polymers in aqueous solutions. This approach leads to macromolecular charge-transfer salts with 10,000× higher electrical conductivities than the pristine polymers, low work function, and excellent thermal/solvent stability, providing a versatile platform for various electronic devices. The resulting conductive, water-processable inks demonstrate exceptional performance in non-fullerene organic solar cells, organic electrochemical transistors, inventors, and artificial neurons. This breakthrough offers a practical solution for achieving large-scale and sustainable implementation of organic electronics without the need for traditional chemical modifications.

9:00 AM SB02.08.03

Spontaneous Modulation Doping in Semi-Crystalline Conjugated Polymers Aditya Dash, Shubhradip Guhait, Dorothea Scheunemann, Vishnu Vijayakumar, Nicolas Leclerc, Martin Brinkmann and Martin Kemernink, 1University of Heidelberg, Germany; 2Institute Charles Sadron, France; 3Université de Strasbourg, France

The possibility to control the charge carrier density through doping is one of the defining properties of semiconductors. For organic semiconductors, the doping process is known to come with several problems associated with the dopant compromising the charge carrier mobility by deteriorating the host morphology and/or introducing Coulomb traps. While for inorganic semiconductors these factors can be mitigated through (top-down) modulation doping, this concept has not been employed in organic devices. Here, we show that proper choice of host/dopant combinations can give rise to spontaneous, bottom-up modulation doping, in which the dopants preferentially sit in an amorphous phase, while the actual charge transport occurs predominantly in a crystalline phase with an unaltered microstructure, spatially separating dopants and mobile charges. Combining experiments and numerical simulations, we show that this leads to exceptionally high conductivities at relatively low dopant concentrations.

9:15 AM SB02.08.04

Effective Doping and Effectiveness in Semiconducting Polymers Mohum Jha, Joaquim Mogollon Santiana, Aliyah A. Jacob, Kathleen Light, Megan L. Hong, Michael R. Lau, Leah R. Filardi, Sadi M. Gurses, Coleman X. Kronawitter and Adam J. Moule; University of California, Davis, United States

Molecular doping of semiconducting polymers has emerged as a prominent research topic in the field of organic electronics with new dopant molecules introduced regularly. FeCl$_3$ has gained attention as a p-type dopant due to its low-cost, availability, ability to dope high ionization energy co-polymers, and its use as a dopant that can be used with anion exchange. Here, we use a combination of UV-Vis-NIR spectroscopy, four-probe sheet resistance measurements, and X-ray absorption near-edge structure (XANES) spectroscopy to perform lifetime measurements to assess the stability of the doped polymers over time, which is crucial for evaluating the long-term performance and reliability of the doped films. FeCl$_3$ can cause radical side reactions that damage the conjugated polymer backbone, leading to degradation of the electronic properties. The rate of this degradation is orders of magnitude higher when the film is exposed to air. Anion exchange doping can reduce the [FeCl$_4$$]^{-}$ concentration, but does not necessarily improve the doping lifetime because anion exchange electrolytes can serve as co-reactants for the degradation reaction. By comparison, doping with (2,3,5,6-Tetrafluoro-2,5-cyclohexadiene-1,4-diyldiene)malononitrile (4F4TCNQ) as the reactive dopant results in

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Charge Transport Physics of Organic and Metal Halide Perovskite Semiconductors

Henning Sirringhaus; Cambridge University, United Kingdom

Organic and metal halide perovskite semiconductors are soft functional materials that are emerging as a viable semiconductor technology in industries such as displays, electronics, renewable energy, sensing and healthcare. A key enabling factor has been significant scientific progress in improving the charge transport properties and carrier mobilities of these materials, which has been made possible by better understanding of the structure-property relationships and the underpinning charge transport physics. Here we aim to present a coherent review of how we understand the unique charge transport physics in these two classes of semiconductors and discuss similarities and differences. We are also interested in the use of these materials in thermoelectric devices and we will discuss approaches to their controlled doping and understanding of the relevant thermoelectric physics.

11:00 AM *SB02.09.03
Effects of Nanoscale Morphology on Molecular Doping in Conjugated Polymers

Sung-Joo Kwon1, Rajiv Giridharagopal1, Justin Neu2, Wei You2 and David S. Ginger1; 1University of Washington, United States; 2University of North Carolina at Chapel Hill, United States

Conjugated polymers are inherently nanostructured, with a mixture of crystalline and amorphous domains, investigating the underlying mechanism of doping benefits from nanoscale real-space imaging. Here, we studied the molecular doping on P3HT(2-TT) in solution and thin film using scanning Kelvin probe and conductive atomic force microscopy to visualize the dopant aggregation and heterogeneity of local extent of doping on CPs. We show that the doping efficiency and dopant aggregation are both correlated with the ability of the dopant/solvent solution to swell the conjugated polymer, with combinations that swell resulting in more efficient doping and smoother films with less aggregation. We use these methods to provide a link between optical measurements of doping and local work function variations for films that have been molecularly and electrochemically doped. These techniques provide spatial mapping of topology with work function and time-resolved doping behavior of high resolution (sub-micron scale). Additionally, we investigated further dopant aggregations upon modifying the solvent of the dopant solution, side-chain and crystallinity of CPs; it reveals that swelling of dopant solution, and crystallinity both govern the aggregation of dopant on CPs, thereby limiting the doping efficiency of the CPs. This work will provide significant insight to understand molecular or electrochemical doping of conducting polymers at the microscopic level.

1:15 AM *SB02.09.04
Impact of Chain Conformation and Interchain Contacts on Charge Transport in Conjugated Polymers

Jenny Nelson1, Jack F. Coker, Jarvist M. Frost and Xingyuan Shi; Imperial College London, United Kingdom

Charge transport in organic semiconductors such as conjugated polymers proceeds through a combination of intrachain and interchain charge transfer events. Predicting transport properties for any new material requires an understanding of how the chemical structure and physical organisation of polymer chains influence these processes. The polymer’s conformational phase space influences intrachain charge dynamics through variations in the structure, and hence energy, of polaron states and also influences the type of interchain contacts that can be formed. We consider the case of the stiff, high-mobility indacenodithiophene-co-benzothiadiazole polymer (C16-IDTBT) and use a variety of electrical and structural measurements as well as molecular dynamics, electronic structure calculations and charge transport simulations to probe the nature of the intra- and inter-chain charge transfer processes. We conclude that the polymer’s unusually high connectivity, rather than high interchain coupling, is responsible for its hole mobility. We compare the behaviour with other conjugated polymers including polyfluorenes and polythiophenes, in terms of their chemical structure. We conclude by reviewing the factors that will ultimately limit charge transport in conjugated polymers.

SESSION SB02.09: Charge Transport in Organic Semiconductors I
Session Chairs: Derya Baran and Mariano Campoy-Quiles
Thursday Morning, April 25, 2024
Room 437, Level 4, Summit

9:30 AM *SB02.08.05
N-Doped Conducting Polymer (n-PBDF): Polymerization and Doping Mechanisms

Jianqiu Mgi; Purdue University, United States

n-PBDF has been recently discovered. It distinctly departs from known n-type conducting polymers - being solution-processable, highly conductive, and environmentally stable. In this talk, I will introduce the synthesis of n-PBDF and the mechanistic understanding of its polymerization and doping mechanisms.

10:00 AM BREAK

SESSION SB02.09: Charge Transport in Organic Semiconductors II
Session Chair: Ting Lei
Thursday Afternoon, April 25, 2024
Room 437, Level 4, Summit

1:45 PM *SB02.10.01
Charge Transport Properties of n-Type Conjugated Polymers and Photovoltaic Blends

Samson A. Jereke1, Sarah West and Duyen Tran; University of Washington, United States

Understanding of the charge transport properties of conjugated polymers is central to their applications in organic electronic devices, including organic light-emitting diodes, thick film transistors, electrochemical transistors, organic photovoltaics, thermoelectric devices, etc. Nevertheless, the underlying mechanisms of how molecular and supramolecular factors influence the charge transport properties of semiconductor polymers remain to be fully elucidated. In this talk, I will highlight some examples of our recent work in addressing this knowledge gap for n-type and p-type conjugated polymer films as well as for photovoltaic polymer blend films. Our studies in one area have investigated how polymer molecular weight influences the charge transport properties in two topologically distinct classes of n-type conjugated polymers – those with rigid-rod chain topology and those with semi-flexible chain topology – and found that the chain length dependence of carrier mobility and mechanism of electron transport depend on the polymer chain topology. A detailed characterization of the thin film microstructures of the materials provided insights on the structural disorder and energetic disorder as a function of polymer chain length. How side chain engineering and tuning of the donor-acceptor character on the ladder polymer backbone influences their thin film microstructures and charge transport properties are investigated in a series of n-type conjugated ladder polymers. In another example, we have investigated the charge transport properties of binary blends of interest in all-polymer solar cells, including the roles of the polymer molecular weight, backbone microstructure, and film casting condition and dopants. Firstly, we perform spectroelectrochemistry to calibrate the optical bleaching to known polaron levels, and calculate the doping efficiency of molecular doping. We further perform functional atomic force microscopy (scanning Kelvin probe and conductive atomic force microscopy) methods to visualize the dopant aggregation and heterogeneity of local extent of doping on CPs. We show that the doping efficiency and dopant aggregation are both correlated with the ability of the dopant/solvent solution to swell the conjugated polymer, with combinations that swell resulting in more efficient doping and smoother films with less aggregation. We use these methods to provide a link between optical measurements of doping and local work function variations for films that have been molecularly and electrochemically doped. These techniques provide spatial mapping of topology with work function and time-resolved doping behavior of high resolution (sub-micron scale). Additionally, we investigated further dopant aggregations upon modifying the solvent of the dopant solution, side-chain and crystallinity of CPs; it reveals that swelling of dopant solution, and crystallinity both govern the aggregation of dopant on CPs, thereby limiting the doping efficiency of the CPs. This work will provide significant insight to understand molecular or electrochemical doping of conducting polymers at the microscopic level.

2:15 PM SB02.10.02
Multi-Band Filling and Non-Equilibrium Charge Transport in Conjugated Polymers at Charge Densities on The Order of 10^{21} cm^{-3}

Xinpeng Ren1, Dionisius Hardjo Lukito Tjhe1, Ian Jacobs1, Gabriele D'Avino2, Tarig Mustafa1, Thomas Marsh1, Lu Zhang1, Yao Fu1, Ahmed E. Mansour2, Yuxuan Huang3, Wenjin Zhu1, Ahmet Hamdi Unal1, Vincent Lemaur4, Claudio Quarti1, Jin-Kyun Lee5, Iain McCulloch6, Martin Heeney2, Simone Fratini2 and Henning Sirringhaus1; 1University of Cambridge, United Kingdom; 7Imperial College London, United Kingdom

Charge transport in conjugated polymers and photovoltaic blends is governed by the aggregation of dopant on CPs, thereby limiting the doping efficiency of the CPs. This work will provide significant insight to understand molecular or electrochemical doping of conducting polymers at the microscopic level.

Organic electrochemical transistors (OECTs) provide us a powerful tool for studying charge transport in conjugated polymers over a wide range of charge densities. It has been reported that in
both n-type and p-type OECTs, charge densities on the order of one charge per monomer (~10 cm) can be achieved. At such high charge densities, Coulomb interactions among electrons and between electrons and counter-ions are expected to play a role in charge transport. However, charge transport in this regime, as well as the many-body correlated physics, is still not well understood as charge transport in devices with much lower charge densities (e., organic field-effect transistors).

In this work, we show that in OECTs based on a class of p-type donor-acceptor polymers, it is possible to completely empty the HOMO and eventually access the HOMO-1 orbitals without any degradation, which is supported by a combination of electrical, thermoelectric, and photoemission spectroscopic measurements. More interestingly, under such extreme band filling conditions, by adding a second field-effect back-gate to the OECT, we observe unusual field-effect response when the ionic motions are frozen. Both the shape of the back-gate transfer curve (graphene-like) and the magnitude of drain current modulation (up to 300%) are substantially different from what one would expect from a conventional field-effect device based on an ultra-heavily doped polymer.

Temperature-dependent measurements suggest that the unusual back-gate field-effect response is a non-equilibrium phenomenon, which provides unique insight into the formation of a frozen, soft gap in the density of states driven by Coulomb interactions.

2:30 PM SB02.10.03
Chiral Assemblies of Conjugated Polymers for Controlling Charge and Spin Transport Ying Diao; University of Illinois at Urbana-Champaign, United States

Intimately connected to the rule of life, chirality remains a long-time fascination in biology, chemistry, physics and materials science. Chiral structures, e.g., nucleic acid and cholesteric phase developed from chiral molecules are common in nature and synthetic soft materials. Chiral semiconductors have been long leveraged by Nature to efficiently transduce energy and electron transfer. However, it has been rarely used in synthetic semiconductors due to synthetic challenges. We recently discovered chiral emergence from high performance achiral conjugated polymers, in which hierarchical helical structures spanning nano- to micron scales emerge from a multistep assembly pathway in an evaporating meniscus during coating and printing. We further show that such hierarchical helical structures can be largely modulated by non-equilibrium processing during solution printing as well as by subtle changes in the polymer structure. With the ability to widely tune helical structures, we set out to demonstrate the ability of chiral helical structures in enhancing chemical doping efficiency and conductivity in redox polymers, and in efficiently converting spin to charge promising for spintronic applications.

3:00 PM BREAK

SESSION SB02.11: Organic Thermoelectrics
Session Chair: Jianguo Mei
Thursday Afternoon, April 25, 2024
Room 437, Level 4, Summit Conference Center

3:30 PM SB02.11.01
π-Conjugated Nickel Complexes as n-Type Organometallic Semiconductors for Thermoelectric Generators Michihisa Murata; Osaka Institute of Technology, Japan

Flexible thermoelectric generators, which convert waste heat into electricity, have received increasing attention as convenient and low-cost energy-harvesting devices. π-Type and n-type organic and organometallic semiconducting materials are particularly suitable for thermoelectric materials on account of their very low thermal conductivity, which affords significant advantages not only in realizing high efficiency, but also in generating a temperature gradient. However, the development of n-type organic materials has been hampered partially on account of their instability in air upon doping with an n-dopant.

One promising example of n-type organometallic semiconductors is π-conjugated nickel-ethenetetrathiolate (NIEETT), which exhibits high air-stability and n-type thermoelectric behavior. We envisioned that the new design of π-conjugated ligands in nickel complexes should have a positive impact on the conductivity and the thermoelectric properties. In order to increase the accessibility of this variety of class of complexes, we have developed a versatile method for the synthesis of a variety of π-conjugated Ni complexes and examined their performance. Even though they are insoluble in virtually all common organic solvents, we found that the conductivity of the resulting films can be markedly improved by the choice of the π-conjugated core. For example, a nickel complex containing thiene[3,2-b]thiophene units was designed and synthesized. Composite films of the resulting nickel complex and polyvinylidene difluoride (PVDF), which can be fabricated via a simple solution process under atmospheric conditions, exhibit remarkably high n-type conductivity (>200 S/cm). Moreover, the thermoelectric power factor of the n-type composite film was proven to be air stable. A grazing-incidence wide-angle X-ray diffraction analysis (GIWAXD) indicated a significant impact of introducing the thiene[3,2-b]thiophene core into the backbone of the nickel complex on the orientation within the composite films.

These results on the design and synthesis of air-stable n-type materials should contribute to the generation of advanced materials with potential applications in flexible thermoelectric generators.

4:00 PM SB02.11.02
Controlling Energetic and Structural Disorder of Doped Conjugated Polymers for High-Performance Organic Thermoelectrics Kilwon Chung; Pohang University of Science and Technology, Korea (the Republic of)

Molecular doping is a fascinating technology that can easily increase the electrical conductivity of conjugated polymers. It is actively being explored as a fundamental approach for developing thermoelectric materials and flexible bio-integrated electronics. A variety of dopants, from inorganic salts to molecular dopants and Lewis acids, along with innovative doping strategies, have successfully pushed the electrical conductivity of conjugated polymers to approximately ~1000 S/cm. Despite these noteworthy outcomes, inherent limitations hinder further progress in this field. Conjugated polymers lack a three-dimensional crystal structure and contain structural imperfections, leading to a substantial energetic disorder with a broad distribution of the density of states in their energy landscape. Moreover, the incorporation of dopants introduces structural disorder in crystalline ordering, localizing charge carriers to just a few monomer units. This energetic and structural disorder acts as a significant hurdle to advancing doped conjugated polymers. In this talk, I will present a chemically doped conjugated polymer, indacenodithiophene-co-benzothiadiazole (IDTBT), which is able to maintain low energetic disorder due to the highly planar backbone chain structure. I will thoroughly introduce the relationship between the exceptional charge transport properties revealed by the Kang-Snyder model and narrow-band model, and the polymer chain structure inspected through Raman spectroscopy and DFT calculations. Also, I will discuss a doping strategy aimed at reducing dopant-induced disorder in highly doped conjugated polymers, with a particular focus on a promising Lewis acid dopant, tris(pentafluorophenyl)borane (BCF). The improvements in charge transport properties that result from this strategy will be substantiated through an analysis of structural disorder, energetic disorder, and charge carrier localization, including quantitative investigation using coherence length, paracrystallinity, and paramagnetic susceptibility. Lastly, I will provide a brief overview of the high thermoelectric performance achieved in our research and present the potential of thermoelectric materials based on doped conjugated polymers.

4:15 PM SB02.11.03
Unlocking The Potential of Solution-Processed PEDOT:PSS Thin Films for Efficient Thermoelectric Energy Conversion Juhwang Park and Jeonghun Kwak; Seoul National University, Korea (the Republic of)

Thermoelectric (TE) generation using solution-processable conjugated polymers holds great promise for low-temperature energy harvesting due to their versatility in materials, processes and form-factors. Among these polymers, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is considered a promising candidate owing to its high electrical conductivity, flexibility, and air stability. However, a lack of understanding on the relationship between microstructure and TE charge transport properties has been a significant obstacle, impeding further enhancements in performance of solution-processable PEDOT:PSS. Here, we present a solution-processed, high-performance TE device based on a PEDOT:PSS thin film and thoroughly investigate their microstructure–thermoelectric performance–charge transport property relationships. We first fabricated a highly conductive PEDOT:PSS films using a super acid, where the σ values increased up to ~3600 S cm −1 primarily due to the highly ordered microstructure with PSS removal. Through a successive reduction process, we achieved the highest power factor of 534.5 μW m −1 K −2 with delocalized charge transport properties. Additionally, high electronic tunability of the reduction allowed us to investigate the Seebeck–conductivity relationship over a wide range of n, suggesting that the maximum PF value may surpass the experimentally obtained values. To identify the origin of the discrepancy, we analyzed the macro- and micro-scale charge transport properties using the temperature-dependent σ. Hall effects, and magnetococonductance of the films, together with the morphology, and found out that the connectivity between crystalline domains and the resulting high degree of percolation for transport are important factors toward the theoretically ideal PF.

4:30 PM SB02.11.04
3D-Printed Bulk Organic Thermoelectrics with High Power Output for Stretchable Electronics Francisco Molina-Lopez; KU Leuven, Belgium

Distributed electronics are gaining traction for application in wearables and the Internet of Things (IoT). The increasing complexity of these systems comes with an acute need for energy that batteries struggle to satisfy, either because they are too stiff to be seamlessly integrated into soft wearable electronics, or because their replacement is unfeasible for the numerous and highly
distributed nodes of the IoT. In those scenarios, thermoelectric (TE) materials, which can convert directly waste heat into electrical power, hold great potential. Conveniently, it has been suggested that TE materials are more efficient than other thermal engines for low-power applications[1] like wearables and the IoT. However, the widespread of TE generators (TEG) is hampered by their expensive fabrication process; the use of critical elements such as Bi and Sb; and their limited form factor (rigid, flat, and small).[2] The ubiquity of the IoT nodes and the particular form factor of wearable devices (stretchable and large-area) call for a new technology that strongly relies on clean and abundant materials like polymers, and on scalable and versatile fabrication technologies, like printing. While the development of conducting polymers for organic thermoelectrics (OTEs) has recently witnessed tremendous progress, the reality is that the integration of such materials in actual devices has been seldom attempted, and when attempted, the high performance of the materials did not translate into performing devices. The reason for such lackluster outcome resides in the fact that most OTE materials are developed as thin films using technologies borrowed from organic FETs and photovoltaics. In sharp contrast, performing TEGs (such as commercial Peltier elements) are inherently bulk devices, presenting low internal resistance and capable of sustaining large temperature gradients in the through-plane direction, none of which is possible for thin films.

In my research group, we are working towards the development of high-performing 3D-printed bulk OTEs, which can be directly printed over large areas on flexible/stretchable substrates. In particular, we are developing direct ink writing (DIW) of conjugated polymers, which requires the careful formulation of pastes with very particular rheology, namely shear thinning and high yield strength. Moreover, specific strategies for drying and post-processing are necessary to ensure high shape fidelity. In return, DIW is not only potentially cheap and suitable for soft substrates, but offers also enough processing versatility to tune material morphology while enabling original device architectures that allow on-skin integration (to power wearables using the heat emitted by the human body) and conformability to hot curved surfaces, like hot pipes or engines (to power IoT nodes).

**Acknowledgments**

This work was supported by the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme: Grant Agreement No. 948922 – 3DALIGN.

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A Novel Class of Soft Materials for Neuromorphic Electronics and Wearables: From Conducting Hydrogel to Semiconducting Hydrogel

V. Druet et al

Integrated into adaptable circuits with output controlled by various stimuli, mimicking the function of a neuron. Orders of magnitude wide detection range. While showing the unique characteristics of these devices, I will discuss the possible pathways through which the polymer film generates charges as an effect of counterion size and position relative to the polaron center of charge and conclude that the counterion impact on the polaron can be reduced with larger polaron-ion distances. The use of larger counterions, which sit at longer distances from the polymer backbone, is one way of achieving this.

SYMPOSIUM SB03

Materials, Devices and Systems for Neuromorphic Electronics—From Artificial Synapses to Bionic and Wearable Systems
April 23 - April 25, 2024

Symposium Organizers
Dimitra Georgiadou, University of Southampton
Paschalis Gkoupidenis, Max Planck Institute
Francesca Santoro, Forschungszentrum Jülich/RWTH Aachen University
Yoeri van de Burgt, Technische Universiteit Eindhoven

* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION SB03.01: Mixed Conductors In Neuromorphic Applications
_Session Chairs: Francesca Santoro and Benjamin Tee

Tuesday Morning, April 23, 2024
Room 436, Level 4, Summit

10:30 AM *SB03.01.01
Stable Organic Electrochemical Neurons Simone Fabiano; Linkoping University, Sweden

Recent progress in the design and synthesis of both p-type and n-type organic mixed ionic-electronic conductors (OMIECs) has led to the creation of power-efficient devices for diverse applications, including sensors, nervetrodes, neural interfaces, and artificial synapses. A cutting-edge addition to the biocatalytic toolkit is the organic electrochemical neuron (OECN) with ion-modulated spiking, enabling the development of event-based sensors capable of local sensing, signal processing, and stimulation/actuation. However, the current technology encounters stability challenges, primarily stemming from the degradation of the p-type organic electrochemical transistor (OECT) characteristics. Therefore, achieving stable p-type OMECs is deemed essential for unlocking the full potential of high-performance OECNs. Here, we leverage the inherent stability of rigid ladder polymers, which can sustain a high degree of electrochemical doping. This intrinsic property results in exceptional operational stability, high charge carrier mobility, and large volumetric capacitance. By integrating both n-type and p-type ladder polymers with an engineered backbone to ensure efficient charge transport, we present integrate-and-fire OECNs exhibiting biologically relevant firing frequencies and unparalleled stability. Our findings represent a significant leap forward in OECN technology, addressing previous stability limitations and promising novel opportunities for the advancement of in-sensor computing and the broader field of bioelectronics.

11:00 AM *SB03.01.02
Unlocking The Versatility of n-Type Mixed Conductors For Bioelectronic Applications Sahika Inal; King Abdullah University of Science and Technology, Saudi Arabia

Establishing close interactions between biological systems and synthetic materials is the key to forming biohybrid assemblies that find use in sensors, actuators, and robotics. In this talk, we will present n-type conjugated polymers as multifunctional bioelectronic interfaces. I will show how they can be tailored to form favorable interactions with catalytic enzymes. When this biohybrid is used in an enhancement mode organic electrochemical transistor (OECT), the device detects glucose and lactate in blood serum or saliva with excellent sensitivity and selectivity over six orders of magnitude wide detection range. While showing the unique characteristics of these devices, I will discuss the possible pathways through which the polymer film generates charges as the enzyme reacts with its metabolites. I will then show how these polymers respond to visible and NIR light by generating photocurrents in aqueous electrolytes. This system is then integrated into adaptable circuits with output controlled by various stimuli, mimicking the function of a neuron.

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11:30 AM SB03.01.03
A Novel Class of Soft Materials for Neuromorphic Electronics and Wearables: From Conducting Hydrogel to Semiconducting Hydrogel Shiming Zhang, Dingyao Liu and Yan Wang; The University of Hong Kong, Hong Kong

Thin-film semiconductor-based devices have revolutionized the field of microelectronics. In the realm of biomedical applications, conducting hydrogels have rapidly gained prominence due to their mechanical and biocompatible nature with biological systems. The realization of semiconducting hydrogel materials holds significant value within the field of bioelectronics [1]. Advancing towards flexible and stretchable semiconducting hydrogels can enable direct applications at the interface of soft biological systems [1].

Organic electrochemical transistors (OECTs) are emerging devices in the field of artificial intelligence, as they are able to emulate several synapses functionalities. While short-term processes (short-term plasticity, spike-dependent plasticity, etc.) can be successfully simulated by exploiting peculiar features of OECTs ionic circuit, long-term potentiation (LTP) must be further investigated to increase the retention of the induced neuromorphic states [1]. A recent successful approach is based on electrodeposition occurring in the transistor channel [2].

This contribution describes the use of PEDOT:PSS electrodeposition on the gate electrode to obtain long-term potentiation [3]. The presynaptic signal ($V_{pre}$) is the potential applied to the gate electrode, which acts as a controller of the drain current, that represents the postsynaptic signal ($I_{post}$). The neuromorphic behavior does not stem from the channel employed as a memory element but from an enhancement of the gating efficiency and switching properties. The deposition of PEDOT:PSS film raises the gate capacitance and thus the ability of the gate electrode in modulating the current flowing in the channel. LTP depends on both the number of pulses used and the $V_{pre}$ which generates LTP when a threshold of $+0.7$ V is overcome. The synaptic weight is evaluated by measuring the transconductance, which varies from 0.3 $\mu$S for the native device to 30 $\mu$S for the neuromorphic OECT with the highest LTP. In-operando atomic force microscopy sheds light on operating principle by showing the modifications of the gate electrode induced by $V_{pre}$. The structural strengthening of the artificial synapse is stable for at least two months, and the behavior can be reset by inducing long term depression by applying $V_{pre}$ pulses that leads to a PEDOT:PSS overoxidation and to the formation of a nonconductive layer on the gate electrode.

The artificial synapse also mimics short-term plasticity (STP), and in particular paired pulse depression, with two distinguishable exponential decay phases. The time constants associated with STP in our device, i.e., 0.4 and 2.0 ms, are considerably smaller than those characterizing the decay phases reported in some biological synapses. It is worth noting that PPD and LTP were induced using different shapes of $V_{pre}$ waves with the same experimental setup. These results suggest that the proposed device could combine short-term plasticity and long-term plasticity in a hybrid process. The integration of these devices in neuromorphic circuits could open fascinating perspectives in the realization of advanced neuromorphic circuits based on OECTs.

REFERENCES


SESSION SB03.02: Organic Electrochemical Transistors
Session Chairs: Dimitra Georgiadou and Sahika Inal
Tuesday, April 24, 2024
Room 436, Level 4, Summit

1:30 PM SB03.02.01
Organic-Based Synapses, Neurons and Dendrites
Alberto Salleo
Stanford University, United States

Polymer-based artificial synapses have shown outstanding performance in terms of switching speed, switching energy and endurance. The working principle of these devices leverages the dynamics of ion diffusion in polymers. The same dynamics can be used to fabricate organic circuits that mimic spiking neurons that exhibit adaptive behavior. Furthermore, the same materials are used for device speed, which is most relevant for integrated circuits. Using this figure of merit, we should reduce the channel length and increase charge carrier mobility, or the mobility of the charge carriers. However, the development of semiconducting hydrogels presents challenges, primarily due to the thin-film nature of semiconductors, which are generally less than 1 micrometer in thickness.

Organic electrochemical transistors (OECTs) are excellent building blocks for a new class of neuromorphic devices. Owing to a peculiar switching mechanism based on a redox reaction, ions of an electrolyte couple with the electronic charge carriers of the active material and unique properties absent in other types of thin-film transistors emerge. Among these is often a pronounced switching hysteresis, an attractive feature widely applied as a non-volatile memory. However, its physical origin has hardly been studied.

Organic electrochemical transistors (OECTs) have garnered significant interest due to their ease of fabrication, flexibility, biocompatibility, and suitability for biosignal sensing, including applications in neuromorphic computing. Organic electrochemical transistors (OECTs) have been used to simulate various synaptic phenomena, including short-term plasticity (STP), long-term potentiation (LTP), and depression (LTD). These devices are promising for the development of neuromorphic computing, where the goal is to design artificial systems that can perform tasks similar to biological brains.

Here, we propose a novel top-gate architecture for OECTs in pursuit of higher operational frequencies, power efficiency, and the ability to integrate using low-cost printing techniques. Organic electrochemical transistors can be formed by depositing a thin film of an ionically conducting material on a conducting substrate and applying an electrical potential across the film. The thin film acts as a channel through which ions can diffuse, and the applied potential can control the flow of ions, thereby modulating the electrical properties of the device.

Using a specific electrolyte with the benchmark channel material PEDOT:PSS, we are able to report on OECTs of significantly enhanced hysteresis, as well as an off-state lowered to the regime of nA. Both of these properties, previously sought through complex material modifications, can be achieved here through the simple use of the commercially available liquid [EMIM][EtSO₄], which does not require any further material processing. Based on a thermodynamic framework, we can describe this hysteretic behavior as a bistability and trace it back to the monotonic dependence on temperature. This behavior is contrary to what is expected from classical transistor theory. Going further, we set out to investigate the microscopic origin of the bistability, that is, the interactions underlying the entropic effects. To this end, we have turned to spectroscopic methods, including ex situ XPS, GIWAXS, UV-Vis-NIR and Raman spectroscopy, which allow us to decipher the unique interplay between PEDOT:PSS and [EMIM][EtSO₄].

We find that the liquid ionic phase introduces significant changes to the channel material, as it removes excess dopant and induces an ion exchange, both of which contribute to the device’s exceptional electrical performance. To further study this performance in situ, we employ spectroelectrochemistry, which reveals a unique dep- and dopant behavior compared to other electrolyte systems, and which we can quantify by fitting the spectral signals with a vibronic model. As such, we can draw a conclusive picture of the OECT performance, ranging from the broad ensemble-picture of thermodynamics to the narrow view on microscopic interactions underlying the bistability.

We are convinced that this work will not only expand the understanding of OECT physics, but also provide simple access to devices of remarkable performance based on the mechanisms revealed herein.

2:00 PM SB03.02.02
Unraveling The Bistability of Solid-State OECTs
Lukas M. Bongartz1,2, Garrett LeCroy2, Tyler Quill2, Adam Marks2, Hans Kleemann1, Alberto Salleo2 and Karl Leo1
Technische Universität Dresden, Germany; 2Stanford University, United States

Organic electrochemical transistors (OECTs) have been used to simulate various synaptic phenomena, including short-term plasticity (STP), long-term potentiation (LTP), and depression (LTD). These devices are promising for the development of neuromorphic computing, where the goal is to design artificial systems that can perform tasks similar to biological brains.

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2:15 PM SB03.02.03
Top-Gate Organic Electrochemical Transistors: A New Paradigm for Fast and Energy Efficiency Operation
Ali Solgi and Hans Kleemann
Photonic Materials (IAPP) and Institute for Applied Physics, Technische Universität Dresden, Germany

Organic electrochemical transistors (OECTs) have garnered significant interest due to their ease of fabrication, flexibility, biocompatibility, and suitability for biosignal sensing, including applications in neuromorphic computing. However, power consumption is pivotal in neuromorphic computing and logic circuit applications. The central challenge in these applications lies in identifying the optimal balance between the operational speed of the device and the magnitude of current flowing through the channel, which is ultimately all defined by the transistor geometry. Consequently, much effort has been put into miniaturizing the OECTs, which unfortunately comes with the disadvantage of increasing integration complexity and cost.

Here, we propose a novel top-gate architecture for OECTs in pursuit of higher operational frequencies, power efficiency, and the ability to integrate using low-cost printing techniques seamlessly. We analyze the scaling of these printed, all-solid-state top-gate devices vs. side-gate structures, and we define a figure of merit describing how efficiently transconductance is identified, much effort has been put into miniaturizing the OECTs, which unfortunately comes with the disadvantage of increasing integration complexity and cost.

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Neuromorphic architectures can enable significant power efficiencies in machine learning tasks. The use of soft, organic materials can allow for integration of sensing, actuation and data transmission onto neuromorphic platforms. In this talk, I will share our work on developing asynchronous data transmission systems\(^1\) for neuromorphic in combination with soft flexible electronic materials and devices\(^2\). Using such systems, we can generate unique datasets containing high speed sensory data, for e.g., a MNIST like tactile dataset\(^3\) and apply them to use cases in robotics\(^4,5\).

References


3:00 PM BREAK

SESSION SB03.03: Neuromorphic Devices
Session Chairs: Paschalik Gkoupidenis and Alberto Salleo
Tuesday Afternoon, April 23, 2024
Room 436, Level 4, Summit

3:30 PM SB03.03.01
Modeling Organic Electrochemical Neuromorphic Devices
Ugo Bruno\(^1\), Henrique Frulani de Paula Barbosa\(^2\), Francesca Santoro\(^3\) and Bjorn Lussem\(^2\);\(^1\)Istituto Italiano di Tecnologia, Italy; \(^2\)Universität Bremen, Germany; \(^3\)Forschungszentrum Jülich GmbH, Germany

Organic Electrochemical Transistors are seen as a key element for a fully flexible and wearable sensor technology. In addition, they can be functionalized to show short- or long-term depressive behavior, and long-term potentiation. These devices, often called electrochemical neuromorphic devices (ENODes) have attracted intense research interest in the last couple of years, which led to a continuous increase in device performance.

However, although the progress of the field has been impressive, their fundamental working mechanism is still under debate and an experimentally verified model to discuss ENODE behavior has been elusive. Here, we discuss our progress towards such a model. A focus is put on a correct description of the steady-state and transient switching observed in OECTs, describing important dynamics of ions and holes. In addition, faradaic reactions are introduced in the model, enabling simulations of voltage-driven processes that are usually behind countless sensing applications. Lastly, an outlook is given towards the implementation of charge transfer and ion trapping in the device that form the basis for describing neuromorphic behavior.

4:00 PM SB03.03.02
Electrochemically Controlled Neurotransmitter Delivery for In Vitro Neuromodulation
Craig Milton\(^1,2\), Eric Reed\(^2\), Alena Veigl\(^2\), Tyson Back\(^3\), Nicholas Glavin\(^2\), Rhonda Pitsch\(^2\), Matthew Gregg\(^4\), Tyler Nelson\(^2\) and Steve Kim\(^5\);\(^1\)NRCH Postdoctoral Fellow, United States; \(^2\)Human Performance Wing, Air Force Research Laboratory (AFRL), Wright-Patterson AFB, United States; \(^3\)Materials and Manufacturing Directorate, Air Force Research Laboratory (AFRL), Wright-Patterson AFB, United States

The National Academies of Science and Engineering have issued a grand challenge to “reverse-engineer the brain”. Addressing this challenge requires a more complete understanding of how connections between individual neurons and groups of neurons are formed and maintained, as well as a more thorough elucidation of the signaling processes that drive neural network optimization. However, to achieve this goal, it is first necessary to develop the appropriate fundamental tools and protocols for adaptive biomimicking, bottom-up neuroscience, and neuromodulation, which all involve a tightly coordinated synergy between sensors and specialized devices for neurotransmitter delivery. To date, extensive research efforts have been devoted to neurotransmitter sensing, but relatively little attention has been given to developing methods for electronically controlled in vitro neurotransmitter delivery.

To address this challenge, our research team has developed devices that can both sense and selectively dispense the biochemical cues that drive the formation, regulation, and modulation of in vitro neuronal networks. Here, we report electrochemically controlled dispensing of both excitatory and inhibitory neurotransmitters (e.g. glutamate, GABA, dopamine) from functionalized electrodes that operate at low voltage. The regulated uptake and release of neurotransmitters is mediated by electrochemically controlling the electrostatic affinity between the neurotransmitter and a polarized electrode that has been functionalized with an electroactive affinity molecule.

To optimize our devices, our team tested a variety of electrode functionalization approaches (e.g. alkane-thiol or silane chemistry, layer-by-layer or covalent modification) and a variety of electroactive affinity molecules (e.g. ferrocene, methylene blue, viologens). Our controlled dispensing devices function as a faradaic capacitor -- when the functionalized electrode is anodically polarized, the redox affinity molecule becomes oxidized (i.e. positively charged), and the neurotransmitter loads on the functionalized electrode through electrostatic attraction to the oxidized redox affinity molecule. The neurotransmitter may be conveniently “stored” on the electrode by maintaining the applied electrode potential, and then released on demand by reversing the applied bias using controlled steps or pulses, which reduces the electroactive affinity molecule and releases the neurotransmitter. This controlled adjustment of applied electrode potential permits quantitative biochemical release. In addition, the electrochemical signature associated with the loading of different neurotransmitters permits sensing as well as delivery.

We confirm the operational principle through a variety of analytical and electroanalytical techniques, such as cyclic voltammetry, chronoamperometry, open-circuit potentiometry, continuous enzymatic monitoring, electrochemical quartz crystal microbalance (EQCM), X-ray photoelectron spectroscopy, and triple quadrupole mass spectrometry. We then demonstrate that the functionalized media can be electrically coupled with electrochemical transistors (ECT) for triggered neurotransmitter release in conjunction with changes in the concentration of important physiological ions (e.g. sodium, potassium, calcium) or biochemical messengers.

Finally, we will present the steps we have taken to implement these devices within organ-on-a-chip systems, and demonstrate the utility of our devices for studying the formation and longitudinal evolution of neural networks within in vitro neuronal colonies.

4:15 PM SB03.03.03
Organic Electrochemical Transistors based Decoding Hardware for Near-Sensor Brain Signal Processing
Yuyang Yin and Paddy K. L. Chan; The University of Hong Kong, Hong Kong

As the thriving of brain-computer interface (BCI) technologies, signal decoding algorithm and hardware have been rapidly developing for information interpretation as a crucial part of the BCI system. Although state-of-the-art algorithms can be capable for successful brain wave decoding to realize tasks such as speaking intention prediction or robot arm manipulation, unconventional processing and computing hardware are indeed desired for low-cost and high-speed decoding. Neuromorphic hardware provides solutions in this regard, for which low-complexity protocol and true-hardware implementations have been pursued. Herein, reservoir computing (RC) hardware is constructed based on memristive organic electrochemical transistors (OECTs) for intention of decoding signals from brain. The OECT devices with PEDOT:TOS/PTHF channel layer can be electrically regulated to realize transition from short-term memory (STM) element to long-term memory (LTM) element, which benefits the one-shot fabrication of reconfigurable dual-modal memory device. Based on this merit, the reservoir unit of the RC system is constructed with STM elements and designed as an adjustable network to fit the feature of inputs, at the same time LTM elements are used as trainable weights of the neural network in the readout layer. It is beneficial that the reservoir maps temporal inputs into reduced-size vectors, allowing feasible hardware demonstration of the readout layer in a small network size and leading to desirable short-delay decoding. With this hardware system, simulated epileptic seizure signals can be detected online at decent accuracy, which further direct the generation of stimulus to form a close-loop
Vision plays a crucial role in artificial systems such as surveillance, manufacturing, and robotics. However, the capabilities of conventional cameras are constrained by their design. Planar image sensors often result in significant aberration issues. While complex multi-lens systems can mitigate aberrations, they also increase the size and weight of the camera and limit its field of view. Additionally, the separate light-mapping, memory, and signal-processing units can lead to excessive signal transmission, delays, and high energy consumption—all of which are detrimental to the rapid advancement of artificial intelligence applications.

Drawing inspiration from the natural vision of animals, we have developed bionic eye devices featuring a curved artificial retina equipped with onboard signal processing capabilities. These devices use high-density curved nanowire arrays that emulate a retinal neuron array, endowing the bionic eye with a compact design, superior imaging performance, and an ultra-wide field of view exceeding 540 degrees. We have embedded advanced neuromorphic signal processing functions at the pixel level, including capabilities for color distinction, contrast enhancement, noise reduction, and motion detection. Additionally, we have incorporated electrically switched working modes and adaptive optics to enhance the adaptability of our bionic eyes in a variety of application settings.

Dual-Function IGZO Phototransistor for Rate-Based Encoding and Photonic Synaptic Characteristics in Neural Networks  
Ya-Chieh Huang, Yu-Chieh Chen, Li-Chung Shih and Jen-Sue Chen; National Cheng Kung University, Taiwan

The IGZO phototransistor exhibited the capacity to represent a total of 128 distinct conduction states. Finally, the IGZO was illuminated adjusting the time intervals between them. As the time interval between the light and positive voltage pulse (0.7 V) increased, the drain current of the device decreased. On the other hand, as the time interval between the light and negative voltage pulse (−0.1 V) increased, the current either decreased when the negative voltage pulse was supplied later or increased when the negative voltage pulse was supplied first. Consequently, the IGZO phototransistor was exposed to 405 nm light of varying intensities while simultaneously being subjected to gate voltage pulses of stochastic intensity. These gate voltage pulses were randomly sampled from a Gaussian distribution with a mean (μ) of −0.4 V and a standard deviation (σ) of 0.2 V. Concurrently, the drain terminal generated spikes whenever it exceeded the threshold current (I_{th}). As a result, the light intensity increased, the spike rate also rose, demonstrating the IGZO phototransistor's ability to efficiently encode light intensities into spike rates.

Furthermore, to make the IGZO phototransistor suitable for integration into neuromorphic networks, we conducted tests to assess the photonic synaptic properties. Initially, we examined the temporal effects of light/voltage pulses by exposing the IGZO phototransistor to a 10 ms light pulse with a light density of 77 mW/cm² and a 10 ms voltage pulse of either 0.7 V or −0.1 V, while adjusting the time intervals between them. As the time interval between the light and positive voltage pulse (0.7 V) increased, the current density of the device decreased. On the other hand, as the time interval between the light and negative voltage pulse (−0.1 V) increased, the current either decreased when the negative voltage pulse was supplied later or increased when the negative voltage pulse was supplied first. Subsequently, the IGZO phototransistor was exposed to 64 light pulses (for potentiation) and 64 negative voltage pulses (for depression), aimed at regulating the photonic synaptic weight of the device. As a result, the IGZO phototransistor exhibited the capacity to represent a total of 128 distinct conductance states. Finally, the IGZO was illuminated by 405 nm light for 10 ms at gate voltage of 0.1 V and 1 V, and the retention time after illumination was assessed. The result indicates that the retention time at VG = 1 V is longer than at VG = 0.1 V, suggesting that the photonic retention capability of the device can be adjusted by the gate voltage.

The results of the experiments discussed above reveal that the IGZO phototransistor exhibits both spike encoding and photonic synaptic functions, making it a promising candidate for neural networks applications. In our future work, we plan to utilize the IGZO phototransistor to encode the MNIST dataset into spike rates and subsequently train it using spiking neural networks (SNNs). With further development and exploration, our goal is to utilize a single device for perception and encoding, eliminating the need for separate light sensors and enhancing the efficiency of machine vision systems.

**Materials for Neuromorphic Supercomputers**

Jeffrey Shainline, Bryce Primavera, Jeffrey Chiles and Saeed Khan; NIST, United States

Many efforts in neuromorphic computing seek extreme energy efficiency for edge devices by leveraging principles of neural information processing. Fewer efforts aim to capture the full complexity and scale of biological brains, potentially implementing neural principles in technological hardware at a scale that surpasses that of the human mind. For this second thrust, which we term “neuromorphic supercomputing”, the materials challenges are quite unique.

Utilizing existing silicon microelectronics is a natural choice for neuromorphic supercomputing. Yet when implementing neuro-inspired circuits, architectures, and algorithms with existing silicon microelectronic hardware, communication bottlenecks emerge as a major limitation. Biological neurons make thousands of connections to near and distant synapses, whereas silicon neurons cannot achieve this level of fan-out due to wiring parasitics. Address-event representation of spikes is employed with a shared communication infrastructure. As the number of neurons grows, that infrastructure becomes overwhelmed, and the rate at which each neuron can spike drops below the rate of biological neurons, rendering the technological approach inferior to the biological one, even for relatively small systems. This is a severe obstacle for neuromorphic supercomputers.

To overcome this barrier, we use light for communication. A neuron spike is represented by a pulse of photons distributed to synaptic connections via nanophotonic waveguides, circumventing wiring parasitics that prevent direct electrical communication. Superconducting single-photon detectors allow communication to occur at the lowest possible light level for extreme energy efficiency. For computation, the photonic components must be paired with electrical devices and circuits. Using superconducting single-photon detectors requires low temperature operation, so other superconducting elements such as Josephson junctions can be used as well. To realize the full spectrum of synaptic, dendritic, and neural functions, a combination of cryo-CMOS and Josephson circuits are uniquely powerful.

The full hardware stack for this neuromorphic supercomputing platform includes conventional CMOS working in conjunction with superconducting electronics, semiconducting light sources, multiple planes of passive dielectric waveguides, and single-photon detectors integrated with those waveguides. To realize this full stack, multiple challenges in materials science remain. First and foremost, the separation of imaging, memory, and signal processing. Such a feat has been a goal of the industry, yet this context provides one crucial advantage: low-temperature operation. Silicon itself is a reasonable light emitter at low temperature, provided the crystalline lattice is modified to contain emissive centers. The optimization of silicon for this unique optoelectronic purpose represents an important objective of this research. A second objective relates to the single-photon detectors. For scalability, we seek to operate at 4.2K. Polycrystalline materials such as NbTiN make excellent single-photon detectors with superconducting transition temperatures above 4.2K, but the yield and detection plateaus are sub-optimal. Other amorphous materials such as MoSi and WSi have much higher yield and detection plateaus, but they typically must be operated between 1 K and 2K. Finding a material and with high yield that is superconducting is a high goal for the project as well. Finally, to achieve large systems with the number of neurons and synapses as the human brain will require many planes of waveguides and active superconducting devices. Numerous materials integration challenges must be solved to realize this sophisticated microelectronics process at the 300mm scale. If these problems can be solved, the world will have access to a new domain of advanced computational technology for neural information processing, achieving several important fundamental physical limits of cognition.

**Inkjet Printed Metal-Organic Framework Memristors for Non-Volatile Memory and Neuromorphic Applications**

Yan Lin, Franz Fischer2, Hongrong Hu1, Hartmut Glienmann3, Carsten Natzke1, Christof Wöll1, Ben Breitung1 and Jasmin Aghassi-Hagmann1; 1KIT, Germany; 2RWTH Aachen University, Germany

Memristors, as fundamental electronic components, have the unique ability to retain a memory of its past electrical resistance state based on the charge that has flown through it. They have
generated considerable interest in the field of electronics due to their potential to revolutionize memory and computing technology. Moreover, they offer a combination of non-volatile storage, high-speed operation, and the ability to perform analog computation, which can be advantageous in certain computing tasks and artificial intelligence applications.

Metal Organic Frameworks (MOFs) consist of metal ions connected by organic linkers, resulting in intricate structures with well-defined porosities, which leave spaces for ions, vacancies or guest molecules to migration and provides an excellent environment for electrochemical metalization (ECM) memristors.

Integrating MOFs into additive manufacturing techniques like ink jet printing can revolutionize their applicability, opening doors to large-scale production of patterned MOF devices. In this talk, the first demonstration of inkjet printed HKUST-1 directly integrated into a printed electronic device, particularly a memristor, will be presented, marking a significant advancement in the field of printed electronics. Furthermore, the inkjet printed memristors can serve as both, non-volatile memories and artificial synapses, for neuromorphic computing. Additionally, the ability of inkjet-printed memristors to act as artificial synapses for neuromorphic applications under different forms of synaptic short-term plasticity was investigated. This study showcases the potential of inkjet printed MOF memristors and will pave the way for high performance memristors in the field of neuromorphic computing, thus, it will further advance the development of artificial intelligence.

10:00 AM BREAK

SESSION SB03.05: Photonic Computing
Session Chairs: Dimitra Georgiadou and Nripam Mathews
Wednesday Morning, April 24, 2024
Room 436, Level 4, Summit

10:30 AM SB03.05.02
Infrared Nanoimaging of Hydrogenated Perovskite Nickelate Memristive Devices
Sangham Gamage1, Sukriti Manna2, Maciej Zajac2, Steven Hancock1, Qi Wang1, Sarahpreet Singh2, Mahdi Ghafarifard1, Kun Yao1, Tom Twidale4, Tae Joon Park3, David Landau1, Hadan Wen2, Subramanian Sankaranarayanan2, Pierre T. Darancenc3, Shriram Ramanathan2 and Yohannes Abate1; 1University of Georgia, United States; 2Argonne National Laboratory, United States; 3Purdue University, United States; 4J. A. Woollam Inc., United States; 5Rutgers, The State University of New Jersey, United States

Solid-state devices from correlated oxides such as perovskite nickelates are promising for neuromorphic computing by mimicking biological synaptic function. However, comprehending dopant action at the nanoscale poses a formidable challenge to understanding the elementary mechanisms involved. Here, we perform operando infrared nanoimaging of hydrogen-doped correlated perovskite, neodymium nickel oxide (H-NdNiO3) devices and reveal how an applied field perturbs dopant distribution at the nanoscale. This perturbation leads to stripe phases of varying conductivity perpendicular to the applied field, which defines the macroscopic electrical characteristics of the devices. Hyperspectral nano-FTIR imaging with density functional theory calculations unveils a real-space map of multiple vibrational states of H-NNO associated with OH stretching modes and their dependence on the dopant concentration. Moreover, the localization of excess charges induces an out-of-plane lattice expansion in NNO which was confirmed by in-situ - x-ray diffraction and creates a strain that acts as a barrier against further diffusion. Our results and the techniques presented here hold great potential in the rapidly growing field of memristors and neuromorphic devices wherein nanoscale ion motion is fundamentally responsible for function.

10:45 AM *SB03.05.03
Event Driven Optical Sensors based on Perovskites and Organic Semiconductors
John Labram; University College London, United Kingdom

While great progress has been made in visual object recognition in recent years, almost all strategies occur in software, relying on conventional video input. This represents a major bottleneck that could limit the speed at which objects can be identified. Recently, we have demonstrated simple capacitive event-driven sensors inspired by the way that animals perceive visual stimuli. [1] These so-called retinomorphic sensors provide a spiking voltage in response to changes in illumination, but no response under constant illumination. [2]

In this talk I will discuss our motivations for detecting light in this way, strategies to achieve this experimentally, and how we expect arrays of these sensors to interpret the visual field. We have demonstrated sensors which employ both metallic halide perovskites and organic semiconductors as the absorber layer, with each system exhibiting vastly different behavior. Our latest devices can detect objects which spend less than 10 μs in the visual field and generate an output voltage with zero input voltage. [3] I will end my talk by describing a framework to quantify behavior in these devices, evaluate performance limits, and discuss strategies to improve functionality in the future. [4]

References:

SESSION SB03.06: 2D Material Artificial Synapses
Session Chairs: Dimitra Georgiadou and John Labram
Wednesday Afternoon, April 24, 2024
Room 436, Level 4, Summit

2:00 PM SB03.06.02
Exploring the Potential of Combining Polyoxometalates (POMs) and 2D Materials with Nanogap Electrodes for Neuromorphic Computing
Roshni S. Babu1, Emilie Gerouville1,2, Ioannis Zeimpekis1,2, Dimitra G. Georgiadou1,2; 1University of South Hampton, United Kingdom; 2Optoelectronics Research Centre, United Kingdom

Neuromorphic computing, inspired by the human brain's remarkable computational capabilities, has emerged as a promising paradigm for advancing artificial intelligence and cognitive computing systems. In contrast to the Von Neumann computing architecture, the human brain relies on neurons and synapses for both storage and computation. Consequently, there has been a growing interest in exploring nanodevices that mimic synapses to achieve highly efficient computing. Among these nanodevices, memristors have gained a lot of attention due to their advantages, such as low power consumption, high integration density and the capability to replicate synaptic plasticity, which align with the requirements of neuromorphic computing. In this work, we explore two nanomaterial classes, namely polyoxometalates (POMs) and two-dimensional (2D) transition metal dichalcogenide (TMD) materials, to facilitate the development of efficient neuromorphic hardware. POMs, a class of nanoclusters composed of metal and oxygen atoms, exhibit tunable multi-redox properties. Their excellent electron-accepting ability, high stability, and photo-stable redox properties, render them suitable for mimicking synaptic plasticity and being employed in in-memory and neuromorphic computing devices. This study, we have fabricated resistive switching memory devices based on Keggin-type POMs, bearing various counterions, and the role of these cations on memristive switching characteristics was investigated. The POMs are deposited by spin coating or drop casting on cobalt nanogap metal electrodes. The cobalt electrodes of Au and Al separated by a nanogap of 10 nm are prepared by adhesion lithography. This coplanar nanogap geometry is an ideal platform to accommodate such 1-nm sized molecular clusters. Preliminary results showed a resistive switching behaviour with a low operating bias voltage and high endurance and retention, while control over the reversible redox states can be used in neuromorphic and reservoir computing devices. In this study, we have fabricated resistive switching memory devices based on Keggin-type POMs, bearing various counterions, and the role of these cations on memristive switching characteristics was investigated. The POMs are deposited by spin coating or drop casting on cobalt nanogap metal electrodes. The cobalt electrodes of Au and Al separated by a nanogap of 10 nm are prepared by adhesion lithography. This cobalt nanogap geometry is an ideal platform to accommodate such 1-nm sized molecular clusters. Preliminary results showed a resistive switching behaviour with a low operating bias voltage and high endurance and retention, while control over the reversible redox states can be used in neuromorphic and reservoir computing devices. Furthermore, our research involved an investigation into 2D memristors, employing cobalt nanogap electrodes with MoS2 as the channel material. The MoS2 is directly grown on to a Si/SiO2 substrate using atomic layer deposition (ALD) process and transferred onto a cobalt nanogap electrode array. The utilization of MoS2 in memristors fabricated with nanogap electrodes has demonstrated the potential to reduce switching voltages to a crucial minimum. In conclusion, as we delve into nanomaterials, such as POMs and 2D materials, and their incorporation into...
In the last decade, various classes of memristive materials have demonstrated promising properties for emerging information processing technologies such as neuromorphic computing. Among the innovative materials for memristive devices, the class of transition metal dichalcogenides (TMDs) has attracted much attention, due to their excellent physical properties and scalability, which allows scaling to atomically thin layers with defined electronic structure. However, many of the physically relevant properties have so far only been demonstrated on single devices made from TMD flakes produced by exfoliation which commonly suffer low reproducibility with the fabricated flakes/sheets being rather sensitive against ambient influences like humidity and light. Thus, to exploit their full potential in applications, reliable thin-film processes at wafer-level are requested to tailor the materials precisely for the desired application and integrate them into functional devices and systems. It is therefore beneficial to introduce homogeneous layers on a large scale, enabling to encapsulate targeted areas from the ambient and build vertical devices of controllable size fingerprints.

This contribution therefore presents a technology platform that allows TMD materials to be integrated into a thin-film process. In detail, a wafer-level 4-inch thin-film technology for fully encapsulated molybdenum disulfide (MoS2) memristive devices is presented, allowing for a systematic statistical analysis of electrical properties. The developed method, paired with material analyses, further enables us to compare the different material configurations and draw conclusions about the physical switching mechanism and suitability for integration into circuits. MoS2 layers of 10 nm thickness were deposited in a tri-layer process, sandwiching the material between two 30 nm electrodes using magnetron sputtering. Devices were structured using an optical lithography lift-off process, comprising more than 32,000 devices in six different sizes, areas ranging from 10x10 to 50x50 square micrometers. The sputtered MoS2 was found to have an amorphous structure. Devices were encapsulated using high quality chemical vapor deposited silicon dioxide (CVD-SiO2). To understand and tailor the switching mechanism of the memristive devices, the electrode material (active and non-active) was varied and the influence of the encapsulation of the MoS2 were investigated in detail.

Experimenting with different electrode materials, Cu and Ag showed a strong interaction between electrode and MoS2, deploying transmission electron microscopy (TEM). Even though these combinations tend to exhibit switching behavior, they have an undesirably high variability due to the material interactions. Furthermore, comparing the current-voltage characteristics measured on both encapsulated and non-encapsulated devices revealed that in the encapsulated devices, no resistive switching could be observed. In contrast, I-V hysteresis could be found in non-encapsulated devices. To realize the objective of encapsulated, reliable, and reproducible devices, technology was then adapted from tri-layer to bi-layer sputtering, introducing a defined oxidation step for the MoS2 layer before the deposition of top electrode and encapsulation.

The therewith resulting devices were systematically evaluated, studying their current-voltage characteristics, number of resistive states, retention time, on/off ratio, and switching energy. Finally, a model of the switching is proposed, explaining the cause of memristive characteristics in sputtered MoS2 and their link to external influences.

Funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 434434223 – SFB 1461 and the Carl-Zeiss Foundation via the Project MemWerk as well as support by the Center of Micro- and Nanotechnology (ZMN), a DFG-funded core facility at TU Ilmenau, is gratefully acknowledged.

2:30 PM BREAK

SESSION SB03.07: Phase Change Materials
Session Chairs: Simone Fabiano and Dimitra Georgiadou
Wednesday Afternoon, April 24, 2024
Room 436, Level 4, Summit

3:30 PM SB03.07.01
Wearable Neuromorphic Device for Personalized Healthcare
Wei Gao; California Institute of Technology, United States

The rising research interest in personalized medicine presents a tremendous opportunity for developing wearable devices toward predictive analytics and treatment. Emerging neuromorphic computing technologies that mimic the data processing properties of biological neural networks offer a promising solution for handling overflowing data related to personalized healthcare. In this talk, I will first introduce the implementation of a simplified, functionally flexible analog-type operator by physically defining short-term plasticity and long-term plasticity in a crossbar synapse array. The applicability of such neuromorphic processor consisting of short-term synapses and long-term synapses was evaluated by constructing a small-sized analog-type operator to conduct representative data-processing tasks for wearable applications. I will also introduce our latest works on the development of wearable, flexible, and multifunctional bioelectronic systems with multi-modal physicochemical sensing and neuromorphic computing capabilities for personalized healthcare.

4:00 PM SB03.07.02
Reconfigurable Memristive Devices based on Phase Change Materials for Artificial Synapses and Neuromorphic Computing
Sundar Kunwar, Nicholas Cucciniello, Di Zhang, Pinku Roy and Aiping Chen; Los Alamos National Laboratory, United States

Phase change materials such as vanadium oxide (VO2) possess great potentials for artificial neuron application because of its inherent nonlinear characteristics such as metal-to-insulator (MIT) phase transition with an applied electric field and quick relaxation. Recent studies have demonstrated that the VO2 based artificial neurons achieve superior biological neuronal activities at lower energy as compared to those based on the filamentary type devices. Our recent study on the VO2 based memristive devices have suggested that a reconfigurable resistive switching (RS) i.e., both volatile (as neurons) and non-volatile (as synapse) can be achieved, enabling the creation of more energy and area efficient artificial neural networks for neuromorphic computing. In this talk, I will present the case of the VO2/La0.7Sr0.3MnO3 (LSMO) heterostructure devices and their dual RS properties. The movement of oxygen vacancies and the MIT phase change are deemed to be the main driving forces for such dual RS modes. A dual mode RS in a single device holds great promise for the application in memristive neural networks and neuromorphic computing.

4:15 PM SB03.07.03
Investigating The Interplay of Piezoelectricity and Synaptic Plasticity in Se-Based Photodiodes for Optically Controlled Memristors on Flexible Substrates
Taizo Kobayashi1, Kunal Tiwari2, Sergio Giraldo3, Marcel Piaciä2, Axel Gon Medalie2, Arindam Basak2,3, Edgardo Saezoo2 and Zacharia Jehl L-Kan2; 1Ritsumeikan University, Japan; 2Polytechnic University of Catalonia, Spain; 3Kalinga Institute of Industrial Technology, India

Neuromorphic computing, situated at the forefront of the AI revolution, offers the promise of overcoming the Von Neumann bottlenecks in terms of energy consumption while excelling in tasks such as unsupervised learning, analysis of probabilistic and fast changing data. In the era of increasing significance for computer vision, visual learning, and soft robotics, the fabrication of devices on flexible substrates becomes extremely relevant.

This work proposes a pioneering investigation of the synaptic plasticity in Selenium (Se)-based photodiodes with a particular focus on the complex interplay between piezoelectricity and memory. These Se-based photodiodes are fabricated on flexible polyimide substrates, introducing a novel dimension to their functionality by exhibiting a substantial piezoelectric effect, leading to a remarkable variation of the open circuit voltage under different strains as previously reported. Our research methodology involves using both continuous and pulsed light to explore the relationship between piezoelectricity and memory within these Se-based devices. Remarkably, we observe changes in the dark current-voltage (IV) characteristics both before and after a train of illumination pulses, indicative of the device's behavior being very similar to an optically controlled memristor. It should be noted that this change in resistivity is fully reversible and can be induced even at relatively low illumination power densities, as low as 5 mW/cm².

To further investigate the interplay between piezoelectricity and memory, we follow a classic approach of sequential light write pulses and read voltage pulses. This monitoring process involves tracking the current at specific voltage pulses, thus providing indirectly the persistent photocurrent. This dynamic data is collected as a function of time under various bending angles of the devices. Our findings bring important insights on the role played by the interface alignment between the Se absorber and the ZnMgO window layer in driving the piezoelectric effect and affecting the memory effect. Our research makes use of different illumination wavelengths, ranging from 350nm to 1400nm, which shows that the system is also wavelength selective. To assess the synaptic plasticity in these devices, we systematically characterize the device’s short-term and long-term plasticity in terms of the Recovery Time Constant. Additionally, we...
Materials processing and synthetic design serve as ideal avenues to control the transport properties of organic mixed ionic/electronic conductors (OMIECs). Small changes in chemistry can affect the materials electronic mobility, swelling, ion uptake and stability. Devices based on these materials have thus opened up new opportunities in bioelectronics, energy, and neuromorphic computing. Furthermore, volumetric/bulk transport and charging in organic mixed conductors opens up opportunities for less common device form factors that can result in scaled down and co-localized function in circuits. In this talk, I will present on the engineering of OMIECs for artificial synapses, as well as recent efforts to improve artificial neurons by employing highly non-linear responses. I will first present a non-volatile organic electrochemical transistor (OECT) based on a poly(3,4-ethylenedioxythiophene):tosylate (PEDOT:Tos)/Polytetrahydrofuran (PTHF) composite. This device can continuously and reversibly change its conductance state at a write bias less than 0.8 V and the state retention time can be longer than 200 min without decoupling the write and read operation. By incorporating a pressure sensor and a photoreactor into the gate terminal of volatile and non-volatile OECTs, a neuromorphic circuit is proposed with the ability to associate two physical inputs (light and pressure), which may have implications for biomimetic devices like electronics-skin and neuroprosthetics. I will then discuss recent developments in simple co-localized OECTs for on-site amplification, as well as for fine tuning of gaussian (or anti-ambipolar) responses in vertical OECTs for simplified spiking circuits, which present an exciting pathway for fully integrated artificial neurons that can directly interface with biological systems.
In this study, we propose a synaptic weight modulation layer (SML) in oxide semiconductor-based synaptic devices by adjusting the quantity of charge trapping depending on the light irradiation. SML is comprised of ultraviolet (UV)-treated hafnium oxide (HfO₂), which generates varying amounts of oxygen vacancy (Vₜ) sites, acting as charge trap sites, simply by modifying the UV lamp (wavelength of 184.9 nm & 253.7 nm) exposure time. The devices are based on indium-gallium-zinc oxide (IGZO) thin film transistor (TFT) with two types of SMLs: low-synaptic weight modulation layer (L-SML) with 10 min UV-treated HfO₂ and high-synaptic weight modulation layer (H-SML) with 1-hour UV-treated HfO₂ located between the channel of a-IGZO and thermally grown silicon dioxide (SiO₂) from a heavily boron-doped p-type silicon substrate (p+). The hysteresis characteristics are measured to confirm the charge trapping phenomenon by threshold voltage shift (∆Vth). IGZO TFT w/ L-SML and IGZO TFT w/ H-SML showed the ∆Vth of 5.15 V and 10.10 V respectively. This result implies that the increment of ∆Vth is clearly influenced by UV treatment time, which occurs by the difference in charge trap density. To verify the UV effect on the HfO₂ dielectric film, the current density versus electric field (J-E) curve is measured in electron-metal-insulator-metal (MIM) capacitors. The HfO₂ dielectric film shows a dielectric strength of 10.13 MV/cm, L-SML shows 8.88 MV/cm and H-SML shows 7.35 MV/cm. The breakdown electric field decreases while UV exposure time increases. This phenomenon is expected by bond dissociation and X-ray photoelectron spectroscopy (XPS) analysis is performed to investigate the difference of chemical bonds in the HfO₂ between L-SML and H-SML.

In general, the inhibitory post-synaptic current (IPSC) was measured to verify the synaptic characteristics of IGZO w/L-SML and IGZO w/H-SML-based synaptic transistors. These devices showed low synaptic weight characteristics through the ratio of post-synaptic current/pre-synaptic current in different pulse amplitudes. At 5 V, 6 V, and 7 V, the IGZO TFT w/H-SML ratios were 43.7%, 58.0%, and 75.0%, respectively, compared to the IGZO TFT w/L-SML ratios of 19.7%, 32.6%, and 49.8%. Additionally, potentiation and depression characteristics of IGZO TFT w/L-SML and IGZO TFT w/H-SML according to 128 consecutive pulses are verified to verify the difference in learning capability. The post-synaptic current (PSC) change in IGZO TFT w/L-SML and H-SML exhibits a remarkable difference, with an increase from approximately 140 nA to 323 nA (2.3-fold) and 18 nA to 117 nA (6.5-fold), respectively. As a result, it was confirmed that the different characteristics of synaptic transistors via simple light irradiation method might be a candidate for enhancing the learning capability and computational efficiency of neural computing.

References
Electrochemical metallization (ECM) cells operate on the principle of growing and dissolving a conducting filament (CF) in an insulator separating two metal electrodes. Typically, the thickness of the insulator is a few nanometres. The growth (SET) of the CF occurs by applying a positive voltage to the electrochemical active electrode (AE), which leads to oxidation of the electrode and migration of ion hopping within the oxide – also called switching layer (SL) – of the resulting metal ions. Reduction occurs preferentially on a critical nucleus at the inert electrode (IE), leading to growth of the CF. Reversal of the voltage leads to reversal of the above processes and dissolution (RESET) of the CF. A previously published 2D axisymmetric model [1] contains Butler-Volmer equations to describe ionic currents, Simmons tunnel equation for electronic tunnel current between the conducting filament (CF) and the active electrode, Fuchs-Sondheimer model for resistivity of the CF, mechanical stress, to limit the lateral CF growth and a moving mesh approach for growth of the CF. This model was extended with tunnel junction heating, an additional energy dissipation when electronic tunnel currents occur, the dissolution of the anode and the previously current limiting resistor was exchanged by an ideal current limitation. The model was then modified to simulate not only SET but also RESET kinetics. In this work the dissolution of the AE and the combined influence of heating, mechanical stress variations, dissolution of the active electrode, the length of the SET voltage pulse (programming time) and the maximum SET current on the RESET time was investigated. It is shown, that mechanical stress – which crucially affects the lateral size of the CF – and the dissolution of the active electrode have the largest impact on the RESET time and that only tunnel junction heating allows significant heating of the CF even at low currents in the low microampere range. The integration of this findings into compact models should lead to better descriptions of measurement results and thus improving and boosting the design of memristive devices and neuromorphic circuits.

References:

Acknowledgements
This work was supported in part by the Deutsche Forschungsgemeinschaft under project SFB 917 and in part by the Federal Ministry of Education and Research (BMBF Germany) in the project NEUROTEC II under Grant 16ME0398K and Grant 16ME0399.

9:00 AM SB03.09.03
Behavior Guided Design of Materials, Mechanics and Electromagnetics for Biosymbiotic Electronics Philipp Gutruf, University of Arizona, United States

Philipp Gutruf
Departments of Biomedical Engineering and Electrical and Computer Engineering, Bio5 Institute, Neuroscience GIDP University of Arizona, Tucson, AZ 85721, USA;

The concept of digital medicine, which relies on streams of continuous information from the body to gain insight into health status, manage disease and predict onset health problems, is currently relying on biosensors with limited chronic capabilities. [1] Key technological hurdles that slow the proliferation of this approach are means by which clinical grade biosignals are continuously obtained without frequent user interaction. [2] To overcome these hurdles, solutions in power supply and interface strategies that maintain high fidelity readouts and function chronically are critical. Current approaches for high fidelity recordings typically rely on adhesive interfaces that are subject to epidermal turnover, limiting sensor lifetime. Additionally, they rely on electrochemical power supplies which are subject to frequent recharge, add bulk and weight, require user interaction and introduce motion artefacts. Here we introduce a new class of devices that overcomes the limitations of current approaches by utilizing context aware mechanical and electromagnetic design facilitated through digital human behavior assessment to create unique personalized devices optimized toward the wearer. Specifically, we introduce new methods to use behavioral analysis of a user group to shape design to enable indefinite device lifetimes. [4]

These elastomeric, 3D printed and laser structured constructs, called biosymbiotic devices, enable adhesive-free interfaces and the inclusion of high performance, far field energy harvesting to operate over weeks at the time, enable new sensing paradigms such as circumferential muscle strain, high fidelity absolute position sensing, mK resolution thermography and 3D printed optofluidics to capture an encompassing and evolving record of health. The impact of this approach is also showcased in wearable devices that are low profile, soft and can transmit high fidelity biosignal data over tens of miles of distance without cell connection uninterrupted over weeks without user interaction.

References

8:45 AM SB03.09.02
2D Axisymmetric Continuum Model for RESET Kinetic Variations in Electrochemical Metallization Cells Milan Buttberg1 and Stephan Menzel2; 1RWTH Aachen IWE2, Germany; 2Forschungszentrum Jülich GmbH, Germany

Electrochemical metallization (ECM) cells operate on the principle of growing and dissolving a conducting filament (CF) in an insulator separating two metal electrodes. Typically, the thickness of the insulator is a few nanometres. The growth (SET) of the CF occurs by applying a positive voltage to the electrochemical active electrode (AE), which leads to oxidation of the electrode and migration of ion hopping within the oxide – also called switching layer (SL) – of the resulting metal ions. Reduction occurs preferentially on a critical nucleus at the inert electrode (IE), leading to growth of the CF. Reversal of the voltage leads to reversal of the above processes and dissolution (RESET) of the CF. A previously published 2D axisymmetric model [1] contains Butler-Volmer equations to describe ionic currents, Simmons tunnel equation for electronic tunnel current between the conducting filament (CF) and the active electrode, Fuchs-Sondheimer model for resistivity of the CF, mechanical stress, to limit the lateral CF growth and a moving mesh approach for growth of the CF. This model was extended with tunnel junction heating, an additional energy dissipation when electronic tunnel currents occur, the dissolution of the anode and the previously current limiting resistor was exchanged by an ideal current limitation. The model was then modified to simulate not only SET but also RESET kinetics. In this work the dissolution of the AE and the combined influence of heating, mechanical stress variations, dissolution of the active electrode, the length of the SET voltage pulse (programming time) and the maximum SET current on the RESET time was investigated. It is shown, that mechanical stress – which crucially affects the lateral size of the CF – and the dissolution of the active electrode have the largest impact on the RESET time and that only tunnel junction heating allows significant heating of the CF even at low currents in the low microampere range. The integration of this findings into compact models should lead to better descriptions of measurement results and thus improving and boosting the design of memristive devices and neuromorphic circuits.

References:

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8:15 AM #SB03.09.01
Brain-Inspired Electronic Learning Metamaterials Douglas Durbin, Sam Dillavou, Menachem Stern and Andrea Liu; University of Pennsylvania, United States

Neural networks in the brain and artificial neural networks (ANNs) in silico are both able to learn complex functionality. While each artificial neuron is updated based on global information, using a central processor (CPU) and memory, each real neuron in the brain updates itself without external CPU. In this talk I will describe the first laboratory realization of such self-learning without use of CPU or memory. Our systems consist of a network of identical variable-resistive elements that self-adjust using a local rule based on the voltage drops they experience under contrastive boundary conditions. As such, they have many brain-like advantages over ANNs and enable study of learning as a bottom-up emergent process.

References:

SESSION SB03.09: Theory and Modeling of Brain-Inspired Devices
Session Chairs: Paschalis Gkoudelis and Bjorn Lussem
Thursday Morning, April 25, 2024
Room 436, Level 4, Summit

Additively Manufactured 3D Membranes for Wearable Renal Assist Device Natalie Hwee1, Kun Wang2, Sijia Huang1, Donglin Li2, Wade Degraff2, Longsheng Feng1, Sangil Kim2, Jianchao Ye1 and Juergen Biener1; 1Lawrence Livermore National Laboratory, United States; 2University of Illinois at Chicago, United States

More than 400,000 Americans require renal assist devices in the form of hemodialysis machines. This industry costs more than $50 billion dollars a year. Two limitations of current hemodialysis membranes are that they are prone to biofouling and have low packing density of the membrane resulting in a large device. Developing a wearable device that has improved filtration and efficiency would change the lifestyle of thousands of Americans from relying on hemodialysis centers.

We have developed a formulation for a material that has 3 times better biofouling properties than commercial materials while maintaining mechanical robustness. We have used a combination of additive manufacturing (AM) and polymerization induced phase separation (PIPS) to design a 3D membrane with controlled micropore size and two-phase flow. Our membrane has achieved over 10 times higher flow rate compared to commercially available membranes at similar pressure drop. This membrane design enhances filtration capabilities through the membrane wall by creating turbulent flow in the channels. Coupling material formulation and additive manufacturing is a way to develop high packing density membrane for a wearable renal device.

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

Organic-Inorganic Hybrid Memristor for Neuromorphic Electronics, Abdulaziz Aldabayan, Antonio Facchetti and Natalie Stingelin; Georgia Institute of Technology, United States

In the era of big data, there is a growing demand for highly efficient technologies to facilitate the acquisition, storage, and analysis of vast volumes of information. The Resistive Switching Random Access Memory (ReRAM), having non-volatile memory attributes, synaptic-like behavior, and energy-efficient, high-density features, had emerged as a promising tool poised to transform and shape the development of neuromorphic computing and wearable electronics. In this work, an organic-inorganic hybrid poly (vinyl alcohol) titanium oxide hydrate hybrid memristor device is developed. The device of the structure Au/PVA:TiOH/Au exhibits bipolar non-volatile resistive switching characteristics. We hypothesize that the operational mechanism of the PVA:TiOH layer is driven by the formation and rupture of local conductive Ti3+ filaments caused by Joule heating and electric field-assisted reduction of Ti4+, producing dioxygen, that induces a Schottky-like barrier behavior at one interface and a quasi-ohmic contact behavior at the other. This biocompatible memristor presents a compelling case for sustainable memory solutions in the increasing field of neuromorphic electronics.
The conventional von Neumann bottleneck, characterized by the separation of information processing and storage, presents architectural limitations in computational efficiency and energy consumption. As the growing demand for energy-efficient computing systems, neuromorphic systems, inspired by the parallel processing principles of the human brain, have gained significant attention. Within this domain, the memristor, integrating the functionalities of both a memristor and a transistor into a single device, exhibits distinctive memresistive switching characteristics controlled by an external gate terminal.

To enable compatibility with CMOS process technology, we fabricated a metal oxide-based memristor on SiO$_2$/p$^+$ Si substrate. The memristor structure involves the stacking of hafnium oxide (HfO$_x$) as the gate insulator and indium gallium zinc oxide (IGZO) as the active layer. The redistribution of oxygen vacancies within HfO$_x$/IGZO interface can effectively modulate the Schottky barrier height between the IGZO channel layer and the aluminum (Al) metal source/drain (S/D) electrodes. Unlike traditional two-terminal memristors, the single-pulse measurements reveal the ability to manipulate short-term memory decay time by adjusting gate voltage levels, while the drain pulse waveform remains fixed, allowing us to simulate various degrees of short-term memory effects effectively. The Long Short-Term Memory (LSTM) model provides distinct advantages for image recognition through controlled degrees of short-term memory states within the LSTM that adapt to varying image dynamics, ultimately enhancing accuracy and efficiency. In time-series data processing, we divide 4x4-sized black-and-white English letter images into four rows, each containing four pixels. The design of electrical pulse waveforms, based on stroke order, serves as inputs to the LSTM mode, enabling it to capture temporal relationships within image sequences. Our research advances memory and recognition technologies, promising enhanced accuracy and efficiency across diverse fields of application.

**9:30 AM SB03.09.05**

**Brain Inspired Floating Redox Wiring for Neural Networks**

**Roshani Madurawala, Maik-Ivo Terasa, Anna Lina Wyschonk, Soeren Kaps and Rainer Adelung; University of Kiel, Germany**

The human brain is a remarkably complex and adaptable organ and its capability to change and adapt, is due to a phenomenon known as "neuroplasticity." Neuroplasticity in synapses refers to the brain's outstanding ability to change the strength and structure of the connections between neurons, which is crucial for information transfer. This has inspired the design and training of artificial neural networks (ANN), allowing them to learn and improve their performance over time. In the trend of implementing ANN in hardware, one specific challenge is the implementation of plasticity in the artificial synapses. Here we show a concept and a mechanism to incorporate plasticity into a system by means of electrochemical metalization in a liquid matrix, Dimethyl sulfoxide (DMSO). A liquid matrix inspired by the brain has been employed to facilitate the mobility of the ions in addition to its cooling purposes in this ionotronic system. These bio-inspired, dynamic and reconfigurable electronic connections are robust in DMSO while still being prone to manipulation upon applied external stimuli, because they float in DMSO. These connections are wires that grow as dendrites due to the redox reaction taking place at the electrodes. The thickness and the growth conditions of these wires influence their electrical properties, which could be altered by varying the initial experimental conditions such as the applied voltage. The manipulation of these wires could be done during the growth of the wire (filament) between two nodes or more, simultaneously. Furthermore, after the growth of one filament, the filament could be manipulated in a way to induce filament breakage which resembles synaptic properties. This process of plasticity in artificial synaptic connection equivalents, serves as a fundamental step in the refinement of network connectivity. Its replication within artificial systems marks a significant milestone in the quest to emulate the brain's adaptability. Intriguingly, this filament can grow in a span of over 200 µm. What is even more remarkable is their ability to overcome the limitations of traditional 2D growth, as they readily extend their presence into the 3D realm. Growth and manipulation of single 2D and 3D filaments and in extension, a filament network, using external stimuli will be shown along with electrical characterization of these filaments and possible applications. In essence, the groundwork laid in the field of dynamic filament growth within a liquid matrix holds the potential to reshape the landscape of technological advancement. With its capacity for synaptic mimicry, flexible growth, and 3D expansion, this innovation ushers in an era of transformative possibilities, making inroads into fields as diverse as neuromorphic computing, cognitive sciences, and advanced artificial intelligence. [1]


The authors acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 434434223 – SFB 1461

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**9:45 AM SB03.09.06**

**Wireless Implantable Microwave Neural Device for Neural Inhibition**

**Carolyn Marar, Ji-Xin Cheng and Chen Yang; Boston University, United States**

Neuromodulation using electromagnetic waves is a powerful approach to control brain circuits in a minimally invasive manner. To date, researchers have explored a broad spectrum of electromagnetic wave and developed wireless neuromodulation methods. Microwave (MW), with frequencies between 300 MHz and 300 GHz, fills the gap between optical wave and magnetic wave, yet has rarely been explored for neuromodulation. Microwave has much longer wavelength than photons, which have been known to provide >50 mm penetration depth into the human brain noninvasively, while maintaining more than 50% of its energy. Yet, its wavelength is much shorter than that of magnetic wave, promising higher spatial resolution to specifically modulate subcortical regions. Here we will discuss a miniaturized millimeter size microwave antenna as a wireless implantable neural interface to inhibit neural activities in vitro, ex vivo and in vivo. The developed split-ring resonator (SRR) generates a localized and enhanced microwave field at the gap site of the ring with submillimeter spatial precision. The SRR breaks the microwave diffraction limit and greatly enhances the efficiency of microwave inhibition. With the SRR, microwave at dosages below the safe exposure limit are shown to inhibit neurons within 1 mm from the gap site. Importantly, we measured the temperature at the neurons under microwave modulation using mCherry as a temperature reporter and found the temperature increase to be less than 1 degree, confirming a non-thermal effect for microwave inhibition. The inhibition effect was also confirmed in a crayfish nerve model using electrophysiology recording. Application of the microwave SRR to suppress seizures in an in vivo model of epilepsy is demonstrated. These results suggested that the millimeter microwave resonator is a novel platform for wireless, battery-free neuromodulation with high spatial precision. The device operates within safety limits and occupies a volume < 2 mm$^3$. This approach opens up a broad potential of wireless deep neural inhibition through miniaturized microwave implants treating neural disorders as well as managing pain.

**10:00 AM BREAK**

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**SESSION SB03.10: In-Memory Sensing**

Session Chairs: Paschalis Gkoupidenis and Jonathan Rivnay

Thursday Morning, April 25, 2024
Room 436, Level 4, Summit

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**10:30 AM **SB03.10.1.01**

**Memristive Devices for Advanced and Ultra-sensitive Bio/Chemical Sensing Systems.**

**Joulia Tzonouvdaki; Ghent University, Belgium**

Memristive devices and systems, much akin to biological synapses, possess the intrinsic ability to simultaneously carry out computational tasks and store information at significantly reduced volumes and power consumption by modifying their memory state as a function of the integral of the input stimulus. These emerging technologies coupled with biological processes, opened new perspectives in the role of bio-inspired sensors introducing a versatile paradigm for label-free and ultra-sensitive bio/chemical sensing, holding great promise as intelligent bio-interfaces and sensory systems in the biomedical domain. The recent advancements in the transduction and processing of chemical biomarkers of the neural and immune system functions will be discussed while also providing a critical outlook on the prospective role of memristive devices as fundamental building blocks in advanced biosensing systems.

**11:00 AM SB03.10.02**

**Artificial Thermomechanical Receptor for In-Sensor Multimodal Fusion**

**Junhyuk Bang1, Kyun Kyu Kim2 and Seung Hwan Ko*1;2;1Seoul National University, Korea (the Republic of); 2Stanford University, United States**

As wearable devices evolve in complexity, there's a surging demand for advanced multimodal sensing technologies. Especially the acquisition of thermodynamic information is essential, which allows human-like perception, sensor calibration, and hazard detection. While previous studies have succeeded in selectively capturing temperature and mechanical signals, these methods typically required individual measuring units of target stimuli, leading to increased structural complexity, and necessitating extra computational processes for signal matching.
To address these limitations of traditional multimodal sensors, we introduce the neuromorphic sensor for in-sensor multimodal fusion. This innovative design is inspired by the sensory nerve system's efficient computing architecture, which represents multimodal information by interleaving signals across time. To replicate this neural-like computing architecture, we utilize a stretchable memristive nanowire network (the Ag@Cu2O core-shell nanowires) as the sensing material. This random network, with numerous memristive junctions of a metal-metal oxide-metal configuration, experiences a binary phase transition related to material and network geometry during the memristive switching process. In the high-resistance state, the conductivity pathway primarily goes through a dense network of Cu2O shells, while in the low-resistance state, it predominantly goes through a sparse network of conductive filaments. This unique feature empowers active alteration in sensing capability, allowing for the selective extraction of thermal and mechanical signals through a singular resistance measurement unit. Furthermore, by carefully manipulating the signal measurement voltage pulse scenario, thermomechanical information is integrated into a singular interleaving response profile. It enables the spatiotemporal synchronization of thermal and mechanical information itself without the necessity of an external computing unit.

Owing to its design simplicity, our neuromorphic multimodal sensor is much more miniaturized than previous work, achieving a sensing channel size of under 0.1mm² and a device thickness of less than 40 μm. This advancement not only improves its conformability on curved surfaces but also ensures rapid response to external stimuli. To demonstrate the practical application of realizing human-like perception, we integrated our sensor with the deep neural network and recognized random objects. In-sensor multimodal fusion, which captures complex physical characteristics, shows superior recognition accuracy compared to datasets acquired by measuring single information (thermal information or mechanical information). These findings open new opportunities for wearable electronics with wearability, and functionality and pave the way for intelligent multimodal sensor systems.

11:15 AM SB03.10.03
High-Speed Edge Computing Implemented Using Reconfigurable Carbon Nanotube Transistor Memories Jingfang Pei¹, Lekai Song¹, Pengyu Liu¹, Teng Ma² and Guohua Hu¹; ¹The Chinese University of Hong Kong, Hong Kong, China; ²Hong Kong Polytechnic University, China

The constant data transportation from the edges to the centralized cloud computing infrastructure causes considerable constraints over the computational power and latency as well as the energy cost. Decentralization of the computation with the computational tasks distributed to the edges is an emergent solution to address the problem. Processing onsite data in local memories holds great promise to implement the edge computing. Here, we demonstrate edge computing using reconfigurable nonvolatile carbon nanotube transistor memory arrays, and prove high-speed, real-time video processing.

We fabricate the transistors from solution-sorted semiconducting single-walled carbon nanotubes. The transistors exhibit fast switching with the switching times and delays down to tens of nanoseconds, a large switching ratio of over 10⁴; and, particularly, a significant memory window of ~12 V arising from charge trapping in the sensing polymer. The above characteristics endow the transistors with highly-stabilized reconfigurable nonvolatile memory states and a high data processing speed. Owing to solution processing, the fabrication is wafer-scalable, the transistors exhibit uniform characteristic memory metrics, e.g., with 1.8% variation in the memory window, suggesting an industrial-scale manufacturing capability of the fabrication. Using the transistor memories, we design and implement an edge computing device with a convolution unit connecting to a differentiator, and demonstrate the application of the edge computing device in edge detection and motion track tasks of video streams. Particularly, the edge computing device successfully performs local video processing at a speed of 10,000 fps, exceeding the conventional high-speed cameras. The efficacy of the edge computing device, and the scalability of the fabrication, we envisage a promising prospect of realizing large-scale edge computing devices in implementing practical edge computing in, for instance, autonomous driving, virtual and augmented reality, and robotics.

11:30 AM SB03.10.04
Interfacial Engineering of Metal Ion Injection in Threshold Switching Memristor for Neuronal Applications Calvin Lee, Putu Andhita Dananjaya, Eng Kang Koh, Funan Tan, Lingli Liu and Wen Siang Lew; Nanyang Technological University, Singapore

Neural networks composed of artificial neurons and synapses mimicking the biological nervous systems have governed much attention because of their promising potential in high-density memory storage and large-scale neuromorphic computing. In this context, various resistive switching phenomena in memristors such as ionic charge transfer, oxygen vacancy ordering, and electrochemical metallization (ECM) have been utilized to replicate neuronal dynamics. Among them, ECM threshold switching (TS) devices are favorable for realizing complex neural networks due to their simple structure, large on/off ratio, and low operation voltages. However, ECM TS device uniformity is relatively poor, which may affect the accuracy of artificial neural networks, limiting the practical applications of ECM TS memristors. In this work, we experimentally demonstrate a highly-uniform WO₃₋ₓ–based TS device with nanoporous Pt interfacial layer as the high-performance selector, which shows low leakage current (~1 pA), high on/off ratio (>10⁵), and high endurance (>10⁶ cycles). Furthermore, the WₓOₓPt-nanoporous layer TS device exhibits self-oscillation behaviour at low voltage (<1 V), where the oscillation frequency increases with the applied voltage and decreases with the load resistance.

Based on the studies of the nanoporous Pt interfacial layer with WₓOₓ - based TS devices, the overall variability of the operating voltages of TS devices with nanoporous Pt interfacial layer were reduced to levels below that achieved in TS devices without nanoporous Pt interfacial layer. Furthermore, the nanoporous Pt interfacial layer enables the TS devices to operate at higher current compliance levels (~100 μA). The insertion of the nanoporous Pt interfacial layer offers a simplistic technique of metal ions manipulation in ECM TS devices.

11:45 AM SB03.10.05
Revealing Oxygen Donor Level in Tungsten Oxide Films for Neuromorphic Applications with Parallel Dipole-Line Hall System Hyunjeong Kwak¹, Chaeyoun Kim², Byungha Shin², Oki Gunawan³ and Seyoung Kim³; ¹Pohang University of Science and Technology, Korea (the Republic of); ²Korea Advanced Institute of Science and Technology, Korea (the Republic of); ³IBM T.J. Watson Research Center, United States

Electrochemical random-access memory (ECRAM) devices stand as key candidates for realizing analog cross-point array-based AI computation accelerators thanks to its excellent programmability driven by ion movement, high stability, low cycle-to-cycle and device-to-device variation(1). However, there have been limited efforts to investigate fundamental physical parameters of the key channel material, WOₓ₊ₓ, that control ECRAM switching characteristics. Tungsten oxide serves as a channel layer since its conductivity can be modulated depending on the ion concentration, rendering it a fitting choice to realize the analog switching/2). In this work, we fabricate ECRAM devices in a multi-terminal Hall-bar structure and conduct Parallel Dipole Line (PDL) Hall measurements to investigate the essential electrical properties of tungsten oxide films, including resistivity, mobility, carrier density and activation energy. The AC Magnetic PDL Hall system, based on strong magnetic field generation and lock-in detection, offers high sensitivity, allowing for sensing even weak Hall signals from low mobility and high resistivity samples/3). Furthermore, we measure the mobility and carrier density of tungsten oxide as a function of temperature using variable temperature PDL Hall measurements. The observed Hall mobility in WOₓ₊ₓ films reaches to 4.66 cm²/Vs at room temperature. At lower temperatures, a slight decrease in Hall mobility is observed due to impurity scattering from ionized centers. We extract the activation energy of the oxygen donor level in tungsten oxide thin films using Arrhenius plots. Our findings show the experimental access of the key variables that change during switching in ECRAM, which is not only crucial for enhancing ECRAM's performance but also essential for providing vital insights into neuromorphic applications.


Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Noise and Variation in Memristive Devices and Crossbar Arrays

SB03.12.01

Changes in the electronic transport behavior and the MIT caused by the addition of various types of defects introduced into the system. Previous work using He+ ions at low fluences showed different voltage schemes, the Ta2N/Ta2O5/Pt RRAM device demonstrates both filamentary (digital) and interfacial (analog) resistive switching within a single device. A thorough evaluation of its ability to be used as a neuromorphic computing memory device is hindered because the total number of states that can be stored within a single device is restricted. In this work, using Memory (RRAM), or in particular its integration with a transistor, 1T1R (1 Transistor - 1 RRAM) structure, is a popular solution to this problem. These devices emulate storing synaptic image recognition and natural language processing for unstructured data. This leads to a paradigm shift towards a Neuromorphic computing architecture. The Resistive Random Access Switching RRAM as a neuromorphic device element within a chip fabricated using the same fabrication process steps. The devices also demonstrate good scalability (<150 nm), low operational and the oxide switching layer. The coexistence of the two switching mechanisms means it is possible to operate the filamentary switching RRAM as a storage device and the interfacial switching RRAM as a neuromorphic device element within the NDR region. Finally, we aim to harness ion implantation as a technique to induce desired current oscillations or action potential-like behavior in simple neuromorphic computational primitives.

Polycrystalline VO2 thin films were grown on SiO2(100 nm)/Si substrate. These films were implanted with Ge+ ions at 110 keV, and at fluences ranging from 1x1014 to 1x1016 ions/cm2. Photolithography was used to make a variety of 2-terminal and 4-terminal devices on the films to study device switching performance. Implanted devices were then subjected to rapid annealing (RTA) at temperatures ranging from 300°C to 900°C to restore the VO2 crystallinity. This allowed us to identify the RTA temperatures and fluence values that best modified the MIT without amorphizing the film. The present study describes changes to the electrical transport upon Ge+ implantation as well as explores different oscillating behaviors observed within the NDR regions for devices subjected to different implantation conditions. Further exploration on the limits of controlling different aspects of the electrical transport behavior will enable a larger class of materials that can emulate the neuronal functions and diverse neuronal dynamics, and introduce a strategy to engineer biomimetic functionality into computational primitives.

References:
4. R. M. Gurrola et al., “Modulation of electronic transport in VO2 induced by 10 keV helium ion irradiation”. In progress

2:30 PM SB03.11.04

Coexistence of Both Digital and Analog Response in Ta2O5-Based RRAM Devices toward Neuromorphic Hardware

Em Kang Kahl1,2, Putu Andhiita Dananjaya1, Han Yin Poh1,2, Lingli Liu1, Calvin Lee1,2, Young Seon You1 and Wen Siang Lew1; 1Nanyang Technological University Singapore, Singapore; 2GlobalFoundries, Singapore

With the amount of digital data growth in recent years, although the von Neumann architecture-based processors can efficiently conduct logic computations on structured data, they do poorly in image recognition and natural language processing for unstructured data. This leads to a paradigm shift towards a Neuromorphic computing architecture. The Resistive Random Access Memory (RRAM), or in particular its integration with a transistor, 1TIR (1 Transistor - 1 RRAM) structure, is a popular solution to this problem. These devices emulate storing synaptic weights in terms of the conductance. However, an inherent problem is that the RRAM’s switching mechanism typically involves an abrupt switching current response. This means that its ability to be used as a neuromorphic computing memory device is hindered because the total number of states that can be stored within a single device is restricted. In this work, using different voltage schemes, the Ta2O5/Ta2Ox/Pt RRAM device demonstrates both filamentary (digital) and interfacial (analog) resistive switching within a single device. A thorough evaluation of the underlying principles governing both switching modes revealed that the anomalous gradual switching is linked to the modulation of interfacial oxides that form between the active electrode and the oxide switching layer. The coexistence of the two switching mechanisms means it is possible to operate the filamentary switching RRAM as a storage device and the interfacial switching RRAM as a neuromorphic device element within a chip fabricated using the same fabrication process steps. The devices also demonstrate good scalability (<150 nm), low operational voltage (<2.5 V)), endurance (>106 cycles), good retention (85°C at 105s), and the possibility of reversibility of the mechanisms while having good multi-level cell properties. With the duality of these two switching modes, our device is poised for application in both memory storage and synaptic weight-storing applications.

3:00 PM BREAK

SESSION SB03.12: Memristive Circuits and Arrays

Session Chairs: Douglas Durian, Dimitra Georgiadou and Paschalis Giouopoulos
Thursday, April 25, 2024
Room 436, Level 4, Summit

3:30 PM *SB03.12.01

Noise and Variation in Memristive Devices and Crossbar Arrays

Qianfei Xie; University of Massachusetts, United States

Memristors are resistance switches with reconfigurable multilevel resistance states modulated by an electric field. Crossbar arrays of such devices can perform analog computation at the site of data throughput. However, these devices are stored in (memory computing) by directly using physical laws, such as Ohm's law for multiplication and Kirchhoff's current law for summation. Analog in-memory computing reduces the time and energy needed to access system memory. The multiply-accumulate operations can be performed through a single current sensing operation, dramatically increasing the computing throughput. However, ion-based devices have noises due to the random trapping/release of charge carriers at thin-film interfaces or defect sites (random telegraph noise) and the fluctuation of defect concentrations (1/f noise). Together with thermal and shot noises, they impose a fundamental limit on the capability of analog computing. Furthermore, the device-to-
High-Frequency Flexible Organic Thin-Film Transistors

11:00 AM

*SB04.01.02

Photo-Enhanced Output in Memdiodes based on Organic/Inorganic Hybrid Materials for Neuromorphic Synapses

Jacob Lee1, Dhriti Nepal2, John Ferguson2, Ajit K. Roy2 and Xiaojuan Fan1,2, 1Marshall University, United States; 2Air Force Research Laboratory, United States

We report that memdiodes (MDs) have been created based on metal halide-embedded polymeric hybrids in ambient conditions, presenting unusual photo-enhanced electronic transport behaviors. The hybrid materials show unconventional optoelectronic properties, providing alternatives to traditional semiconductors such as silicon. The blending of inorganic metal halides and organic polymers combined with an insulating polymer membrane facilitates resistive memory and diode behaviors. Two-terminal memristive devices are made of a hybrid photoactive layer of CuCl2 and a layer of poly(methyl methacrylate) (PMMA) deposited on substrates to form a pn-junction memdiode. Thin films were characterized using ATR-FTIR, SEM, UV-Vis-NIR microspectrophotometer, and IV curves. Cyclic voltage sweepings present polarity-related current curves, which manifest the MD characteristics as the current stays near zero in negative voltages, but significantly increases in positive voltages. Cyclic IV curves also present a moderate hysteresis, featuring a memory device. Surprisingly, the current magnitude increases by 4 times when the light radiation turns on, implicating that the electronic output is significantly enhanced by photoexcitation. The resistive transport mechanism is hypothetically attributed to electron-ion couplings, where both electronic mobility and ionic-hopping contribute to carrier transport as electrons migrate in an ionic "train", where dielectric dipoles induce IV hysteresis. All materials in the MD devices are bio-compatible, stable, and flexible, potentially applicable to bio-electronic circuits, artificial neuromorphic synapses, and brain-inspired quantum computing.

SYMPOSIUM SB04

Innovative Device and Characterization Concepts for Organic Electronics
April 23 - April 26, 2024

Symposium Organizers
Paddy K. L. Chan, University of Hong Kong
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Journal of Materials Chemistry C
Proto Manufacturing

* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

10:30 AM *SB04.01.01

Probing The Microscopic Origins of Device Performance and Stability in Organic Semiconductors through Trap Density of States Spectroscopy

Oana D. Jurchescu; Wake Forest University, United States

Organic semiconductors (OSCs) are highly susceptible to defect formation, owing to their weak intermolecular interactions, leading to trap states in the band gap that can drastically alter their optoelectronic properties. Characterization techniques that can elucidate the mechanisms of defect formation and evolution are essential for guiding the processing and design of high-performance stable OSC devices. In this presentation I will discuss a highly efficient methodology to elucidate the microscopic processes occurring within the OSC when deliberately exposed to different external stimuli. The methodology relies on real-time access to the trap density of states (t-DOS) spectrum of the OSC using organic field-effect transistor (OFET) measurements. The t-DOS spectrum provides detailed information about the origin and energetic distribution of electronic traps in OSCs, as well as their time evolution. Several different trap states will be discussed as case studies, including those arising from impurities and isomer coexistence, microstrain at device interfaces, environmental and bias stress. Methods for minimizing the trap density to enhance performance and stability will be presented. Finally, the exploitation of trap formation for the development of radiation dosimeters for cancer treatment will be discussed.

11:00 AM *SB04.01.02

High-Frequency Flexible Organic Thin-Film Transistors

Hagen Klauk; Max Planck Institute for Solid State Research, Germany

Organic thin-film transistors (TFTs) are potentially useful for flexible electronics applications, as they can typically be fabricated at temperatures no higher than approximately 100 °C and thus not only on glass, but also on polymeric substrates and even on paper. An important TFT performance parameter is the transit frequency, which is the highest frequency at which a transistor is able to switch or amplify electrical signals. The transit frequency of organic TFTs depends mostly on the contact resistance and on the lateral TFT dimensions (channel length, gate-to-contact overlaps). A better understanding of the factors that determine the contact resistance of organic TFTs has made it possible to fabricate organic TFTs that have a contact resistance within three orders of magnitude of the theoretical limit and an experimentally measured transit frequency of 21 MHz (at 3 V). Any significant further reduction of the contact resistance of organic TFTs to the levels commonly achieved in inorganic field-effect transistors now hinges mainly on the elimination of the Fermi-level pinning induced by metal-induced gap states at the metal-semiconductor interfaces. In terms of decreasing the lateral TFT dimensions, flexible organic TFTs with channel lengths and gate-to-contact overlaps below 1 μm were recently demonstrated that display reasonable static characteristics (turn-on voltage of 0 V, subthreshold swing below 100 mV/decade, on/off current ratio greater than 10^4), but suffer from a relatively large contact

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With the increased burden on healthcare workers in recent years, point-of-care medical devices for the gastrointestinal tract that do not need external supervision (neither during ingestion nor for their retrieval) could be crucial for safe and early diagnosis, monitoring and treatment of many diseases. Edible electronics can enable such a vision through devices that are not only ingestible but are indeed digestible just like food, as they are made up of food-grade materials, thus zeroing the risks and health hazards posed by device retention and therefore the need for supervised administration. To turn this vision into reality, research efforts are steering towards functional edible electronic devices that can enable active signal monitoring and control of drug release inside the human body.[1]

In this work, we present a printed fully edible transistor operating at low voltage (<1V). Inert metallic source-drain and gate staggered electrodes were inkjet-printed on top of an ethyl-cellulose edible substrate, while the chitosan solid electrolyte and the edible semiconductor Copper Phthalocyanine (CuPc) were drop-casted and thermally evaporated, respectively. The devices were characterized in terms of transport characteristics, air stability and reproducibility, showing performances comparable to conventional transistors based on the same semiconductor, an air stability of at least 12 months and a high degree of reproducibility. To realize a proof-of-principle logic gate, the transistor was connected with a commercial resistor to create an inverter. We believe that the results of this work can pave the way to the development of edible circuitry for a broad range of future applications in the medical, food and entertainment industry. We recognize the importance of x-y-z).


11:45 AM SB04.01.04

Development of Strain-Induced Organic Single-Crystalline Transistors Mizuki Abe, Taiki Sawada1, Yu Yamashita1,2, Naotaka Kasuya, Shun Watanabe, and Jun Takeya1,2,3, The University of Tokyo, Japan; 2National Institute for Materials Science, Japan; 3JST CREST, Japan

Organic single crystals (OSC) are known as flexible, processable, lightweight, and potentially low-cost materials which are applied in many electronic devices. There is considerable interest in developments in organic thin-film transistors (OTFTs) for applications such as flexible displays, sensors, and IC tags. Rapid developments in synthetic chemistry and device engineering allow us to explore high performance devices. However, there is limited study to improve static (DC) and dynamic (AC) performances of organic devices without employing synthesis and complicated device integration.

A strain is used to control the electronic structure. Particularly in the case of single-crystalline OSCs, it has been demonstrated that a slight compressive lattice strain can modify the electronic structure via uniformly modified crystal structure, and enhances carrier mobility.[1][2]. However, the method to apply strain into OSCs has been limited; bending substrate has been only the way to systematically control the strain in OSCs. Therefore, a novel method to introduce a persistently strain into OSCs particularly on a planar substrate will be highly desirable.

Here, we establish a general method to persistently and uniformly induce compressive strain into single-crystalline OTFTs to enhance the performance of OTFTs. OTFTs with single-crystalline films of 3,11-diocytldinaphtho[2,3-d:2,3-d]benz[1,2-b:4,5b]dithiophene (C8–DNBDT–NW) as the active layer were fabricated on 15 μm thick polyimide (PI) substrate. To induce uniaxial compressive strain into OTFTs semi-permanently in a planar substrate, we developed following next method. First, OTFTs fabricated on PI substrate were adhered onto a convexly bent thick mother substrate (polyethylene terephthalate) by using cyanoacrylate adhesive. The OTFTs adhered on the extended surface of the bent mother substrate were compressed semi-permanently when the mother substrate is recovered in a flat state. In this method, the surface strain ε of the bent film was calculated by the following equation: \( \varepsilon = h / (2R + h) \), where \( h \) is the thickness of mother substrate and \( R \) is the curvature radius of bent substrate.

By applying this modulation, the carrier mobility by the introduction of uniaxial compression is observed. By changing the curvature of mother substrate, the ratio of compressive strain into OTFT changes accordingly. In this measurement, the maximum compressive strain induced into OTFTs is evaluated to be 3.1\% along c-axis. The intrinsic mobility increases monotonically by inducing compressive strain by a factor of 150\% when compressive strain reaches 3.1\%. This large enhancement of intrinsic mobility agrees quantitatively with our previous study,[1], and originates from the suppression of molecular vibration, rather than from the effect of effective mass; a reduction of lattice constant of C8–DNBDT–NW directly restricts the molecular vibration which contributes particularly to electron-phonon interaction.

The enhancement of dynamic performances of OTFTs by the strain is observed consistently in strain-induced OTFTs. Cutoff frequency \( f_c \), the parameter which determines operation speed of OTFTs, improves by a factor of 140\% when 1.0\% compressive strain is induced into OTFTs. Theoretically, cutoff frequency is proportional to the carrier mobility of OSCs. Therefore, this result indicates that enhancement of carrier mobility by the introduction of strain also improves dynamic properties of OTFTs. From these results, strain-induced OTFTs showed high carrier mobility and improved cutoff frequency. Inducing even larger strain is expected to further improve both static and dynamic properties of OTFTs. This simple, but versatile method will open opportunities for further developments in high frequency operation of OTFTs.


1:30 PM SB04.02.01

Charge Transport and Thermoelectric Properties of High Mobility Doped Conjugated Polymers Henning Sirringhaus; Stanford University, United Kingdom

Doped conjugated polymers are critical to emerging device applications, including field-effect transistors, thermoelectrics, bioelectronics, and neuromorphic computing devices. We will present recent advances in controlling doping processes and understanding the resulting charge transport properties of doped polymers. This will include discussion of the role of Coulomb interactions between carriers and the counterions at high doping densities, new experimental methods to study the electronic structure and transport properties of these doped polymers as well as recent advances in improving the electrical stability of FETs and thermoelectric performance.

2:00 PM SB04.02.02

Charge Carrier Transport in Crystalline Organic and Hybrid Perovskite Semiconductors Investigated with a High-Resolution ac-Hall Technique Vitaly Podzorov; Rutgers University, United States

The importance of Hall effect measurements in evaluating the charge carrier mobility of novel materials is being increasingly recognized in materials science, semiconductor physics, and electronics. Hall measurements are advantageous over other mobility measurement techniques in that they: (a) allow a direct access to the mobile carrier concentration and mobility in a steady-state charge transport regime; (b) provide an alternative for mobility evaluation in systems where other techniques are hard to implement; (c) provide means of distinguishing between different transport mechanisms (e.g., hopping, band-like, or their combination); and (d) help disentangling the contributions of various carrier types or trap states. However, in many intrinsically low-mobility materials and devices, conventional dc Hall measurements are extremely hard to carry out due to typically weak Hall signals (and, thus, low signal-to-noise ratio).

High-resolution ac Hall and photo-Hall measurements recently developed in our group have resulted in a significant progress in our understanding of the charge transport and photophysical properties of organic semiconductors and lead-halide perovskites.[1,2] In this talk, I will discuss a few examples of the transport physics studies using Hall-effect measurements. For instance, Hall measurements have led to elucidation of the role of grain boundaries in high-performance polycrystalline organic field-effect transistors (OFETs), where capacitively charged grain boundaries lead to an “underdeveloped” Hall effect.[3] In another example, the Hall measurements have led to elucidation of the role of grain boundaries in high-performance polycrystalline organic field-effect transistors (OFETs), where capacitively charged grain boundaries lead to an “underdeveloped” Hall effect.[3] In another example, the Hall measurements have led to elucidation of the role of grain boundaries in high-performance polycrystalline organic field-effect transistors (OFETs), where capacitively charged grain boundaries lead to an “underdeveloped” Hall effect.[3] In another example, the Hall measurements have led to elucidation of the role of grain boundaries in high-performance polycrystalline organic field-effect transistors (OFETs), where capacitively charged grain boundaries lead to an “underdeveloped” Hall effect.[3] In another example, the Hall measurements have led to elucidation of the role of grain boundaries in high-performance polycrystalline organic field-effect transistors (OFETs), where capacitively charged grain boundaries lead to an “underdeveloped” Hall effect.[3] In another example, the Hall measurements have led to elucidation of the role of grain boundaries in high-performance polycrystalline organic field-effect transistors (OFETs), where capacitively charged grain boundaries lead to an “underdeveloped” Hall effect.[3] In another example, the Hall measurements have led to elucidation of the role of grain boundaries in high-performance polycrystalline organic field-effect transistors (OFETs), where capacitively charged grain boundaries lead to an “underdeveloped” Hall effect.[3] In another example, the Hall measurements have led to elucidation of the role of grain boundaries in high-performance polycrystalline organic field-effect transistors (OFETs), where capacitively charged grain boundaries lead to an “underdeveloped” Hall effect.[3] In another example, the Hall measurements have led to elucidation of the role of grain boundaries in high-performance polycrystalline organic field-effect transistors (OFETs), where capacitively charged grain boundaries lead to an “underdeveloped” Hall effect.[3] In another example, the Hall measurements have led to elucidation of the role of grain boundaries in high-performance polycrystalline organic field-effect transistors (OFETs), where capacitively charged grain boundaries lead to an “underdeveloped” Hall effect.[3] In another example, the Hall measurements have led to elucidation of the role of grain boundaries in high-performance polycrystalline organic field-effect transistors (OFETs), where capacitively charged grain boundaries lead to an “underdeveloped” Hall effect.[3]
Effect of Structural Dynamically Induced Disorder on Charge in Molecular Materials

Lisa A. Fredin; Lehigh University, United States

Describing charge carrier anisotropy in small molecule crystalline semiconductors with ab initio methods is challenging because of the weak intermolecular interactions which lead to both localized and delocalized charge hopping interactions. Hopping models (localized) are generally used to describe materials with small charge carrier mobilities, while periodic band models (delocalized) are used to describe materials with high carrier mobilities. Noncovalent interactions between the molecular components mean that dynamic disorder in these materials can have a large impact on the electronic properties of these materials at room temperature. In particular, dynamically induced structural disorder can lead to non-linear changes of the electronic response. Here we build new real temperature computational methodologies based on either Marcus Theory (hopping) or the Boltzmann Transport Equation (band transport) that allow for direct prediction of electronic response of single crystal organics while capturing the weak electrostatic interactions between n-interacting organic molecules, the surrounding crystal environment through periodic symmetry, delocalization of charge in a single calculation, and zero-point energy corrections. In particular, very small atomic displacements can sometimes have a large effect on the localization of electronic density and thus charge transport.

3:00 PM BREAK

SESSION SB04.03: Materials I
Session Chairs: Ting Lei and Simon Rondeau-Gagne
Tuesday Afternoon, April 23, 2024
Room 435, Level 4, Summit

3:30 PM SB04.03.01
Understanding The Device Stability Through The Lens of Semiconductive Polymer's Chain Dynamics

Xiaodan Gu; University of Southern Mississippi, United States

Organic semiconductors were widely studied due to their unique optoelectronic and mechanical property. They are the key component in various functional electronic devices, as organic photovoltaic devices, flexible displays, wearable sensors, neuromorphic computing, and more recently bioelectronics. Despite tremendous progress being made in improving the charge carrier mobility and optimizing energy bandgap, the conjugated polymer's physical property was not widely studied, particularly the glass transition phenomenon. However, it is important for device stability, preventing wide adoption of polymer-based organic devices.

In my talk, I will outline past works on studying the polymer dynamics for semiconductive polymers and provide an overview of our effort in this area using a wide range of unique characterization tools, from thin film to bulk. I will discuss the challenge associated with accurately measuring the glass transition temperature for rigid conjugated polymers. I will also discuss our approach to address this challenge using thin-film calorimetry and ellipsometry tools, as well as using molecular dynamic simulation and cheminformatics to accurately predict the glass transition temperature. Lastly, I will cover how dynamics could impact thin film morphology and device performance at different operation temperatures and should be carefully considered when designing new polymers and devices.

4:00 PM SB04.03.02
Nanomechanics of Materials used in Flexible Electronics

Deepak Venkateshvaran and Leszek Spalek; University of Cambridge, United Kingdom

Organic semiconductors are multifunctional soft electronic materials that play an impactable role in the flexible electronics industry. Their use spans printed electronic circuits, large area displays, flexible solar energy harvesters, and implantable bioelectronics. For their competitive optical, electronic, thermoelectric, and spin-based properties, these soft electronic materials attract significant academic engagement, seeding new technologies for the future. [1, 2, 3]

Although macroscopic flexibility on the centimetre to metre scale is a unique selling point for organic semiconductor technology, not much is known about their mechanical properties on the nanoscale. Quantification of these nanomechanical properties, together with an understanding of nanoscale stiffness tunability and homogenisation, holds significant potential for fundamental and applied science. [4, 5]

During the last decade, the development of high precision atomic force microscopes has made it possible to quantify the mechanical properties of organic polymers on the scale of a few polymer chains. Techniques such as higher eigen mode imaging make it possible to visualise molecular ordering on the nanoscale under ambient conditions with ease. These techniques allow one to correlate molecular ordering with the stiffness that such ordering manifests.

In this talk, the science and technology of precision nanoscale measurement of mechanics will be spotlight. The interrelation between molecular organisation and nanomechanical properties in high-performance polymers used for organic electronics will be shown. [6, 7] A quantification of differences in strain within organic nanocrystal polymers will also be demonstrated. The measurement techniques demonstrated in this talk are extendable to a wide variety of multifunctional materials with a broad range of elastic properties and have significant use in both academia and industry.


4:30 PM SB04.03.03
Discovering New Molecules for Organic Electronics from The Chemical Supply Chain

Alessandro Troisi and Omer Omar; University of Liverpool, United Kingdom

We present our methodology to discover novel active molecular compounds for organic electronics combining high-throughput virtual screening and knowledge of the chemical supply chain. The talk with provide new recent examples of the discovery of (i) dual emitters, (ii) molecules with inverted single-triplet gap and (iii) low energy emitters. In all cases the discovery take places in two steps, the exploration of a large chemical space of pre-computed properties followed by a refinement of the search through more computationally demanding screening steps. The approach is designed to allow facile experimental verification of the predictions and some verifications will be presented as part of the lecture. The web platform enabling similar workflows to be adapted to different properties is presented.
Material degradation poses a significant concern for both material scientists and engineers, leading to costly repair efforts and more extensive consequences than mere failure. As a result, there is a growing interest in developing self-healing materials to eliminate the need for maintenance. In contrast to their inorganic semiconductor counterparts, organic semiconducting materials possess notably low Young's moduli, making them exceptionally well-suited for integration into wearable electronic devices that can be directly applied to the human skin [1]. However, wearable electronics are exposed to a myriad of environmental stressors, including mechanical wear, chemical exposure, temperature fluctuations, and radiation. The relentless impact of these stressors can lead to the deterioration of the chemical structure, ultimately resulting in the degradation and eventual loss of the material's physical properties.

Within this context, we will delve into our strategic approach to mitigating the loss of physical properties through the development of intrinsically self-healing polymers. This significant achievement was made possible by harnessing the principles of supramolecular chemistry, with a particular emphasis on the utilization of intramolecular hydrogen bonds [2-4]. To gain a comprehensive understanding of how hydrogen bonding affects the viscoelastic and electrical characteristics of organic semiconductors, we devised two distinct material sets. The first consists of a conjugated polymer with integrated hydrogen bonding functionality, while the second involves a composite material comprising a conjugated polymer embedded within a self-healing polysiloxane matrix.

Our discussion will comprehensively cover the effects of these distinct approaches on charge transport and self-healing capabilities. Furthermore, we will outline how we can leverage the observed disparities to not only customize the electronic properties but also fine-tune the self-healing and mechanical attributes of the material to align with the specific demands of diverse applications.

Charge Carrier Trapping in Organic Semiconductors

The efficiency and stability of single-layer polymer light-emitting diodes is compromised by unbalanced charge transport, absence of triplet-exciton harvesting and low photoluminescence quantum efficiencies. Especially charge traps have a triple negative effect: they give rise to non-radiative trap-assisted recombination, they associate singlet excitons leading to a reduced photoluminescence quantum yield and due to confinement of the emission zone at an electrode they lower the optical outcoupling efficiency. A strategy is developed that precludes trapping in large band gap organic semiconductors. We demonstrate that using thermally activated delayed fluorescence emitters in combination with trap-free transport high external quantum efficiencies for single-layer blue OLEDs can be obtained. Our results show that OLEDs with a simplified single-layer structure can rival the efficiencies of complex multilayer stacks.

First, we engineer spin qubits based on high-spin multieexcitons photogenerated in organic semiconductors using singlet fission. We engineer the packing of tetracene molecules within single crystals by using tailored linking groups to demonstrate multie excitons that exhibit promising spin qubit properties, including a coherence time, $T_2^*$ of 3 μs at 10 K, a population lifetime, $T_{pop}$ of 130 μs at 5 K, and stability even at room temperature. The single-crystal platform also enables global alignment of the spins and, consequently, individual addressability of the spin-sublevel transitions. Decoherence mechanisms, including exciton diffusion, electronic dipolar coupling, and nuclear hyperfine interactions, are elucidated, providing design principles for increasing the spin coherence lifetime and operational temperature of the multie exciton spin qubits. By dynamically decoupling the qubits from the surrounding spin bath, $T_1$ of 10 μs is achieved. This material system provides an exciting path to realize dense arrays of optically addressable qubits that are generated on demand at specific locations.

Second, we harness a new class of organic framework materials, known as ion-paired frameworks, to develop atomically precise arrays of molecular spin qubits. We learn how to control the density of the paramagnetic Cu(II) porphyrin spins by engineering the linker groups and crystal growth conditions. Pulse-electron paramagnetic resonance (EPR) spectroscopy is used to probe the spin coherence of these single crystals at temperatures up to 140 K. The crystals with the longest Cu--Cu distances exhibit a spin coherence time, $T_2^*$, of 207 ns and a spin–lattice relaxation time, $T_1$, of 1.8 ms at 5 K, which are records for qubits in an atomically precise molecular system. The mechanisms of spin decoherence and spin-lattice relaxation will also be discussed. Incorporating molecular electronic spin qubits in ion-paired frameworks enables control of composition, spacing, and interqubit interactions, providing a rational means to extend spin relaxation times for next-generation quantum technologies.

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High-mobility single crystal organic semiconductors are important for applications in advanced organic electronics and photonics. Photogeneration and transport of mobile carriercarriers in these materials, although very important, remain underexplored. For sustained progress in the field, understanding the intrinsic (i.e., not limited by static disorder) charge transport properties of crystalline organic semiconductors is important. The Hall effect represents one of the most efficient experimental tools for assessing intrinsic charge transport, as Hall effect in single crystal materials probes band-like (i.e., delocalized) mobile charges. The photocarrier generation by light allows circumventing the challenging problem of carrier injection from contacts (especially when measurements of both electrons and holes are pursued), avoiding carrier trapping and scattering associated with the interfacial charge transport as in OFETs, and preventing added disorder associated with chemical doping. Therefore, photo-Hall effect opens new opportunities in probing the intrinsic charge transport in organic semiconductors.

The photo-Hall measurements in pristine, ungated organic semiconductors pose an even greater challenge than the Hall measurements in OFETs or chemically doped samples, because a much lower carrier density (and, thus, much higher sample’s resistances) is typically generated by light. By taking advantage of a sensitive ac-Hall methodology previously developed in our group, we have performed reliable photo-Hall effect measurements in a benchmark organic semiconductor rubrene. We present the first clear demonstration of a photo-Hall effect in organic semiconductors, using a benchmark molecular crystal rubrene as an experimental platform. The concept of a photo-Hall effect allows probing the intrinsic transport properties of pristine semiconductor materials in stand-alone crystals, free from the problems associated with charge injection from contacts, interfacial transport, or additional disorder typically encountered in the conventional approaches based on OFETs or chemically doped materials. In photo-Hall measurements, the steady-state carrier density and mobility are measured independently, with no assumptions regarding the photocarrier generation efficiency or lifetime, thus providing a direct experimental access to these important parameters. We find that under a cw illumination in the visible range, only mobile holes are generated in pristine rubrene crystals, leading to a substantial p-type surface photococonductivity with the hole mobility $n_{photo-Hall} = 11 \pm 1 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and the density that follows a power law $n_{photo-Hall} = \alpha P^\beta$, with the power exponent $\alpha = 1/4–1/3$. In addition, by intentionally inhibiting the surface transport via the gauge effect, we observed a small residual bulk photocarrier density governed by a bimolecular electron-hole recombination ($\alpha = 1/2$) with a higher true-bulk hole mobility of $n_{photo-Hall} = 16 \pm 1 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1}$.

These experiments significantly advance our fundamental understanding of charge transport and photocarrier mobility in rubrene, based on triplet excitation diffusion and surface dissociation, in which the latter process is shown to be governed by electron trapping with a release of mobile hole. Overall, our work demonstrates that the photo-Hall effect is a powerful tool for addressing the intrinsic charge transport in organic semiconductors and potentially other emergent semiconducting materials.

References:


The Photo-Hall Effect in High-Mobility Organic Semiconductors Vladimir V. Bruevich and Vitaly Podzorov; Rutgers University Physics Department, United States

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Vertical transistor architectures offer sub-micrometer channel dimensions and hence, high-frequency operation, without the need for advanced patterning techniques. However, while the fabrication procedures for lateral thin-film transistors matured, fabrication techniques for vertical organic transistors are less developed and as a consequence, yield, uniformity, and reliability of such devices remain poor. Furthermore, reports with vertical organic transistors addressing circuits and advanced device functionalities are rare.

For more than one decade, we have been developing organic permeable base transistors (OPBTs) – a vertical transistor structure that resembles a solid-state triode where nano-scale pinholes allow the current to pass from the emitter to the collector electrode through a control base. Starting with investigations on the fundamental device physics, we advanced the performance of these devices towards the ultra-high-frequencies region, and recently, we demonstrated the integration of complementary inverters with adjustable tripping point. In this contribution, I will discuss recent significant progress concerning device integration using large-area electrochemical anodization. In particular, using this technique, the yield of fabrication is close to 100%, allowing us to integrate circuits. Furthermore, the anodization gives us control over leakage currents, and device capacitance, and increases the tolerances against thickness variation, resulting in an excellent current gain of $>10^7$. Moreover, the anodization technique is vital for the realization of devices with advanced functionalities such as vertical memory or reconfigurable devices, opening up the perspective for the design of ultra-high-frequency application-specific circuits based on organic semiconductors.

4:00 PM *SB04.07.02 High-Speed Organic Integrated Circuits and Applications Jun Takeya1,2, The University of Tokyo, Japan; 2P-Crystal Inc., Japan

Electronic devices in the future sustainable societies require maximum function with minimum amount of constituent materials and energy cost for production. Electronic functions are often originated from two-dimensional material properties so that device components of large area and small thickness saves material consumption. The fundamental electronic functions of both analogue and digital circuits mostly rely on only a nanometer-scale thin layer at the very surface of the semiconductor material due to the very short penetration length of electric field. The presentation focuses on material bases, methods of circuit fabrication, dynamic operation of the devices, and several applications for commercialization.

Recently developed ultrathin organic semiconductor single crystalline films is suitable for large-area production with low energy consumption; the films are easily formed to large area from solution at relatively low temperature at 80 degrees centigrade [1]. Extremely thin crystal films are controllably grown to a few molecular layers with the thickness of only 10 nm, so that material cost can be highly limited. Due to a careful material design for restricting harmful molecular vibration, very high carrier mobility more than 10 cm²/Vs is achieved. Furthermore, development of technologies for printed integrated circuits provides a manufacturable process for low-cost platforms for RFID tags and sensing circuitries. Finally, a technology for large-area light-weight display sheets will be demonstrated.

A dynamic transistor model is developed using device parameters such as channel length and overlap length of gate and source electrodes, so that high-frequency transistors are physically designed appropriately including charge-injection resistance [2]. A high cut-off frequency above 45 MHz is actually achieved which are composing elements of organic integrated circuits. Typical integrated circuits using only a few hundred transistors can be realized using newly developed high-frequency organic rectifiers to operate an RFID tag with the NFC frequency [3].

Such prospect bears increasing reality because of recent research innovations in the field of material chemistry, charge transport physics, and solution processes of printable organic semiconductors. With excellent chemical and thermal stability in recently developed new materials, we are developing simple integrated devices based on CMOS using organic p-type and n-type polymeric thin-film FETs. Particular importance is now processing technologies for continuous growth of the organic single-crystalline semiconductor “wafers” from solution and for lithography patterning of semiconductors and metal electrodes. Successful rectification and identification are demonstrated at 13.56 MHz with printed organic CMOS circuits. Future ten-micrometer scale large-display also needs to be more “two-dimensional” to save materials and save energies to carry and equip on billboards.

A Persistent Challenge in Organic Electronics: How Does Structure Affect Electronic Transport? **Alberto Salleo**

University of California, United States

Linking microstructure to transport remains the grand challenge preventing the rational design of new organic semiconductors. Indeed overcoming this hurdle might unleash the full power of organic synthesis to make materials with “designer” properties, be they electronic, excitonic or ionic transport. We have spent years developing complementary techniques that allow us to analyze the microstructure at different length-scales and from complementary points of view. In particular, the use of XRD, TEM and UV/Vis spectroscopy allows to understand order from the molecular to the device level. We use these techniques coupled with transport measurements to understand the role of intra vs. interchain order as well as mesoscale order. These techniques can be extended to mixed conductors where the electrolyte controls order and provides one more knob to study the relationship between order and transport.

Electrochemical Transistors: A Platform for Exploring Carrier Transport and Ion-Carrier Correlations at High Charge Densities in Organic Semiconductors **Daniel Frisbie**

University of Minnesota, United States

Electrochemical transistors are a powerful platform for fundamental investigations of hole and electron transport in organic semiconductors as a function of continuously tunable charge up to very large densities of order 0.1-1 carrier per molecule. There is increasing evidence that ion-charge carrier interactions are profoundly important in these devices. This talk will describe ongoing experiments to examine transport in electrochemical transistors based on single crystals and thin films of organic semiconductors. In one study, electron transport on the surface of electrolyte-gated C60 single crystals is measured as a function of cation radius in the gate electrolyte. For small cations, surface conductivity versus electron density exhibits a peak near 0.5 electron/C60. Conductivity is completely shut down at 1 electron/C60. As cation size increases, this peaked conductance behavior becomes less prominent and average electron mobility increases, indicating that cation-electron interactions at the surface of the C60 crystal play an important role. For devices gated with the largest cations, temperature dependent transport shows the gate-induced electrons are significantly delocalized. In a second experiment, transport is examined in a series of polythiophenes as a function of side-chain length. Again, a strong peak in conductance versus carrier density is observed, with the peak occurring near 0.15 hole/monomer for all of the polymers. Further, there is a marked dependence of the conductance on side-chain length, with longer side chains giving higher conductances. The results are interpreted in terms of ion-charge Coulomb interactions and the implications will be discussed.

In-Operando Spectroscopic Characterization of Non-Equilibrium States in a Highly Doped Polymer **Enrique Jacoby**

University of California, United States

Highly doped organic semiconductors are critical to a variety of applications, including thermoelectrics, bioelectronics, and neuromorphic computing devices. Recent advances have enabled the routine doping of polymer films to extremely high carrier densities on the order of one charge per polymer repeat unit. In this regime charge transport is comparably poorly understood due to the non-negligible effects of electron-electron and electron-ion interactions, in addition to the ever-present role of static and transient disorder.

Here, we report on dual-gated indacenodithiophene-co-benzothiadiazole (IDBT) organic electrochemical transistors (OECTs) and corresponding ion-exchange doped films, in which a second field-effect gate enables us to modulate the carrier density independently from the ion density. These devices show unusual behavior: at low temperatures, field effect transfer curves are highly non-linear and in many cases even ambipolar, while at high temperatures a purely linear curve is obtained. Using solid-state NMR and infrared charge modulation spectroscopy, we demonstrate that this non-linearity at low temperatures is a signature of a non-equilibrium state resulting from freeze-out of ionic motion. Under these conditions, we see an enhancement in charge delocalization, electrical conductivity, and Seebeck coefficient, pointing to a new pathway to enhanced thermoelectric performance.

Electrochemical Doping Induced Crystallinity in Organic Mixed Ionic/Electronic Conductors **Lucas Flagg**

University of Delaware, United States

Organic mixed ionic-electronic conductors (OMIECs) are an exciting class of new materials with a range of potential applications including biosensors, electrochromics, and neuromorphic computing. These applications all require ion transport from an electrolyte into the organic active layer during operation. Characterization of this electrolyte and ion swollen state is essential to understanding device operation on a fundamental level. However, this swollen state is particularly difficult to study because it requires development of in-situ techniques. Here, we utilize in-situ Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) to study the crystallinity of the swollen state of OMIECs as a function of applied potential. We study a variety of conjugated polymer active layers and find consistent doping induced crystallinity across a variety of different polymer backbones. Interestingly, we find a maximum in the crystallinity as a function of doping level for some polymers. At moderate doping levels the crystallinity is enhanced relative to the undoped state, but then at the highest doping levels achieved the crystallinity decreases. Finally, we use organic electrochemical transistors (OECTs) to correlate the electronic conductivity with these doping induced morphological changes. These results demonstrate the importance of in-situ characterization to develop a better understanding of organic electronic devices.

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Novel Extended Chromophores as Organic Transistor Materials

1:30 PM SB04.08.08

N-Type Semiconducting Hydrogel Peiyun Li, Wenxi Sun and Ting Lei; Peking University, China

Hydrogels are an attractive category of biointerfacing materials with adjustable mechanical properties, diverse biochemical functions, and good ionic conductivity. Despite these advantages, their application in electronics has been restricted due to their lack of semiconducting properties, as they have traditionally only served as insulators or conductors. We develop single and multiple network hydrogels based on a water-soluble n-type semiconducting polymer, thereby endowing conventional hydrogels with semiconducting capabilities. These hydrogels show good electron mobilities and high on/off ratios, enabling the fabrication of complementary logic circuits and signal amplifiers with low power consumption and high gains. We demonstrate that hydrogel electronics can sense and amplify electrophysiological signals with enhanced signal-to-noise ratios. Our work could enable more optoelectronic properties and greatly expand the applications of hydrogels in bioelectronics.

3:00 PM BREAK

2:00 PM SB04.09.02
Chiral Organic Semiconductors Yves H. Goetz1,2, 1University Libre de Bruxelles, Belgium; 2International Solvay Institutes of Physics and Chemistry, Belgium

I will report on our latest results on the design, the synthesis, and the characterization of crystalline organic semiconductors with achiral and chiral pi-systems. Chiral induced spin selectivity (CISSeffect and electrical magnetochiral anistropy (MChA) have been investigated in organic field effect transistors (OFETs) with these materials. [Adv. Sci. 2023, 10, 2301914]

2:30 PM SB04.09.03
Deciphering The Difference between Flexible Chain and Hairy-Rod Polymer Semiconductors Natalie Stingelin; Georgia Institute of Technology, United States

Organic electronic materials possess unique opto-electronic and processing properties that provide broad opportunities for use in light-emitting diodes, solar-energy harvesting systems, to next-generation sensors and neuromorphic computing devices. These technologies have been continually improving over the past decades, aided by advancements in materials chemistry and processing innovation. State-of-the-art polymer semiconductors typically have an electron donor-acceptor (D-A) backbone structure with a number of fused ring moieties, and complex aliphatic or, e.g., ethylene-oxide side chains that decorate the backbone to provide solubility. It is important to recognize that the physical properties of the side chains are substantially different from the backbone, constituting an amphiphilic-like characteristics transverse to the backbone reminiscent of phospholipid and surfactant molecular analogs, and simple classical descriptions of amorphous vs. semicrystalline structure no longer apply. Here, we discuss how the FSC technique can be used for the identification of thermodynamic transitions of next generation D-A polymers commonly used in the organic solar cell area to obtain important structural information of this new class of materials and, in turn, establish processing guidelines towards materials of specific optical or electrical characteristics, and improved materials design for organic optoelectronic devices.

3:00 PM BREAK

SESSION SB04.10: Optoelectronics III
Session Chairs: Paddy K. L. Chan and Deepak Venkateshvaran
Thursday Afternoon, April 25, 2024
Room 435, Level 4, Summit

3:30 PM SB04.10.01
Novel Extended Chromophores as Organic Transistor Materials John Anthony; University of Kentucky, United States

The field of organic electronics benefits from the synthetic diversity of conjugated chromophores, which can be further functionalized to tune everything from optical gap to crystal packing. The ability to vary structure allows an impressive variety of related compounds to be compared, enhancing our understanding of design rules for the development of new semiconductor materials. For example, we know that two-dimensional electronic coupling is critical to high-mobility devices, as it is a layered / lamellar motif for the 2D interacting layers. Design guidelines beyond that are now emerging - such as a desire for isotropic electronic coupling within the 2D interacting layers, and functionalization that minimizes core vibration in the solid state. With these emerging notions in mind, I will present an array of new and exotic aromatic backbones and functionalization schemes designed to further explore these newer potential design guidelines, to attempt to determine their impact on performance in organic transistors. In particular, the impact of chromophore twisting / curvature on charge transport studies will be discussed.
Harnessing Exciton Transitions for Sensing Devices: OLED and Transistor-Based Magnetic Field Sensors

Emily G. Bittle; NIST, United States

The study of excitons has advanced optoelectronic device control and efficiency. Now, there is a growing interest in harnessing the unique exciton transitions of long-lived high-binding energy excitons (HBEEs) for developing new device functionality. Our research has demonstrated the feasibility of using exciton dynamics in organic light-emitting diodes (OLEDs) as magnetic field sensors in fully electronic devices1. Additionally, wide-field optical detection of OLED output in a graded magnetic field has been demonstrated that shows the promise of sub-micron sensing using excitons2. By integrating exciton properties and functionality into LEDs and other electronic devices, we envision the potential for developing screens and lighting with built-in sensing capabilities. We are actively exploring the use of transistor-based sensors to refine exciton-based measurements within electronic devices3,4. The flexibility of controlling parameters in transistors, such as traps, interfaces, field, structure, etc, offers a versatile approach to enhancing exciton properties for optimal field sensing. Our ongoing work investigates material and device properties to enhance signal sensitivity, extending beyond the conventional focus on optoelectronic efficiency studies.


Highly Efficient Intrinsic Stretchable OLEDs from Thermally Activated Delayed Fluorescence

Cheng Zhang, Wei Liu and Sihong Wang; Pritzker School of Molecular Engineering, United States

Light-emitting devices are crucial for human-machine interfaces, which would function as read out displaying platform, health sensors, therapy unit, or optical neurotransmitter in optogenetics. Considering the operation scenario of these devices, mechanical stretchability and electroluminescence (EL) performance are two of the key aspects of device design. To achieve stretchability, we have reported a feasible method that is copolymerization soft chain with conjugated functional unit. To achieve decent EL performance, among current light-emitting technologies, organic light-emitting diodes (OLEDs) stand out for their high efficiency, and bright, and low working voltage. To the best of our knowledge, most of the reported stretchable OLED are based on fluorescence emitters, 1st generation of OLED emitter. This kind of emitter has relatively simple requirements since it only harvest its singlet excitons, which leads to a theoretical internal quantum efficiency (IQE) as 25%. In contrast, thermally activated delayed fluorescence (TADF) emitters, the 3rd generation of OLED emitters, are more preferred due to its organic constituents as well as a near-unit IQE. However, its complicated device structure and requirement of energy alignment make the realizing of highly efficient fully stretchable TADF devices very challenging. Here, we want to bring up with a fully stretchable OLED devices based on TADF mechanism reaching an external quantum efficiency (EQE) around 20% and crack-onset strain exceeding 120%.

SESSION SB04.11: Poster Session
Session Chairs: Paddy K. L. Chan, Katelyn Goetz, Ulrike Kraft and Simon Rondeau-Gagne
Thursday Afternoon, April 25, 2024
Flex Hall C, Level 2, Summit

On-Site Amplification of Neural Signals by Organic Field-Effect Transistors

Wanho Cho, R. Geng, A. Mena, W. J. Pappas and D. J. Gundlach; Instrumentation Centre, Hong Kong

In the field of brain-computer interface, the transducing elements play a pivotal role in monitoring and recording neural signals. Compared to noise-sensitive microelectrodes, the high transconductance of organic electrochemical transistors enables on-site signal amplification, leading to an enhanced signal-to-noise ratio (SNR). However, the ion exchange process restricts its capability to record high-frequency (> 1 kHz) neural signals. Although lack of direct communication with the ions in the body, organic field-effect transistors (OFETs) exhibit not only high transconductance (up to 1 mS), low sensitivity to noise (down to 1 nA), and remarkable mechanical flexibility but also high operating speed (> 10 kHz). These combined merits may broaden the potential for full-frequency brain signals recording using active electrodes. In this study, we developed a ultra-conformal OFETs (5 µm channel length) featuring a top-gate bottom-contact structure, achieving a transconductance of 100 µS and a cut-off frequency of 10 kHz. In comparison to microelectrodes (SNR ~ 10 dB), the electrocorticogram signals amplified by OFETs exhibit a superior SNR (over 50 % improvement) and an enhanced temporal resolution. The pre-ictal brain signals (500 µV) associated with epilepsy are effectively monitored by our OFETs array. With proper encapsulation, the devices demonstrate excellent stability and biocompatibility. We believe that the flexible organic electrode paves a promising path for disease prediction and high-frequency neural signals recording.

Highly Efficient Intrinsically Stretchable OLEDs from Thermally Activated Delayed Fluorescence

Cheng Zhang, Wei Liu and Sihong Wang; Pritzker School of Molecular Engineering, United States

Light-emitting devices are crucial for human-machine interfaces, which would function as read out displaying platform, health sensors, therapy unit, or optical neurotransmitter in optogenetics. Considering the operation scenario of these devices, mechanical stretchability and electroluminescence (EL) performance are two of the key aspects of device design. To achieve stretchability, we have reported a feasible method that is copolymerization soft chain with conjugated functional unit. To achieve decent EL performance, among current light-emitting technologies, organic light-emitting diodes (OLEDs) stand out for their high efficiency, and bright, and low working voltage. To the best of our knowledge, most of the reported stretchable OLED are based on fluorescence emitters, 1st generation of OLED emitter. This kind of emitter has relatively simple requirements since it only harvest its singlet excitons, which leads to a theoretical internal quantum efficiency (IQE) as 25%. In contrast, thermally activated delayed fluorescence (TADF) emitters, the 3rd generation of OLED emitters, are more preferred due to its organic constituents as well as a near-unit IQE. However, its complicated device structure and requirement of energy alignment make the realizing of highly efficient fully stretchable TADF devices very challenging. Here, we want to bring up with a fully stretchable OLED devices based on TADF mechanism reaching an external quantum efficiency (EQE) around 20% and crack-onset strain exceeding 120%.
conductivity. This network structure is also tolerant to mechanical deformation. Furthermore, Ag NWs can be dispersed in various solvents and applied to flexible substrates using solution-based methods. Despite these advantages, the widespread use of AgNWs in commercial applications has been limited. One key challenge is the need for scalable processing methods to create precise and high-throughput AgNW networks that meet industrial standards. One common approach is the surface-energy-controlled transfer printing of AgNW networks onto target substrates, but this method faces challenges related to uniformity and fidelity. Photolithography, a prominent microfabrication technology, is also considered a reliable and scalable patterning technique for AgNWs. However, traditional photolithography methods, involving pre-patterned photoresist and subsequent etching or lift-off processes, are not fully compatible with AgNW networks due to their porous nature and poor adhesion to substrates. To address these issues, we developed a direct photopatterning method for AgNW networks. This method requires only a small amount of photoreactive silver ink (~3 wt%). A crosslinker, (oxybis(ethane-2,1-diyl))(oxy)(bis(ethane-2,1-diyl))bis(4-azido-3,5,6-triazafluorobenzoate (2Dx-AEO), was designed and synthesized to induce crosslinking between AgNWs upon ultraviolet (UV) irradiation. This crosslinking approach allows for the precise patterning of AgNWNs. To further enhance the electron characteristics of the AgNW network, polystyrene sulfonate (PEDOT-PSS) was selectively coated onto the AgNW patterns. The unique roughness-assisted wetting phenomenon facilitated the deposition of PEDOT-PSS, resulting in hybrid bilayer electrodes with low roughness, high oxidation resistance, and high mechanical stability. These AgNW/PEDOT-PSS hybrid transparent electrodes were used to create various electrochemical devices. Organic electrochemical transistors (OECTs) were employed as driver transistors, and they exhibited improved performance when using the hybrid electrodes compared to pristine AgNW network electrodes. This improvement was attributed to the low contact resistance and smooth surface of the hybrid electrodes. Furthermore, the AgNW/PEDOT-PSS hybrid electrodes were integrated into electrochromic (EC) devices, demonstrating their stability and suitability for applications involving charge transfer reactions. The devices exhibited reversible color changes and maintained their performance over numerous voltage cycles. Finally, a seven-segment active-matrix EC display was developed by integrating seven EC cells with their own operating OECTs. This display showcased the potential of the Ag NW/PEDOT-PSS hybrid electrodes for use in more complex optoelectronic devices.

5:00 PM SB04.11.06 Intrinsicly Stretchable Full-Color Light-Emitting Films via Elastomer Blend for Polymer Light-Emitting Diodes MinWoo Jeong1, Jin Hyun Ma1, Jae Seung Shin1, Jun Su Kim1, Guorong Ma2, Tae Uk Nam2, Phuong N. Vo3, Kyu Ho Jung3, Xiaodan Gu4, Seong Jun Kang4 and Jin Young Oh4, Kyung Hee University, Korea (the Republic of); 5University of Southern Mississippi, United States

For skin-like display, intrinsically stretchable light-emitting materials are key components. However, the previously reported materials have been still restricted super yellow series materials, which could be emitting just green-like yellow lights. Therefore, three primary light-emitting materials such as red, green and blue (RGB) are necessary to develop skin-like full-color displays. Herein, we report stretchable three primary light-emitting films enabled by polymer blend between conventional RGB light-emitting polymer semiconductors and a non-polar elastomer (SEBS). Through nano-phase separation, these films are composed of multi-dimensional nanodomains that are interconnected in an elastomer matrix for efficient charge transport and light-emitting performance under strain. The polymer light-emitting diode (PLED) exhibited over 1,000 cd/m² luminance with low turn-on voltage (< 5 Von) and the stretched blend films on rigid substrate preserved their light-emitting performance up to 100% strain even after 10,000 multiple stretching cycles.

5:00 PM SB04.11.07 Silicono-Induced Micro lithography of Small-Molecule Phosphorescent Emitters for High-Resolution Micro-OLEDs Sowoon Lee1, Hyukmin Kweon1, Borina Ha1, Ryungyu Lee2, Seokwun Kim2, Seunghan Lee2, Hyobin Ham2, Hayoung Lim3, Moon-Ki Jeong2, Gyu Rim Park1, Joon Hak Oh2, Moon Sung Kang2, Youngmin You3, Jeong Ho Cho3, BongSoo Kim3, Hojin Lee4 and Do Woon Kim2, 1Hanyang University, Korea (the Republic of); 2Soongsil University, Korea (the Republic of); 3Yonsei University, Korea (the Republic of); 4Seongnam University, Korea (the Republic of); 5Ulsan National Institute of Science and Technology, Korea (the Republic of); 6Seoul National University, Korea (the Republic of)

Organic light-emitting diodes (OLEDs) have emerged as a leading display technology, known for their exceptional color purity, rapid response time, slim design, and expanded color gamut. In the group of OLED materials, small-molecule phosphorescent OLEDs, referred to as host-dopant systems, are favored for their superior luminous efficiency. These materials efficiently capture both singlet and triplet excitons, resulting in enhanced quantum efficiency and prolonged operational lifespans. This heightened efficiency makes phosphorescent OLEDs a preferred choice for a wide range of applications, including microdisplays for augmented reality, virtual reality, and mainstream commercial displays. Patterned small-molecule-based phosphorescent materials conventionally rely on fine metal masks (FMM) for deposition-based techniques. Recent demonstrations have achieved resolutions up to 3,000 pixels per inch (ppi) for small-molecule OLED microdisplays using FMM. However, FMM-based approaches have inherent limitations, including shadow effects caused by factors such as vapor path, deposition angles, and mask thickness. Alternative methods like template-directed growth and inkjet printing have been explored, but they often exhibit issues related to resolution, pattern fidelity, and fabrication yield which necessitates the exploration of novel approaches to achieve high-resolution patterning.

To address these challenges, there is growing interest in utilizing reactive ion etching (RIE)-based photolithography for high-resolution patterning. RIE-based photolithography shows promise in achieving precise patterning. Nevertheless, the intrinsic limitations of small-molecule phosphorescent materials, characterized by their poor physico-chemical durability, have hindered their compatibility with RIE-based photolithography. This incompatibility leads to pattern degradation and compromises luminous properties, impeding the realization of high-resolution OLED microdisplays. Herein, we designed a novel paradigm by incorporating silicono into phosphorescent small-molecule networks. This silicone-integrated phosphorescent organic light-emitting network (Si-pOLED), in which silicone molecules are homogeneously crosslinked with small-molecule light-emitting materials, can efficiently achieve ultrahigh-resolution patterns via the photolithography process without degradation of their exceptional phosphorescent emission efficiency. On the basis of the weak interactions between the Si-OH and the OLED materials, we demonstrate ultrahigh-resolution patterns of Si-pOLEDs as low as 1 um. This approach leads to improved OLED microdisplays and promises both high resolution and improved luminescence properties. It marks a significant advance in the field of display technology, offering the potential to maximize performance and resolution to unprecedented levels.

5:00 PM SB04.11.09 Identity of T° Matters! Improved kISC by Modulating Locally Excited Triplet State in TADF Emitters Madalasa Mondal and Ratheeesh K. Vijayaraghavan; ISIKA, Indore

Abstract: Effective triplet exciton utilization efficiency is an essential factor for constructing low-power operational OLED devices with high luminescence efficiency and durability. Thermally activated delayed fluorescence assists this 100% triplet harvesting by converting dark triplet excitons into radiative singlet excitons via a reverse intersystem crossing process. The enhancement of this TISC (kISC) rate (kISC) is primarily realized by the low energy offset between lowest S & T state; to pursue an extremely large kISC, the involvement of high energy locally excited triplet states has become a hot topic in TADF-OLED research in present days. However, the regulation of the 3LE states to match precisely with the 1CT energy level by suitable molecular design is still under progress. Here, we demonstrated an effective electronic coupling between 1CT & 3LE or hybridized triplet state in a series of newly designed and synthesized TADF emitters with strongly twisted D-A structure. The detailed theoretical and experimental investigation reveals that the addition of peripheral donor units to the core D-A backbone incorporates multiple triplet excited states of locally excited or hybridized nature between S1 and T1 states, and the close alignment of 1CT & 3LE states accelerates the spin-flip process and the sizeable radiative rate results in suppressed efficiency roll off with short (ns) delayed lifetime. On the contrary, the isoenergetic alignment of 1CT & 3LE states realized due to the near orthogonal structure promotes the ISC mechanism. Our work highlights the pivotal role of the electronic nature of the intermediate triplet states in controlling the kISC, a thorough photophysical investigation was also performed by manipulating 3LE states by introducing variable donor units to the D-A backbone.

5:00 PM SB04.11.10 Investigating The Mechanisms of Nucleation and Growth of [1]Benzothieno[3,2-b] Benzothiophene (BTBT) and its Derivatives Using Molecular Dynamics Simulations Sashen Chambikara, D. Karunasena and Chad Risito; University of Kentucky, United States

[1]benzothieno[3,2-b] benzothiophene (BTBT) and its derivatives are of interest as the building blocks of organic semiconductors (OSC) for thin-film transistors. OSC charge-carrier mobility is influenced by the crystallinity and the molecular arrangements of molecules in their crystal lattice. To understand relationships between molecular structure and solvents used to process OSC, we investigate the nucleation and growth mechanisms of BTBT and its derivatives using constant chemical potential molecular dynamics (CpMD) simulations. We explore how concentration, solvent, and temperature affect the nucleation and growth of crystals along different crystallographic (template) planes, then quantify and analyze atomistic-scale thermodynamic and kinetic properties of crystallization. Our goal is to provide atomic-scale insights that can be used as guides for OSC design and processing.
Interfacial modifier 

between the electron transporting layer and the active layer has yielded improved photovoltaic performance in both fullerene and non-fullerene based OSCs.


References 

Electrophoretic sensing is a crucial functionality that provides valuable information in clinical diagnosis and treatment. Recent advances in wearable electronics enabled tracking electrophysiological information such as electrocardiogram (ECG) in daily life. However, conventional elastomer substrate-based devices suffer from the lack of long-term adhesion and conformability to human skin to provide a promising approach for applying organic semiconductors in various electronic devices.

Keywords: Conjugated polymers, Integrated circuits, Organic electronics, backbone engineering

Acknowledgement : This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2022R1C1C1006036). Also, this research was partially supported by Korea Institute for Advancement of Technology (KIAT) grant funded by the Korea Government (MOTIE) (P0012451, The Competency Development Program for Industry Specialist).

Reference


5:00 PM SB04.11.12

Skin-Conformable Electrochemical Sensor Devices with Tailored Negative Poisson’s Ratio Hyun Seok Kang, Yung Lee, Somin Kim, Jang-ung Park and Byeong-Soo Bae

1Korea Advanced Institute of Science and Technology, Korea (the Republic of)
2Yonsei University, Korea (the Republic of)

Electrophoretic sensing is a crucial functionality that provides valuable information in clinical diagnosis and treatment. Recent advances in wearable electronics enabled tracking electrophysiological information such as electrocardiogram (ECG) in daily life. However, conventional elastomer substrate-based devices suffer from the lack of long-term adhesion and conformability to human skin to provide a promising approach for applying organic semiconductors in various electronic devices.

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Acknowledgement : This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2022R1C1C1006036). Also, this research was partially supported by Korea Institute for Advancement of Technology (KIAT) grant funded by the Korea Government (MOTIE) (P0012451, The Competency Development Program for Industry Specialist).

Reference


5:00 PM SB04.11.13

The Host-Guest Interaction Effect in all Organic Room Temperature Phosphorescence Light-Emitting Electrochemical Cells Hee Jung Kim and Eunkyung Kim; Yonsei University, Korea (the Republic of)

A series of metal-free dyes, rooted in bromofluorene (BrF4) were synthesized to harness phosphorescence at room temperature within amorphous films and light-emitting devices (LEDs). By incorporating aliphatic and aromatic side groups onto the bromofluorene structure, we achieved substantial control over the resulting color and fine-tuned the intensity of the room temperature phosphorescence (RTP). Our selection of host materials, including 3,3'-di(9H-carbazol-9-yl)-1,1'-biphenyl and poly(9-vinyl carbazole) was guided by their energy bandgap and their ability to facilitate energy transfer to BrF4, with the aim of achieving high electrophosphorescence (BrF4) with the aim of achieving high electrophosphorescence in BrF4 based LEDs. The intensity of the electrophosphorescence was strongly reliant on the chosen host. In-depth investigations employing theoretical computations based on density functional theory, infrared studies, and single-crystal X-ray diffraction unveiled the crucial nature of the interaction between the host’s ring structure and the guest material in influencing electrophosphorescence. This study sheds light on the impact of host-guest interactions and the role of energy transfer within the host material in endowing room temperature phosphorescence in a device.

5:00 PM SB04.11.14

Metal Nanoclusters as an Interfacial Modifier in Organic Solar Cells Yousuf Alishan1,2, Alvin Joseph1, Anitha B1, Aparna R.K.1, Ranjini Sarkar2, Sudip Chakraborty3, Sukhendu Mandal1, and Manoj Nambuothiri1, 1Indian Institute of Science Education and Research Thiruvananthapuram, India; 2Indian Institute of Technology-Madras (IIT Madras), India; 3Harish-Chandra Research Institute (HRI) Allahabad, India

Novel and diverse strategies are constantly under development to boost the efficiency and stability of organic solar cells (OSCs). Interface engineering involving various functional materials is currently a research focus because of its promising potential to enhance the device performance of OSCs. Atomically precise metal nanoclusters, with tunable properties and notable dipole moments resulting from surface ligand interactions that provide stability to the nanoclusters, can be a promising candidate as an interfacial modifier. Copper nanoclusters (Cu NCs), synthesized by a one-pot synthesis method, are shown to exhibit dipole moment and can cause work function modification on a surface. Through this information, the devices are tailored to match the PR of the human skin. The negative PR of the device is achieved by the auxetic structured glass-fabric reinforced substrate with optimized geometric parameters. Also, a soft elastomer with extreme modulus difference with the glass-fabric reinforced film fills the perforations of the auxetic structure to form a continuous surface. The advantage of the proposed methodology, we employ high precision 3D printing technique to fabricate liquid metal-based electrocardiogram (ECG) sensors and electrotactile stimulators with simple configurations. The liquid metal electrodes maintain their conductivity during up to 30% of stretching and 100 times of repeated stretching. The resulting devices exhibit increased sensitivity and stability even under dynamic motion of the wrist thanks to their enhanced adhesion and conformability compared to pristine elastomer substrates. Precisely, the ECG sensors maintain signal to noise ratio of over 20 dB after 30 times of wrist bending, while pristine PDMS-based sensors showed degradation to 13 dB. Moreover, the electrotactile stimulators showed high consistency of perceived sensation for 6 stimulated perception levels, even stable under bending.

References

Effects of Coffee Grounds in Modified Natural Rubber Thin Film on Resistive Switching Memory Characteristics

Research opens new avenues for continuous, real-time monitoring and early disease detection, addressing a critical need in healthcare and paving the way for improved patient outcomes.

For example, a wearable organic piezoelectric electronic patch is being developed to non-invasively monitor breathing parameters. This wearable respirometer offers high accuracy and resolution, making it suitable for diagnosing respiratory and cardiovascular diseases. Our method leverages descriptors extracted from breathing signals captured using a pump-probe experimental configuration. In addition, steady-state thermoreflectance (SSTR) technique is used to compose a map of thermal conductivity as a function of spatial location.

To achieve precise and robust disease predictions, we conducted an extensive examination of various machine learning algorithms. Among these, gradient boosting regression emerged as the most suitable choice for predicting Chronic Obstructive Pulmonary Disease (COPD). Notably, our method achieved an accuracy of over 94% in predicting different COPD diseases. This research opens new avenues for continuous, real-time monitoring and early disease detection, addressing a critical need in healthcare and paving the way for improved patient outcomes.

Metal-Dielectric Photonic Crystal Organic Light Emitting Diodes

A periodic array of stacked microwire organic light emitting diodes (OLEDs) creates a photonic crystal comprising alternating metal and dielectric layers, a metal-dielectric photonic crystal (MDPC). In these MDPC-OLEDs, the semitransparent metal layers serve dual function as both mirrors and either the anode or cathode in the OLED device enabling simultaneous electroluminescence from each unit cell. The angle-resolved electroluminescence spectra of the MDPC-OLED reflects the photonic dispersion of the crystal with rich, energy, momentum, and polarization-dependent behavior depending on the physical geometry of the crystal and the optical properties of the constituent materials. The number of states in the band, the bandwidth, and mid-band Peierls distortion can be controlled by varying the physical dimensions of the crystal through additive manufacturing. Line-widths of the photonic states are reduced by improving the optical symmetry of the unit cell. Crystal defects can be included to introduce mid-gap photonic states. These properties are modeled using a computational transfer matrix simulation and experimentally verified. Lastly, we develop an analytical model based on coupled mode theory and quasi-normal mode theory to determine the relationship between optical constants (index of refraction and extinction coefficient) of the metal and organic layers to the resulting photonic band structure.

Magneto-Electroluminescence Responses mediated by Magneto-Conductance in Thermally Activated Delayed Fluorescence Emitter-Based Light Emitting Diodes

We characterize the magneto-electroluminescence (MEL) responses of polymer and thermally activated delayed fluorescence emitter-based light-emitting diodes (PLEDs and TADF LEDs) under constant voltage and current regimes to elucidate that the current as regulated by magneto-conductance (MC) mediate MEL of devices. Through the analytical fitting of MC and MEL curves, we disclose that MC (as interpreted by the polar pairs model) partially involves the changes in the curve features, magnitudes, shapes, etc. of MEL responses. We observe a sharp W-shape curve feature in the MEL response of the TADF LED under the electric bias at the low magnetic field regime in our study. This result should be attributed to the mediation of the MEL by the negative MC response due to the unbalanced carrier dynamics of the device. While the carrier dynamics were balanced, the specific feature of the sharp W-shape curve disappeared. Our work clearly depicts an accurate analysis of MEL with MC response based on the polaron pairs model for studying the insights of the light-emitting LEDs and that the assessment of MEL is reliable if conduct the measurement at the constant current regime.

Thermal Conductivity Switch due to Topochemical Polymerization of Organic Material

A material that exhibits significant change in thermal conductivity due to external stimuli can be used as a thermal switch and can allow the active control of heat flow. These materials are of high importance in various thermal management applications such as refrigeration and waste heat recovery. Due to their sensitivity to external stimuli, organic materials are considered as a promising class of materials in this regard. This study shows a potential thermal switching mechanism due to topochemical polymerization of [2,2′-bi-H-indene]-1,1′-diol-3,3′-dihydroxy-carboxylate (BIT-Hep). The forward polymerization reaction of BIT-Hep monomer to polymer, P(BIT-Hep), occurs when exposed to light. Since polymerization alters the interchain interactions, breaking and reforming of bonds between repeat units can affect the thermal conductivity.

The thermal conductivities of these samples are measured using time domain thermoreflectance (TDT). TDT is a transient, non-contact, optical thermometry technique that utilizes a pump-probe experimental configuration. In addition, steady-state thermoreflectance (SSTR) technique is used to compose a map of thermal conductivity as a function of spatial coordinate for individual monomer and polymer crystallites. The complementary characterizations of these samples confirms that the topochemical polymerization of BIT-Hep(p) to P(BIT-Hep)(p) changes the bond order which affects the planarity of the repeat unit. Thus, the decrease in thermal conductivity due to this topochemical polymerization is likely due to a greater extent of disorder present in P(BIT-Hep(p)). This study finds that the thermal conductivity within the crystallites differs significantly and reports the average values of 0.478±0.065 W/mK and 0.110±0.060 W/mK for the monomer and polymer, respectively.
Polymer dielectrics hold great potential for power applications and advanced microelectronics. Unfortunately, they exist commonly in semicrystalline form with disordered architectures, which limit their dielectric performances, including breakdown strength, dielectric loss, and temperature stability. Efforts to improve their performances are often hindered by the lack of understanding of the diverse dielectric properties in the complex structures of these semicrystalline polymer dielectrics (SPDs). Circumventing these gaps in knowledge by crystallizing homogenously-ordered SPDs to remove these disorders has yielded little success to date. Here, taking a typical and widely used dielectric, polyethylene (PE) as a model, big homogeneously-ordered SPDs as lamellar single crystals are successfully crystallized and studied for their dielectric properties. We obtain high-quality PE single crystals by controlling the crystallization kinetics in a self-seeding method. Nanoscale MIM capacitors built on these crystals using a non-destructive strategy exhibit a high dielectric breakdown strength and low dielectric constant, with the measured values among the best-known for PE. By exemplifying a crystallization strategy for the ordered SPDs and elucidating the origins of their outstanding dielectric properties, this work illuminates a path for deepening the fundamental understanding and enhancing the electrical performance of SPDs.

### 5:00 PM SB04.11.28

Controlling Rigidity of The Conjugated Backbone Using Plasticizing Molecular Additives to Enhance Deformability in Organic Semiconductors

Seimin Cheung and Kilwon Cho; Pohang University of Science and Technology, Korea (the Republic of Korea)

Plastic electronics, featuring deformable polymer layers, have emerged as a promising technology in recent decades. Researchers have been focusing on enhancing the deformability of polymer films by fine-tuning both the intrinsic molecular structure, such as the conjugation length of the polymer backbone, and the characteristics of functional side chains, including their length, branching points, and hydrogen bonding capabilities. However, it has become evident that chemical tuning alone has its limitations in overcoming the inherent trade-off relationship between electrical performance retention and mechanical deformability. To address this trade-off phenomenon, recent studies have introduced intrinsically aids into conjugated polymers, which encompass elastomeric polymers, crosslinkers, dopants, and various molecular additives. This research explores the impact of the chemical structures of plasticizing molecular additives (PMAs) on the mechanical, thermal, and electrical properties of films containing PMAs under deformation. For the purpose of a comprehensive comparison, our study employs a solution-based rheology and small-angle neutron scattering (SANS) technique to elucidate the adjusted persistence length of conjugated polymer, Poly[2,5-(2-octyldecyloxy)-3,6-diketopropyrrole-alt-5,5-(2,5-dihiten-2-yl)thiene-[3,2-b]-thiophene] (PDDPTTT-TT-OD) interacting with various species of PMAs. Our findings reveal a significant influence of the modified persistent length of PDDPTTT-TT-OD on the thin films’ mechanical deformability, as determined through pseudo-free standing tensile testing. Based on our systematic analyses, we propose that the uniform distribution of PMAs within a conjugated polymer substantially enhances the deformability of thin films. These results are anticipated to offer valuable insights into the establishment of design principles for plasticizing molecular additives in the realm of plastic electronics.

### 5:00 PM SB04.11.29

Improving The Performance of Organic Photodetectors with Removable Ultrathin Top Electrodes

Kosei Sasaki, Takao Someya and Tomoyuki Yokota; The University of Tokyo, Japan

Recently, Organic photodetectors (OPD) with removable top electrode have attracted much attention for systematic analysis of the degradation of the device. This new structure of OPD consist of a bottom and top electrode sheets. The bottom electrode sheet was fabricated by forming a transparent electrode, electrode transport layer (ETL) and active layer on a glass or flexible substrate. The top electrode sheet contains an electrode and hole transport layer (HTL) on another substrate. The top electrode sheet can be attached to the bottom electrode sheet by intermolecular forces. The top electrode sheet can be easily removed from the bottom electrode sheet without damaging the organic semiconductor layer. Using this structure, our group has succeeded in directly and continuously evaluating the electrical properties of the OPD and the crystallinity and chemical analysis of the interface between active layer and HTL before and after operating the device by removing the top electrode sheet.[1] In previous report, the thickness of the top electrode sheet is 1 mm. This thicker substrate shows the weak adhesion between the active layer and HTL.[2] So, the device cannot be operated as an OPD without applying pressure. However, continuous pressure distorts the active layer and accelerate the degradation and possibly change the crystallinity.[2] Therefore, it is important to develop OPD with removable top electrode that can be operated without applying any pressure. In this study, we developed OPD with removable top electrode that can be operated without pressure by using an ultrathin rubber sheet as a substrate of top electrode. The ultrathin rubber sheet is an extremely tough, self-adhesive and gas-permeable polydimethylsiloxane (PDMS) nanofilm with a thickness of approximately 700 nm, fabricated by dip coating a thin polyurethane nanofiber sheet with PDMS.[3] The fabricated OPD shows 67% EQE at 550 nm and ~5 V (light intensity is 6.7 * 10^-3 mW/cm²) without applying pressure. The specific detectability of OPD is as high as 2.9 * 10^13 Jones. The photocurrent and dark current at -2 V were changed 42.9% and 117%, respectively after 100 cycles of lamination and delamination the top electrode sheet.

### 5:00 PM SB04.11.30

Efficient Electron Injection and Transport in Fully Stretchable OLEDs

Wei Lin and Shihong Wang; The University of Chicago, United States

Fully stretchable electroluminescent devices have gained significant research attention due to their transformative potential in applications ranging from wearable displays to implantable light sources. Among the various approaches, OLEDs based on the thermally activated delayed fluorescence (TADF) mechanism hold much allure because of their unity internal quantum efficiency and environmental-bio-compatibility. However, the performance, based on the identical emitter, in stretchable OLEDs falls significantly short of that achieved in traditional rigid devices due to feeble n-type materials available for efficient electron injection and transport. Here we propose innovative solutions to bridge this efficiency gap. First, we develop a stretchable electron transport polymer that simultaneously achieves decent electron mobility, suitable HOMO/LUMO levels, high triplet state, good solution processability, and high stretchability. Secondly, we propose a stretchable cathode design with an extremely low work function that is on par with the conventional rigid cathode, which is unprecedented with previously stretchable cathode based on silver nanowires, carbon nanotubes, conducting polymers, and others. Based on those innovations, we remarkably narrow the efficiency gap and eliminate the turn-on voltage differential between the fully stretchable TADF-OLEDs and their rigid counterparts.

### 5:00 PM SB04.11.31

Accessing New Optoelectronic Devices and Architectures through The Solid-Phase Processing of Conjugated Polymers

Guillermo Esparriza, Darren J. Lipomi and David Fenning; University of California, San Diego, United States

Optoelectronic materials and devices are ubiquitous in the modern world. Thin-film processing of these materials is essential in a tremendous range of applications such as consumer electronics, healthcare, defense, scientific instrumentation, and renewable power generation and storage to name a few. Among optoelectronic materials, conjugated polymers are of significant technological interest and are typically processed from either the vapor, liquid, or solution phases. Unfortunately, all of these techniques come with various downsides and limitations. Processing restrictions (such as solvent orthogonalitiy) or device architectures (such as wetted surfaces) impose potential processing incompatibilities and therefore limits on the devices which may be realized. For this reason, exploring novel processing routes is pivotal to unlocking the full potential any material.

Processing and application of thin films directly from the solid phase (that is, the creation of standalone thin films which are subsequently transferred onto a substrate or undergo other processing) has not been well explored, but has the potential of addressing various pitfalls that arise in conventional processing methods. This talk will be focused several techniques in this category, which have utilized pre-formed thin-films to form coatings on non-planar surfaces, coat sensitive substrates without exposure to heat or liquid solvents, as well as serve as a sacrificial vehicle in preimpregnated coats which would otherwise damage the rest of a device stack. Special emphasis will be given to how these approaches can outperform conventional processing methods as well as how they can be leveraged to enable devices which may have been previously impossible to realize.

### 5:00 PM SB04.11.32

Continuous Production of Ultratough Semicrystallizing Crosslinking Polymer Fibers with High Electronic Performance

Zhi Zhang and Ting Lei; Peking University, China

Conjugated polymers have demonstrated promising optoelectronic properties, but their brittleness and poor mechanical characteristics have hindered their fabrication into durable fibers and textiles. Here, we report a universal approach to continuously producing highly strong, ultratough conjugated polymer fibers utilizing a flow-enhanced crystallization (FLEX) method. These fibers exhibit an order of magnitude higher tensile strength (~200 MPa) and toughness (~80 MJ m⁻³) than traditional semicrystallizing polymer fibers and films, outperforming many synthetic
fibers, ready for scalable production. These fibers also exhibit unique strain-enhanced electronic properties and exceptional performance when employed as stretchable conductors, thermoelectrics, transistors, and sensors. This work not only highlights the influence of fluid mechanical effects on the crystallization and mechanical properties of conjugated polymers but also opens up exciting possibilities for integrating these functional fibers into wearable electronics.

5:00 PM SB04.11.35
Improved Thermally Activated Delayed Fluorescence Devices using Vacuum Processed Carbazole based Self-Assembled Monolayer Niraj Gaur, Manas Misra, Kashish Hossain and Dinesh Kabra; Indian Institute of Technology Bombay, India

Engineering of the interface between organic emissive layer thin films and charge transport layers has fuelled the development of Organic light emitting diodes (OLEDs) over the past decade. This paper shows a comparative study between conventional poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT: PSS) vs carbazole functional groups based self-assembled monolayer (SAM) as hole-injection layer (HIL). SAM enables an improved interface to achieve the charge carrier balance and reduced interfacial recombination to enhance the external quantum efficiency in the p-i-n OLEDs. An industry compatible vacuum processed SAM-HILs ((4,4-Dimethyl-9H-carbazol-9-yl)-butyl) phosphonic acid (Me-4PACz) as a hole transport layer in thermally activated delayed fluorescence (TADF) based OLEDs is reported for first time, which facilitate to overcome the issues of poor device stability. Deeper highest occupied molecular orbital (HOMO) (~ -5.3 eV) of Me-4PACz enables the efficient hole injection with reduction in leakage current by 1 to 2 orders of magnitude compared to PEDOT: PSS (HOMO (~ -5.0 eV)) HIL based OLEDs. Also, built in potential is 1.3 times reduced to 2.45 V for Me-4PACz based OLEDs. With the further optimized thickness of Me-4PACz (d= 6 nm), OLED maximum external quantum efficiency (EQE) gets enhanced from 18.30 % to 20.79 % with luminous efficiency 62.79 cd/A. Further, the Me-4PACz is also investigated on the basis of its -5.00 eV) HIL based OLEDs. Also, we incorporated SAM-HTLs to complete OLED demonstrates comparable efficiency to their solution-processed counterparts. Furthermore, vacuum deposition SAM as HIL based OLEDs is found to provide a five-fold enhancement in the operational stability 60% ($LT_{60}$) of the initial luminance $L_0$ of the OLED in comparison to PEDOT: PSS as HIL based OLED. This study is further extended to a blue TADF OLED, with almost similar finding.

5:00 PM SB04.11.36
Development of Next-Generation OPLS Force Field for Accurate Modeling of Phosphorescent OLED Materials Steven Dajnowicz, Edwin Madin, Hadi Abrosahen, Shaun Kwak, Mathew D. Halls and Edward Harder; Schrodinger, United States

To address the inherent challenges of modeling organometallic complexes, which are commonly used as phosphorescent emitters in OLEDs, the OPLS4 force field is extended in order to achieve a more suitable formal function. These new developments include a fluctuating charge model to describe charge transfer, a Morse potential to describe the metal-ligand bonding, and an angular overlap model to describe d-orbital effects. The initial force field coverage is centered around common chemistries found in Pt(II) and Ir(III)-based emitters. Our model accurately represents geometries when comparing against DFT and crystal structure references. In addition, the model was validated on a series of organometallic emitters doped into an organic host layer, generating configurations from molecular dynamics simulations that are used to predict photoelectronic properties. Future developments include the extension of chemical coverage in the effort to more broadly aid in material design.

5:00 PM SB04.11.38
Interactions in GO/P3HT Layered Nanostructures: Spectroscopic Investigation for Organic Solar Cells Fokotsa V. Molefe1, Bakang M. Mothudi2, Mokhotjwa S. Dhlamin2 and Mmanetsae M. Dialet;1 University of Pretoria, South Africa; 2University of South Africa, South Africa

Herein, a simple and effective approach has been followed to probe deposit poly (3-hexylthiophene) (P3HT) and GO/P3HT layered nanostructures and fabricate their devices. Different structural, morphological, spectroscopic, and electrical techniques were used to probe P3HT and GO/P3HT layered nanostructures properties. The X-ray diffraction (XRD) spectrum of GO/P3HT revealed a highly crystalline reflection of GO which is slightly shifted to higher diffraction angles as evidence of interaction with P3HT. As a proof of concept of interactions, the smooth surface morphology of P3HT translated to wrinkled structure for GO/P3HT presenting the existence of GO sheets in scanning electron microscopy (SEM). Fourier Transform Infrared spectroscopy (FTIR) confirmed the alteration of P3HT structure upon interaction with GO where the average conjugation length decreased from ~1.20 to ~1.12. The UV/VIS/NIR spectrum of GO/P3HT has an observable decrease in percentage reflectance leading to enhancement of the light absorption ability of P3HT with the inclusion of GO nanostructures. Furthermore, the bandgap energy decreased and resulted in decrease in energetic driving force. The fluorescent decay curves revealed a decrease in excited diffusion length. Our findings suggest that the energetic driving force induced the mechanism involved during chemical interaction at the GO/P3HT interface. However, the calculated energetic driving force suggests that the interface between GO/P3HT should be tuned, which agrees with J-V results where the GO/P3HT device revealed a low power conversion efficiency (PCE) of 3.07 %.

5:00 PM SB04.11.39
Pentacene Two-Dimensional Crystals with Layer-Derived Morphologies and Mobilities Grown via Confined Molecular Flow Deposition Zhichao Cheng and Xiaomin Xu; Tsinghua University, China

Pentacene has gained significant attention as a material component in organic field-effect transistors (OFETs). In most cases, the mobility, a key performance metric of the device, is evaluated for the entire film. However, there is limited understanding of its layer-dependent electric transport properties in the two-dimensional (2D) limit, particularly when compared to inorganic 2D materials that have been more thoroughly investigated. Furthermore, in OFETs, the growth of molecules is especially crucial at the initial stage, as the electrical conduction predominantly occurs in the few molecular layers adjacent to the dielectric surface. Herein, we successfully grew pentacene 2D crystals with 1, 2, and 3 molecular layers on thermally oxidized wafer surfaces using the confined molecular flow deposition method, under conditions of both high deposition rates and elevated substrate temperatures. The electric transport properties of these crystals were measured, and the results aligned well with the theoretical calculations. In addition, the growth mode of these pentacene 2D crystals differs from the classical models: layer-by-layer, layer-plus-island, and island growth modes. This deviation arises because the nucleation of pentacene under these conditions does not follow the classical nucleation process. Instead, it develops through two distinct steps. Initially, pentacene molecules nucleate as liquid clusters with the molecules adopting a lying-down orientation. Subsequently, these liquid nuclei transition to a solid crystalline state, where the molecules flip upright. The final number of molecular layers in the pentacene 2D crystals corresponds to the layer number in their solid nucleus, with each layer within the crystal growing synchronously. Additionally, the crystals with different numbers of layers exhibit distinct shapes: ellipses, rounded hexagons, and hexagons for one, two, and three layers, respectively. This phenomenon can be explained by phase field modeling. We believe our work not only verifies the electric transport properties of 2D pentacene crystals with different molecular layers, but also may pave the way for exploring new physics using small molecules.

5:00 PM SB04.11.40
Record-High Surface Potential by Spontaneous Orientation Polarization in Organic Semiconductors Albin Cakaj, Alexander Hofmann and Wolfgang Bruetting; University of Augsburg, Germany

Molecular orientation in organic semiconductors has many different facets, such as optical anisotropy leading to birefringence, alignment of their optical transition dipole moments (TDMs) and/or their permanent electrical dipole moments (PDMs) [1]. While TDM alignment is well established and readily exploited to improve light coupling in organic light-emitting diodes (OLEDs) [2], PDM alignment and the resultant spontaneous orientation polarization (SOP) is by far less investigated, and it is not fully clear yet if it is beneficial or detrimental for device application [3]. SOP is observed in evaporated films of polar organic molecules and leads to a so-called giant surface potential (GSP), which can be measured by Kelvin probe, impedance spectroscopy or the displacement current method [4]. In general, the GSP slope is roughly proportional to the magnitude of the molecule’s PDM. However, despite their very high PDM, many molecules exhibit only small SOP because they tend to aggregate in pairs with antiparallel alignment. Thus, the order parameter (i.e., the degree of net PDM alignment) is typically less than 10%. Here we report a new class of materials with drastically enhanced PDM alignment, exceeding 30% for films grown at room temperature [5]. These phosphate oxides exhibit a highly polar phosphoxygen bond, which leads to large SOP despite the presence of different structural conformers. By evaporating them on a cooled substrate in combination with dilution of the polar species in a non-polar host, record-high GSP slope of almost 300 mV/nm (with an equivalent electric field of 3x10^8 V/m) can be achieved. This opens new perspectives for application of organic semiconductors in energy harvesting devices.


5:00 PM SB04.11.41
Color Tunable Stacked QD-OLED Hybrid Devices Sung-Cheon Kang, Eun-young Choi and Jang-Kun Song; Sungkyunkwan University, Korea (the Republic of)
Organic light-emitting diodes (OLEDs) and quantum dot light-emitting diodes (QLEDs) stand out as highly promising display technologies due to their notable advantages, including high efficiency, rapid response speed, and a high contrast ratio. Typically, flat panel displays incorporate distinct red, green, and blue subpixels placed side-by-side to replicate a full spectrum of colors. However, this design exhibits drawbacks such as a low geometric fill factor, reduced efficiency, and challenges in fabricating high-resolution displays. A potential solution to address these limitations lies in a multicolor-emitting pixel structure, enabling the selective emission of more than two colors from a single pixel. AC-driven color-tunable devices present a promising avenue to achieve this goal. In an AC tandem device, the emitted light's color is determined by the applied signal's polarity, resulting in different colors emitted under forward and reverse bias voltages. In this presentation, we introduce AC-driven multi-color OLED-QLED hybrid pixel structures. The foundational unit comprises two-pixel QLEDs, fabricated using an inkjet process, with an OLED layer deposited atop these QLEDs. Through the combination of these three pixels, a full-color display is achieved. Efficiency optimization is achieved by fine-tuning the materials and structure within the charge transport and charge generation layers. This device configuration features two horizontally arranged pixels and another vertically stacked pixel, enhancing the fill factor by 1.5 times. As a result, this approach holds promise for future display applications, offering high efficiency and flexibility.

9:00 AM SB04.12.02 Stable and High Performing n-Type and Ambipolar Organic Electrochemical Transistor for Next-Generation Bioelectronics Wei Lin Leong, Nanyang Technological University, Singapore

Organic mixed-ionic-electronic conductors (OMIECs), which are capable of efficiently transporting and coupling ionic and electronic charge, have gained significant attention in recent years as emerging organic materials suitable for bioelectronic, neuroimplantable, and energy storage systems. One emerging device that uses these OMIECs is the organic electrochemical transistor (OECT), which offers the advantages of low operation voltage (<1 V), high sensitivity, and excellent aqueous operating capability. To date, OECTs have predominantly been p-type devices, with their n-type counterparts lagging behind in performance and stability, hampering their adoption in complementary circuit designs, electrochemical energy storage, and sophisticated bioanalytical sensing. A potential solution to address this is the development of a transducer that can enable high-performance, high-throughput, and reliable operation in aqueous environments. In this talk, we will present our recent progress on developing a new class of OECTs with enhanced performance and stability. These devices demonstrate high sensitivity, fast response, and reliable operation in aqueous environments, making them suitable for a wide range of applications in bioelectronics, neural prosthetics, and energy storage.

9:30 AM SB04.12.03 Electroluminescent Quantum Dot Light-Emitting Diodes Integrated in Solid-State Organic Electrochemical Transistors for Monitoring Neurological Activity Deniz Zou, 1, 2, and Paddy K. L. Chan 1, 2, University of Hong Kong, Hong Kong; 1 Advanced Biomedical Centre Limited, Hong Kong

Electroluminescent quantum dot light-emitting diodes (EQLDs) have emerged as promising candidates for detecting neurophysiological activity due to their efficient light emission and rapid response times. These devices are suitable for both in vivo and in vitro applications, enabling non-invasive monitoring of brain activity. In this talk, we will present our recent progress on developing high-performance EQLD-based devices for monitoring neurological activity. We will discuss the design and fabrication of EQLDs with enhanced performance, enabling high-speed and high-resolution monitoring of neural activity. These devices demonstrate excellent electrochemical stability, long-term operation, and low power consumption, making them ideal for real-time monitoring of brain activity in both laboratory and clinical settings.


Alzheimer's disease is a progressive form of dementia, which affects more than 50 million people worldwide and is expected to impact three times more by 2050. Although its cause and progression mechanisms are still not fully understood, Alzheimer's disease is associated with the misregulation of certain biomarkers. The quantification of these biomarkers requires expensive equipment, substantial expertise, and time-consuming analysis due to their low concentrations in blood. A much faster, cost-effective, and more convenient in-vitro method with very high sensitivity and specificity is needed to advance Alzheimer's research and diagnostics.

SESSION SB04.12: Bioelectronics
Session Chairs: Lucas Flagg, Katelyn Goetz, Ulrike Kraft and Simon Rondeau-Gagne
Friday Morning, April 26, 2024
Room 435, Level 4, Summit
Organic electrochemical transistors (OECTs) have emerged as a promising point-of-care testing platform for enzymatic biosensing due to their exceptional signal amplification properties, stability in aqueous environments, and biocompatibility. 1,2 However, due to their high sensitivity, OECTs are susceptible to signal drifts caused by changes in the surrounding environment, such as variations in pH levels, temperature fluctuations, and the presence of interfering species in the sample of interest. In this work we present a new OECT configuration design to achieve real-time on-device calibration. This configuration is designed to effectively compensate for signal drifts and faulty analyte detection, thereby ensuring stability and reliable results.

Three-terminal OECTs have been designed and microfabricated with a poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) channel. This ion permeable channel is extremely sensitive to biochemical reactions occurring in the electrolyte placed directly on top of the device for testing. 2 The design of the device incorporates two gates, and it has been optimised to create highly sensitive enzymatic sensors. 3 An enzyme is immobilised via bioconjugation on the first gate electrode, while the second gate electrode acts as a reference. The system is tested in real-time by addition of varying concentrations of the target compound in the electrolyte, while the changes in current are recorded. This test allowed the on-device calibration of our OECTs, enabling the reliable measurement of the compound with high sensitivity and specificity. This is a new promising platform for achieving stability against signal drifts in the OECTs and robustness against interfering analytes in enzymatic sensors, outlining the pathway to very high sensitivity and low limit of detection of brain biomarkers.


10:00 AM BREAK

10:30 AM #SB04.12.05
Retinomotoric Motion Sensors and Integrated Energy Storage Systems Based on Donor-Acceptor Polymers

Tse Nga Ng
University of California, San Diego, United States

Organic retinomorphic sensors offer the advantage of in-sensor processing to filter out redundant static background and are well suited for motion detection. To improve this promising photodetector, here we studied the key role of interfacial energetics in promoting charge accumulation to raise the inherent photoreponse of the light-sensitive capacitor. Specifically, incorporating appropriate interfacial layers around the photovoltaic layer was crucial to extend the carrier lifetime, as confirmed by intensity-modulated photovoltage spectroscopy. Compared to its photodiode counterpart, the retinomorphic sensor showed better detectivity and response speed due to the additional insulating layer, which reduced the dark current and the RC time constant. Lastly, three retinomorphic sensors were integrated into a line array to demonstrate the detection of movement speed and direction, showing the potential of retinomorphic designs for efficient motion tracking.

In addition to enabling motion detector, the class of donor-acceptor polymers showed highly delocalized redox states and operated as stable n-type anodes in energy storage devices. The redox polymer was used in supercapacitors and achieved a high areal power density of 227 mW/cm², allowing rapid charging and high power delivery. The capacitance retention was 84% after 11,000 full redox cycles, offering the critical benefit of long cycle life. This work demonstrated the application of a new class of stable redox-active materials suitable to meet the energy storage needs for short-range wireless electronics.

11:00 AM SB04.12.06
Organic Electronic Platform for Enhancing Plant Growth

Eleni Stavrinidou
Linköping University, Sweden

To cover the food demands of the growing population in the changing climate we need to increase crop yield in a sustainable manner. Hydroponics cultivation minimizes water and fertilizers use while it can be integrated in the urban environment. However so far, the substrates used in hydroponics mainly offer support to the root system. Here we developed an active, organic electronic platform that stimulates the growth of plants in hydroponics culture. We demonstrate that Barley, one of the most important crops, grows well within the bioelectronic platform. When stimulated, the biomass of the Barley increases by 40%, and the effect is evident in both root and leaf development during the growth period after the stimulation treatment. Results also show that stimulated plants reduce and assimilate NO3 more efficiently than controls, a finding that can have implications on minimizing fertilizers use. Our work opens the pathway for enhancing plant growth in hydroponics settings using organic electronics that may result in more sustainable food production.

11:15 AM SB04.12.07
Spontaneous Recording of Cardiomyocytes’ Action Potential by Electrolyte-Gated Field Effect Transistors: A Simple, Planar, Printed In-Vitro Platform for Cardiovascular Drugs Screening

Giulia Z. Zemignani1,2, Adrica Kyndiah1, Luca Sala2, Aleksandr Khudiakov3, Carlotta Ronch1, Gabriele Tullii1, Giuseppina Iachetta4, Rosalia Moreddu4, Stefano Chioldini1, Francesco De Angeli4, Maria Rosa Antognazza1 and Mario Cairoi1
1Center for Nano Science and Technology, Istituto Italiano di Tecnologia, Italy; 2Politecnico di Milano, Italy; 3Center for Cardio Arhythmias of Genetic Origin, Laboratory of Cardiovascular Genetics, IRCCS Istituto Auxologico Italiano, Italy; 4Institute Italiano di Tecnologia, Italy

In the context of cell-based biosensors, extensive endeavours have been dedicated to find accurate, in-vitro bioelectronic platforms capable of directly recording the electrical activity of electrogenic cells, namely neurons and cardiac cells, in a non-invasive way.

The amplitude, shape and duration of the Action Potentials (APs) contain significant information on the viability of cells. These attributes, in turn, facilitate the exploration of cardiac pathologies and the impact of novel pharmaceutical products.

To date, the available methodologies used to assess APs predominantly involve patch clamp techniques or complex 3D nanostructured electrodes, frequently combined with electro-opto- poration, thereby rendering them very invasive in nature.

To this end, the principal objective of this study is to propose a simple and cost-effective device able to record the electrical activity of in-vitro cell cultures in a non-detrimental manner.

Within this research, we have accomplished for the first time the spontaneous recording of intracellular action potentials of human induced pluripotent stem cells-derived cardiomyocytes (hiPSC-CMs) by fabricating plating or seeding of cells on top of the channel of our printed, planar Electrolyte-Gated Field Effect Transistor (EGFET). The EGFETs were fabricated employing carbon-based semiconductors via a simple and cost-efficient printing technique, aiming to facilitate large-scale production.

The cardiac cells APs were obtained by simply recording the transistor current at a fixed gate voltage $V_{GS}$ corresponding to the maximum transconductance. The natural APs of cardiomyocytes are able to change the effective gate voltage applied, which is transduced in a modulation of the source-to-drain current $I_{DS}$ in our device. Remarkably, this modulation occurs without the need of any external stimulus.

Our planar architecture was able to record signals with shape and duration comparable with patch clamp performed on the same batch of cells, confirming the fact that we recorded a major fraction of the intracellular action potentials (estimation in the range of 40-60 mV).

The exceptional sensitivity of our device made it possible to detect the APs perturbations induced by the addition of different drugs targeting specific ion channels. The Action Potential Durations (APDs) recorded in our device exhibit close congruence with those attained with patch clamp techniques, thus positioning our platform as an ideal candidate for long-term monitoring of cardiac arrhythmias, chronic disease and the screening of cardiovascular drugs.

The optimal EGFET-cell coupling enabled by our planar, close printed, carbon-based semiconductors, reveals high stability and quality of the signal transduced, achieving excellent reproducibility over more than a hundred tested transistors. Such an high-throughput device is opening the path to deeper comprehension of fundamental transduction mechanisms at the bio-electronic interface and possesses the potential to be further developed into a future cost-effective diagnostic tool.

11:30 AM SB04.12.08
Design of Injectable, Self-Adhesive and Highly-Stable Conductive Polymer Electrode for Sleep Recording

Hailian Wang1
The University of Texas at Austin, United States

High-quality and continuous EEG monitoring is desirable for sleep research, sleep monitoring and the evaluation and treatment of sleep disorders. Existing continuous EEG monitoring technologies suffer from fragile hydrogel electrode for long-term EEG applications. Specifically, our electrodes have a long-term low impedance on hairy scalp regions of 17.53 kΩ.

To this end, the principal objective of this study is to propose a simple and cost-effective device able to record the electrical activity of in-vitro cell cultures in a non-detrimental manner.

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11:45 AM SB04.12.09
Selective Response of Organic Electrochemical Transistor by a Potentiodynamic Approach

Isseuco Guandalin1, Federica Mariani1, Luca Salvigni2, Francesca Cescardi1, Danilo Arcangeli1,
Organic electrochemical transistors (OECTs) are finding growing interest in the field of biological and chemical sensing. Although the OECT transduction is based on electrochemical reactions, the transistor architecture offers several advantages as compared to amperometric sensors such as signal amplification, use of easy and cheap readout electronics, low supply voltage (usually \(< 1\) V), low power operation (\(< 100\) \(\mu\)W), bio-compatibility. Moreover, OECTs can be easily miniaturized and adapted to non-flat, flexible and even textile devices [1]. Since electrochemical transduction usually detects all redox-active compounds in a sample, selectivity remains an open issue that should be addressed to achieve a reliable measure. Our group has developed a potentiodynamic approach for the selective detection of dopamine (DA) in the presence of interfering compounds (ascorbic acid, AA, and uric acid, UA) [2]. The trans-conductance curves allow linear calibration plots for AA, UA and DA and to separate the redox waves associated with each compound with performances comparable or even better than those obtained by differential pulse voltammetry. This contribution describes the recent achievements of OECT sensors, based on the potentiodynamic approach, to the design of robust and selective devices able to perform real-time analyses that do not strictly rely on laboratory facilities. The detection of the fat-soluble Vitamin A has been carried out in organic environment [3]. The OECT behaviour was thoroughly characterized, its structure was optimised and both potentiostatic and potentiodynamic detections were investigated. The potentiostatic determination exhibited a gain of 100 with respect to the electrochemical signal represented by Vitamin A oxidation current and the limit of detection was as low as \(115\) nM, but it did not address selectivity issues. On the other hand, the potentiodynamic approach showed a higher detection limit, but the sensor displayed selectivity in the presence of \(\alpha\)-Tocopherol. Excellent performances were found when analyzing commercial food fortifiers and a multivitamin premix powder, encouraging results to these bioelectronic devices beyond the watery part of life and biology, where they have already proved to provide uniquely performing electrochemical interfaces. Finally, ongoing research deals with potentiodynamic determination of uric acid in saliva with the aim to estimate oxidative stress.

REFERENCES


SYMPOSIUM SB05

Materials and Systems for Fully Implantable Organ Interfaces
April 22 - May 9, 2024

Symposium Organizers
Eric Glowacki, Central European Institute of Technology
Philipp Gutruf, University of Arizona
John Ho, National University of Singapore
Flavia Vitale, University of Pennsylvania

Symposium Support
Bronze
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* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION SB05.01: Neural Interface Technology
Session Chairs: Philipp Gutruf and John Ho
Monday Afternoon, April 22, 2024
Room 434, Level 4, Summit

3:00 PM *SB05.01.01
Fiber-Based Tools to Probe Brain-Body Physiology Polina Anikeeva, Massachusetts Institute of Technology, United States

Complex interplay between the brain and the other body system governs our behavior, immunity, and disease progression. Yet, probing of the brain-body circuits is challenging, as peripheral nerves and organs are in continuous motion and are subject to stringent immunosurveillance. Our group applies fiber-fabrication methods in combination with traditional solid-state electronics to create multifunctional wireless interfaces with peripheral organs such as the gastrointestinal tract to probe physiological functions with cell-type and regional specificity. Concomitantly, we create fibers to interface with multiple brain regions, and develop materials-based approaches to enable straightforward surgical placement of multi-regional neural interfaces spanning multiple organs.

3:30 PM SB05.01.02
Magnetic Guidewires Driven Deployable Electronics for Minimal Invasive Epidural Electroocorticographic Brain-Computer Interface Tao Zou1,2, Na Xiao1,2 and Paddy K. L. Chan1,2;
1University of Hong Kong, Hong Kong; 2Advanced Biomedical Instrumentation Centre Limited, Hong Kong

Electroocorticographic Brain-Computer Interface (ECoG-BCI) has significantly contributed to both fundamental neuroscience research and clinical applications, including brain function recovery, speech neuroprostheses, epilepsy detection, and traumatic brain injury prognosis. Improving the recording coverage and density of ECoG-BCI are particularly valuable for analysing the activities correlations among the multiple brain regions and identifying the actual neural disease foci accurately. Traditionally, the deployment of large-area coverage devices commonly
necessitates an equally substantial cranial opening, which expose significant brain tissue and could potentially cause brain tissue swelling, inflammation, heighten risk of cortical damage, and infection. As a result, diminishing the acceptance of these implants among BCI users.

Here we present a deployable ECoG-BCI platform operated via magnetically controlled guidewires in minimally invasive approach. The ECoG-BCI platform comprises a high-density array of flexible PEDOT:PSS/pHEMA electrodes (28.4 electrodes cm\(^{-2}\)) covering a large surface area (9 cm\(^2\)), sub-millimeter soft magnetic polymer guidewires, a robotic arm equipped with a permanent magnet for guiding the magnetic guidewire, and an automatic control system. The folded flexible electrode array can traverse the craniootomy and be unfurled by tracking the guidewires. The thin, 10 μm thick polymer based electrode array, featuring perfusion holes, ensures excellent conformability and close contact with the curved brain surface. We deploy the proposed ECoG-BCI platform within area V1 of the visual cortex in a macaca fasicularis, demonstrating chronic neural signal recording and cortical electrical stimulation capabilities. The monkey has responses to the phosphenes induced by the visual cortex stimulation. This deployable ECoG-BCI platform has the potential to restore effective vision for the blind with minimal invasive implantation injury.

3:45 PM *SB05.01.03
Miniature Battery-Free Implants for Distributed Bioelectronic Networks Jacob T. Robinson; Rice University, United States

Direct neural and cardiac stimulation is a powerful method to treat disorders when drug therapies are ineffective, or their side effects are intolerable. Unfortunately, traditional implantable stimulation technologies are based on wires that connect the stimulator to the target, which can lead to challenges for writing the wires, lead fractures, migration, and infection. This is particularly true when attempting to interact with a network of devices.

Here, we describe how magnetoelectric materials enable construction of distributed network interfaces with each node the size of a pea or smaller and capable of digitally programmable stimulation. With robust wireless data and power transfer it is possible to make miniature implants less than 1 cm across with the ability to deliver biphasic stimulation powerful enough to drive neural activity from above the dura. As an example, we show applications in brain and cardiac stimulation neuromodulation where minimally invasive devices can form a network of precisely timed stimulators. Our data from large animal and human studies show the kind of good misalignment tolerance and high-power bioelectronics capabilities that would enable networks of wireless, battery-free, neuromodulation technologies.

4:15 PM *SB05.01.04
Soft and Flexible Bioelectronics for Brain-Machine Interfaces Ha Lin; Harvard University, United States

Large-scale brain mapping through brain-machine interfaces is important for deciphering neuron dynamics, addressing neurological disorders, and developing advanced neuroprosthetics. Ultimately, brain mapping aims to simultaneously record activities from millions, if not billions, of neurons with single-cell resolution, millisecond temporal resolution and cell-type specificity, across three-dimensional (3D) brain tissues over the course of brain development, learning, and aging. In this talk, I will first introduce flexible and soft bioelectronics with tissue-like properties that can track electrical activity from the same neurons in the brain of behaving animals over their entire adult life. Specifically, I will discuss the fundamental limitations of the electrochemical stability of soft electronic materials in bioelectronics and present our strategies to overcome these limitations, enabling a scalable platform for large-scale, long-term, stable brain mapping.

Then, I will discuss the creation of “cyborg organisms”, achieved by embedding stretchable mesh-like electrode arrays in 2D sheets of stem/progenitor cells and reconfiguring them through 2D- to 3D-organogenesis, which enables continuous 3D electrophysiology during the development of human stem cell-derived brain organoids and animal embryonic brains. Next, I will highlight our current efforts that merge 3D single-cell spatial transcriptomics, machine learning, and electrical recording, enabling cell-type-specific brain activity mapping. In conclusion, I will envision the fusion of soft and flexible electronics, spatial transcriptomics, and AI for a comprehensive brain cell functional atlas to enhance future brain-machine interface applications.

4:45 PM *SB05.01.05
Soft Implantable Bioelectronics for Heart Disease Dae-Hyeong Kim1,2; 1Institute for Basic Science, Korea (the Republic of); 2Seoul National University, Korea (the Republic of)

Recent advances in soft electronics have attracted great attention due to large to its potential applications in personalized bio-integrated healthcare devices. The mechanical mismatch between conventional electronic devices and soft human tissues/organs oftentimes causes various challenges, such as the low signal-to-noise ratio of the biosensors, inflammations and/or excessive immune responses near the implanted devices, and unsatisfactory electrical/chemical stimulations in feedback therapies. Therefore, the ultra-flexible, stretchable, and bioresorbable electronic devices have been developed and applied, since their mechanical and material properties are compatible with the in-vivo environment and thus they have a high potential to solve the aforementioned issues. To develop such bioelectronic devices, nanomaterials, their composites, and biodegradable materials have been researched. In this talk, the unconventional electronic material and device strategies and their applications to the treatment of heart diseases are presented. The integration of wireless technologies with the unconventional bioelectronics could provide additional opportunities, and the related results of the wireless bioelectronics are also briefly introduced. These efforts in the development of various unconventional materials and bioelectronic devices are expected to contribute to addressing many unsolved issues in clinical medicine.

SESSION SB05.02: Cardiovascular Biointerfaces
Session Chairs: Philipp Gutruf and John Ho
Tuesday Morning, April 23, 2024
Room 434, Level 4, Summit

10:30 AM SB05.02.01
Rubbery Bioelectronic Patch for The Heart Cunjiang Yu; The Pennsylvania State University, United States

Electronics that can seamlessly integrate with human body could have significant impact in medical diagnostic, therapeutics. However, seamless integration is a grand challenge because of the distinct nature between electronics and human body. Conventional electronics are rigid and planar, made out of rigid materials. Human body are soft, deformable and curvilinear, comprised of biological materials, organs and tissues. This talk will introduce our solution to address the challenge through the recent development of a new class of electronics, namely rubbery electronics. Rubbery electronics is constructed all based on elastic rubber electronic materials of semiconductors, conductors and dielectrics, which possesses tissue-like softness and mechanical stretchability to allow seamless integration with soft deformable tissues and organs. Rubbery electronic materials (semiconductors, conductors, dielectrics) and device innovations set the foundation. This presentation will describe the development the recent advances of rubbery electronics and rubbery bioelectronics. As a platform technology, rubbery electronics could address many challenges in biomedical research and clinical studies.

10:45 AM SB05.02.02
Effects of Leaflet Design on Structural Integrity and Pump Efficiency of Heart Valves Yu-En Yu1, Lilian Lin1, Ching-Chang Huang2 and Hao-Ming Hsiao1; 1National Taiwan University, Taiwan; 2National Taiwan University Hospital, Taiwan

Heart valve disease results in inadequate blood supply from the heart to the body and could cause many complications, including heart attack, stroke, blood clots, heart arrhythmia, or even sudden death. Conventional heart valve treatments often involve risky and lengthy procedure that requires thoracotomy (open chest). In recent years, interventional transcatheter heart valve products have been launched on the market and becomes popular. The procedure includes deploying a transcatheter heart valve to the lesion site through a micro-catheter to restore normal blood flow.

This study proposed a novel design methodology for transcatheter heart valve leaflets. Unlike most transcatheter heart valve leaflets today, our heart valve designs deviated from conventional 3D molding techniques and used 2-D quadrics sketches instead to save manufacturing cost. Polytetrafluoroethylene (e-PTFE) and e-PTFE with the addition of Polyethylene Terephthalate (e-PTFE + PET) were employed as the leaflet materials due to their high blood biocompatibility. The heart valve has to maintain appropriate valve orifice area during opening and ensure secured seal when closed. In addition, it is essential to withstand large dimensional changes and significant deformations during crimping (inside catheter) and deployment (to heart chamber). An interventional transcatheter heart valve was integrated by combining a nitinol scaffold with an expanded e-PTFE leaflet.

A series of tasks including design, computer simulation, laser cutting and its associated heat treatment, and bench testing were conducted. Ten leaflet designs were sketched using 2-D quadrics and cut from e-PTFE fabrics. Finite Element models were developed to facilitate the design iterations and evaluate the heart valve structural integrity from the crimping into a catheter to the deployment inside the heart chamber for both leaflet and nitinol scaffold. Computational Fluid Dynamics were also analyzed to evaluate the pump efficiency of the heart valve pre vs. post replacement. Laser cutting, heat treatment, electro-polishing, and bench testing were implemented to manufacture and test the prototypes for the proof of concept. Results showed that the leaflet...
design affected the pump efficiency of the heart valve and the 2-D quadriceps leaflet designs were able to provide good performance with reduced cost.

11:00 AM SB05.02.03
Materials Considerations Enabling Chronic Validation of a Wirelessly-Powered, Implantable Drug Delivery System Joanna L. Ciatto1,2, Abraham Vazquez-Guardado1,2 and John A. Rogers1,3,4,1 Northwestern University, United States; 2North Carolina State University, United States

Chronically implanted drug delivery devices face significant challenges that affect tolerance and effective dosage upon implantation in living organisms. Foreign body reaction, for instance, is a well-known adverse response to implants and various materials strategies have been proposed to circumvent it, including surface coatings, topography, and morphology, but often they are limited to non-functional implants. Herein, we present a wireless and battery-free, fully-implantable drug delivery device capable of on-demand drug release enabled by rational materials selection. The system relies on electrolytic pumps for drug delivery, which necessitate optimization of surface degradation mechanisms to allow for long-term stability in-vivo. Materials choice, design, and fabrication techniques will be discussed, as they pertain to facilitating the chronic implantation and tolerance of devices. Carefully engineered devices have demonstrated excellent biocompatibility in studies as long as 4 months post-implantation, and successful drug delivery to the bloodstream from the subcutaneous implant after many weeks implanted.

SESSION SB05.03: Organic Electronic Organ Interfaces
Session Chairs: Philipp Gutruf and John Ho
Tuesday afternoon, April 23, 2024
Room 434, Level 4, Summit

2:00 PM SB05.03.01
Conducting Polymer-Based Bioelectrodes with Enhanced Wet Adhesion and Stretchability Jiwan Jeon and Jin-Woo Park; Yonsei University, Korea (the Republic of)

Bioelectronic devices are mounted on human skin and tissue to get physiological information, enable electrical stimulation, and treat diseases. To fulfill these challenging roles, bioelectronic devices must possess the same mechanical properties as tissues that are soft, stretchable, and conform to the tissue surface. Also, it requires high conductivity and tough adhesion for high-quality electrical communication with devices and organizations. However, traditional bioelectronic devices are typically constructed using rigid metals, carbon nanotubes (CNT), or graphene, which offer excellent mechanical conductivity but suffer a significant mechanical mismatch when interfacing with biological tissues. This disadvantage leads to non-conforming electrode-tissue interfaces and can trigger pronounced inflammation. To address these issues, recently, soft bioelectronic devices have been developed that aim at improving compatibility between the devices and tissues and reducing inflammations by replacing rigid components with soft materials that closely mimic the characteristics of natural tissues. Therefore, bioelectronic devices composed of conducting polymers within a soft matrix have been thought as one of the ideal choices of materials. This combination offers excellent biocompatibility, mechanical properties resembling natural tissues, and desirable electrical characteristics. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)(PEDOT:PSS) has been studied extensively in soft bioelectronics. However, pure PEDOT:PSS is brittle because PEDOT:PSS network cannot effectively dissipate strain energy. The methods for preparing stretchable electrodes using PEDOT:PSS can be broadly categorized into two main approaches: A) involves the design of geometrical structures, while the other entails blending with plasticizers, ionic liquids (IL), or polymers. Forming a second network within the existing PEDOT:PSS network to create an interpenetrating polymer network, can enhance the stretchability of the composite electrode. Polyurethane is a hydrophilic polymer that easily mixes with PEDOT:PSS. Blending with polyurethane can make low modulus and high stretchability, but it reduces electrical conductivity with increasing amounts of insulating polymer. A higher proportion of PEDOT:PSS. However, this may result in a more rigid and less stretchable blend due to the inherent properties of PEDOT:PSS. Here, we report a double-network conducting polymer electrode consisting of PEDOT:PSS and polyurethane with high electrical conductivity and large stretchability by using an additive method that effectively reduces the modulus of the material and increases conductivity. We use Triton-X as an additive material. Triton-X effectively infiltrates the space between PEDOT:PSS chains and the polymer matrix, thereby increasing the free volume within both PEDOT:PSS and the polymer. This augmentation in free volume contributes to enhanced stretchability. Additionally, serving as a secondary dopant, Triton-X plays a crucial role in elevating the conductivity of PEDOT:PSS. When compared to DMSO, it has shown a more substantial improvement in conductivity. However, erroneous Triton-X content can weaken the property of reverting to its original length, making it essential to incorporate an appropriate amount to maintain elastic characteristics. Subsequently, for effective attachment to tissues, wet adhesive properties are essential for signal measurement and stimulation. Polyacrylic acid (PAA) and N-hydroxy succinimide (NHS) have been employed in this regard. PAA-NHS forms covalent bonds on the tissue surface, resulting in robust adhesion. Using this approach, we demonstrated the electrodes that exhibit a low modulus, excellent stretchability, and effective wet adhesion properties, which can be utilized for implantable bioelectrodes for nerve stimulation and implantable sensor for ECG.

2:15 PM SB05.03.02
Materials Science of a Multifunctional/Low Cost / Optimum Bicompatible Ultrananocrystalline Diamond (UNCDTM) Coating and Applications to New Generation Implantable Medical Devices/Prostheses and Biological Treatments Orlando Auciello1,2,1 The University of Texas at Dallas, United States; 2Original Biomedical Implants, United States

The presentation will focus on discussing materials science / technological applications of a unique material named ultrananocrystalline diamond (UNCDTM) in film form integrated into new generations of medical devices/prostheses, as described below: UNCDTM coatings, developed/patented by Auciello and colleagues, are grown on many substrates by low-cost Microwave Plasma Chemical Vapor Deposition (MPCVD) and Hot Filament Chemical Vapor Deposition (HFCVD) techniques, using a patented Ar/CH4 gas flow into high vacuum chambers, coupling microwave power, or current-induced heating (~2000 °C) of tungsten filaments. Both processes produce C, C6, C10, C14 of (x= 1, 2, 3) species, which establish chemical bonds on substrates’ surfaces, inducing nucleation/growth of polycrystalline diamond films with the smallest (2-5 nm) grains of polycrystalline diamond film available today, thus, the name UNCDTM (TM means trademark). UNCDTM coatings exhibit lower friction coefficient (0.02-0.04) compared with metals (≥0.5) currently used in friction-prostheses like hips, knees. UNCDTM exhibits unique biocompatibility, because it is made of C atoms (element of life in human DNA, cells, and molecules). Original Biomedical Implants (OBI-USA and OBI-México) companies are developing new medical devices/prostheses based on the UNCDTM coating, namely: 1) UNCDTM-coated silicon-microchip implantable inside the eye as key component of the future artificial retina (The Argus II device, implanted outside the eye, connected to the human retina from outside has been marketed in USA /EU, since 2011, returning partial vision to people blind by genetically-induced degeneration of photoreceptors); 2) New generation implantable prostheses (e.g., dental implants, hips, knees) coated with UNCDTM eliminates failure of current metal-implants due to mechanical wear / chemical corrosion by body fluids (Clinical trials, since 2018, implanting UNCDTM-coated dental implants (DI) in 51 patients in clinic in Queretaro-México, demonstrated transformational UNCDTM-coated DI performance); 3) UNCDTM-coated masks may trap COVID-19 virus better, due to ≤20 nm pores vs micron size pores in current masks, and surface C atoms trapping COVID virus more efficiently; 4) Unique electrically conductive/water corrosion resistant Boron-doped UNCDTM-coated metal electrodes passing electrical current through water, generate ozone (O3) on the surface of the UNCDTM coating, enabling O3 killing all virus, bacteria, and pathogen in water; also, ozonated water jets enable disinfection in 5-10 minutes of surgical instruments without heating them to high temperature for extensive time as currently done.

2:30 PM SB05.03.03
Stand-Alone Conformable Implantable Bioelectronics Based on Internal Ion-Gated Organic Electrochemical Transistors Don Khodaghoo; Columbia University, United States

It is increasingly appreciated that individual variability can strongly affect response to clinical treatments, motivating approaches that enable long-term monitoring of physiologic signals and delivery of responsive therapeutics. Implantable bioelectronic devices are often critical components of such approaches. The incompatibility of traditional electronic components with physiologic media, risk of device-related tissue disruption, and limited means by which to interface and power implanted devices are key hurdles. Organic electronics can be biocompatible and conformable, enhancing the ability to interface with tissue. However, limitations of speed and integration have thus far necessitated reliance on silicon-based technologies for advanced processing, data transmission, and device powering. Here, we create a stand-alone, conformable, fully organic bioelectronic device capable of realizing these functions. This device is based on a novel transistor architecture that incorporates a vertical channel and minimized hydration access conduit to enable MHz signal range operation within densely packed integrated arrays in the absence of crosstalk (vertical internal ion-gated organic electrochemical transistor, vIGT). vIGTs demonstrated long-term stability in physiologic media, and were used to generate high performance multi-stage amplifiers, oscillators, multiplexers, and rectifiers. We leveraged the high speed and low voltage operation of vIGTs to link them with an ion-based powering and data transmission approach that provides power to the transistor in the form of MHz range alternating current and permits signal extraction via modulation of this applied current. The resultant stand-alone device was implanted in freely moving rodents to acquire, process, and transmit neurophysiologic brain signals. Such fully organic devices have the potential to expand the utility and accessibility of bioelectronics to a wide range of clinical and societal applications.

3:00 PM BREAK
SESSION SB05.04/SB08.04: Joint Session: Bioelectronic Technologies
Session Chairs: Philipp Gutruf and Huiliang Wang
Tuesday Afternoon, April 23, 2024
Room 434, Level 4, Summit

3:30 PM *SB05.04/SB08.04.01
Transient Bioelectronic Implants John A. Rogers; Northwestern University, United States

Recently developed classes of electronic materials create an opportunity to engineer ‘transient’ electronic devices that dissolve, disintegrate, degrade or otherwise physically disappear at triggered times or with controlled rates. This talk describes the latest work in bioreabsorbable classes of transient devices, designed as temporary implants with therapeutic function. Presented examples range from ultraminiatuized, self-powered cardiac pacemakers, to electrical stimulators of the diaphragm, phrenic nerve and spinal cord - each with well-defined envisioned uses in clinical care.

4:00 PM *SB05.04/SB08.04.02
Technology for Bioelectronic Medicine George G. Malliaras; University of Cambridge, United Kingdom

Neurological conditions affect nearly one in six people in the world, imposing significant health, economic and societal burden. Bioelectronic medicine aims to restore or replace neurological function with the help of implantable electronic devices. Unfortunately, significant technological limitations prohibit these devices from reaching patients at scale, as implants are bulky, require invasive implantation procedures, elicit a pronounced foreign body response, and show poor treatment specificity and off-target effects. Over the past decade, new devices made using methods from microelectronics industry have been shown to overcome these limitations. Recent literature provides powerful demonstrations of thin film implants that are miniaturised, ultra-conformal, stretchable, multiplexed, integrated with different sensors and actuators, bioreabsorbable, and minimally invasive. I will discuss the state-of-the-art of these new technologies and the barriers that need to be overcome to reach patients at scale.

4:30 PM SB05.04/SB08.04.03
Minimally Invasive Neuroelectronics Anqi Zhang; Stanford University, United States

Neuroelectronic interfaces have enabled significant advances in both fundamental neuroscience research and the treatment of neurological disorders. However, current neuroelectronic devices have a clear trade-off between invasiveness and spatial resolution, and are unable to achieve seamless integration into the nervous system with cell-type specificity. In this talk, I will first introduce an ultra-small and flexible endovascular neural probe that can be implanted into sub-100-micron scale blood vessels in the brains of rodents without damaging the brain or vasculature. Second, I will describe a biochemically functionalized electronic probe that enables cell type- and neuron subtype-specific targeting and recording in the brain. Third, I will present a bottom-up approach for constructing neural interfaces from the cell surface, where neurons are genetically programmed to express membrane-localized enzymes that catalyze in situ assembly of functional materials. Finally, I will discuss future advances toward clinical translation of minimally invasive neuroelectronic interfaces capable of long-term monitoring and treatment of neurological disorders.

8:00 AM *SB05.05.01
Advancing Bi-Directional Electrophysiological Studies on The Intact Retina with Soft Multi-Electrode Arrays Yael Hanein; Ieva Vebrinaite-Adereth and Chen Bar-Haim; Tel Aviv University, Israel

The intricate nature of neural tissues presents formidable challenges in the realm of electrophysiological investigations, particularly when examining intact neural circuits. This challenge is amplified when studying the intact retina, where achieving bi-directional electrophysiological interfacing remains a significant hurdle, and currently available methods fall short of addressing this issue. In this presentation, a novel approach is introduced, leveraging cutting-edge soft multi-electrode arrays to enable comprehensive bi-directional electrophysiological studies on the intact retina. This endeavor involved the development and testing of soft electrode arrays meticulously designed to establish stable electrical connections with the retina. These soft probes were crafted to seamlessly conform to the curvature of the retinal structure within the eye, providing an unprecedented opportunity to study the retina in its anafated state. Notably, this presentation demonstrates, for the first time, the concurrent capabilities of electrical recording and stimulation directly from the intact retina. Of particular significance is our achievement in mapping retina responses to electrical stimulation. This revelation of the retina's responses under electrical stimuli unveils a strikingly strong, both in direct and indirect responses, in stark contrast to ex-vivo conditions. Our findings propose an intriguing scenario in which intact retinas exhibit superior stability and resilience compared to their ex-vivo counterparts, positioning them as a more suitable substrate for effectively mapping responses to electrical stimulation. These results not only enhance our comprehension of intact neural circuits but also inaugurate fresh avenues for pioneering research in the field.

8:30 AM *SB05.05.02
NeuroEdge: Graphene Nanoedge Electronics for Monolithic and Chronic Recording at Neuronal Density Yuxin Liu, Yuxin Jin and John S. Ho; National University of Singapore, Singapore

Recording electrophysiological signals from very closely spaced individual neuron over long durations is crucial for understanding the brain micro-circuit and functionalities at the cellular level. However, existing probe technologies are limited by sparse sampling of neurons in the intralaminar plane due to large interelectrode spacing and the need for surface modification materials, which are susceptible to instability over time, in order to have small dimensions and low impedance. Here, we report a monolithic graphene-edge probe array (NeuroEdge) that achieves a density of >2000 electrodes/mm², approaching cortical neuronal density. NeuroEdge is composed of self-aligned reduced graphene oxide nanoflakes with well-exposed nanoedges and electrolyte-filling nanochannels at the end, achieving impedance < 0.2 MΩ at neuronal size. Owing to its monolithic material composition and exceptionally low impedance, NeuroEdge provides stable electrophysiological recording with a high signal-to-noise ratio > 20 dB over 6 months. We demonstrate the utility of NeuroEdge for interrogating closely packed neurons by revealing the heterogeneity of acoustic-triggered activity in mouse auditory cortex. NeuroEdge provides a tool for accurately discriminating spikes from neighboring neurons in microcircuits in vivo.

9:00 AM *SB05.05.03
Scaling Effects on The Electrochemical Performance of Ti3C2T x MXene Thin-Film Bioelectronics for Neural Recording and Stimulation Spencer R. Averbeck, Raghav Garg and Michael S. Beauchamp; University of Pennsylvania, United States; 2Dxcel University, United States

In the last few decades there has been a growing interest in the development of technologies for neural recordings and therapeutic electrical brain stimulation. In these applications, microelectrode arrays offer the advantage of high-selectivity and sensitivity approaching the spatiotemporal scales of individual neurons. Recently, 2D Ti3C2T x MXene has emerged as a promising candidate for microscale recording and stimulation, due to its high electrical conductivity and volumetric capacitance. Here, we investigate the scaling effects on the electrochemical performance of thin-film 2D Ti3C2T x MXene microelectrodes with diameters ranging from 500 µm to 25 µm and film thicknesses varying from 100 nm to 700 nm. Prior to all electrochemical characterization measurements, we measured contact diameters, surface roughness, and thicknesses with confocal microscopy, atomic force microscopy (AFM), and 2D profilometry, respectively, in order to accurately assess geometric surface areas and available volumes. We then tested the electrodes with electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), voltage transients (VT), as well as 10,000 continuous cycles of biphasic stimulation pulses. Through these experiments, we calculated impedance modulus at 10 Hz and 1 kHz, charge storage capacity (CSC), and charge injection capacity (CIC) across the various electrode contact sizes and thicknesses. We also investigated the effects of pulse-width and waveform asymmetry on the calculated CIC values to determine the optimal stimulation parameters for the safe and effective delivery of electrical stimulation in thin-film Ti3C2T x MXene microelectrodes. We found there was an expected increase in the magnitude of impedances at 1 kHz as the contact diameters decreased from 500 µm to 25 µm with an average thickness of 100 nm, increasing from 9.1 ±
Orbit Symmetry Breaking in MXene Implements Enhanced Soft Bioelectronic Systems

Wednesday Morning, April 24, 2024

11:00 AM SB05.06.02
Implantable Bioelectronic Systems for Early Detection of Kidney Transplant Rejection Surabhi Madhavapathy1, Jiao-Jing Wang1, Heling Wang2, Manish Patel3, Anthony Chang4, Xin Zheng5, Yonggang Huang1, Zheng Jenny Zhang1, Lorenzo Gallon1 and John A. Rogers1; 1Northwestern University, United States; 2Tsinghua University, China; 3University of Illinois at Chicago, United States; 4The University of Chicago, United States

Early-stage organ transplant rejection can be difficult to detect. Percutaneous biopsies occur infrequently and are risky, and measuring biomarker levels in blood can lead to false-negative and -positive outcomes. We developed an implantable bioelectronic system capable of continuous, real-time, long-term monitoring of the local temperature and thermal conductivity of a kidney for detecting inflammatory processes associated with graft rejection, as demonstrated in rat models. The system detects ultradian rhythms, disruption of the circadian cycle, and or a rise in kidney temperature. These provide warning signs of acute kidney transplant rejection that precede changes in blood serum creatinine/urea nitrogen by 2 to 3 weeks and approximately 3 days for cases of discontinued and absent administration of immunosuppressive therapy, respectively.

11:15 AM SB05.06.03
Wireless, Battery-Free Bioelectronics for Fully Implantable, Living Medical Devices Siddharth Krishnan, Matthew Bochenek, Suman Bose, Claudia Liu, Amanda Facklam, Nima Khatib, Ben Walters, Derin Gumustop, Laura O'Keefe, Robert Langer and Daniel Anderson; MIT, United States

Living cells are a novel class of therapeutics that offer possibilities in long-term protein replacement. Primary cells such as pancreatic islets can offer functional cues for Type I Diabetes via responsive insulin secretion, as can stem-cell derived products. Immortalized cell lines can be engineered or transfected to secrete nearly any protein of choice, to address a broad range of conditions from blood-borne disorders to degenerative neural disease and cancer. Two core challenges limit the clinical translation of these cell therapies: first, the potential for recognition and attack by the host immune system necessitates the use of chronic immunosuppressants to maintain graft viability, with mixed success. Second, the formation of fibrotic capsules around transplanted cells isolates them from native vasculature, resulting in hypoxia. In this work, we demonstrate a wireless battery-free device system capable of housing and supporting therapeutic cells in vivo by providing both immune-isolation and oxygen supply. Transplanted cells are separated from host tissue by nanoporous membranes that prevent infiltration and attack by immune cells, obviating the need for immune suppression. A multilayer materials system comprising a proton-exchange membrane electrolyzer and an elastomeric encapsulation allows for direct splitting of molecular water into oxygen and hydrogen. Oxygen is stored in an elastomeric chamber that diffuses directly into regions containing transplanted cells. The entire reaction is sustained by a wireless power harvesting circuit based on resonant inductive coupling, at a frequency (13.56 MHz) chosen for its low specific absorption rate in biological tissue and compatibility with existing commercial infrastructure for two-way data and power transfer. Systematic numerical modeling, benchtop testing, and in vitro experimentation highlight key aspects of device and materials performance.

In vivo studies demonstrate high levels of performance. HEK293T cells engineered to secrete a model protein system (erythropoietin, EPO), demonstrate sustained, significantly elevated levels of protein production when transplanted in O2-Macrophages relative to cells encapsulated in non-oxygenated control devices over several weeks. Xenogenic rat islets transplanted into immune competent, diabetic C57BL/6J mice resulted in complete diabetic reversal for several weeks, with explantation studies revealing viable, glucose response islets. Notably, all of these studies involved transplantation into minimally invasive subcutaneous sites, that are clinically attractive owing to their easy accessibility for implantation and explantation procedures.
Toward Implantable Biohybrid and Regulated Cell Therapies

Jonathan Rivnay
Northwestern University, United States

The union of bioelectronics with engineered mammalian cells is a transformative opportunity in regulated, personalized therapeutics. This approach involves combining the strengths of synthetic biology – namely biological specificity that leverages the natural machinery of cells – with bioelectronic systems, which offer precision timing, dose control, and communication with established sensing technologies and clinical feedback. To this end, we show how implanted biohybrid devices rely on bioelectronics to initiate the production of native peptides, control therapeutic dose, and support the health and productivity of these “cell factories”. We demonstrate optogenetic induction of drug production, fluorescence feedback via photometry to probe cell factory viability, and on-site electrocatalytic oxygenation for maintenance of implanted cell health at high cell density. Current efforts focus on regulation of circadian rhythms; however, the biohybrid cell therapy concept can be broadly applied to chronic diseases including Type I diabetes, obesity, and cancer immunotherapies.

2:30 PM BREAK

SESSION SB05.08: Central Nervous System Interfaces II
Session Chairs: Philipp Gutru'f and Flavia Vitale
Wednesday Afternoon, April 24, 2024
Room 434, Level 4, Summit
Active optical metasurfaces, capable of dynamically manipulating light in ultrathin form factors, enable novel interfaces between humans and technology. Miniaturized implantable devices for light delivery open new applications in biophotonics, including minimally invasive sensing, endoscopic imaging, and optogenetic stimulation. The next generation of human-photonic interfaces will require mechanically adaptive, minimally invasive devices that can dynamically manipulate the shape of optical wavefronts and their spectral properties. In such interfaces, soft materials bring many advantages based on their flexibility, compliance, and large stimulus-driven responses.

Here, we realise electrochemically-mutable, soft (EmUs) metasurfaces that capitalise on the swelling of soft conducting polymers to alter the shape and associated resonant response of metasurface elements. Previous approaches to dynamic metasurfaces that rely on index-tuning of materials are fundamentally constrained by Kramers-Kronig relations, which prescribe that significant index tuning (i.e. index changes) naturally comes with notable absorptive losses. By leveraging the deformability of soft materials to modulate geometry we circumvent these limitations, allowing for effective, low-loss phase tuning. Using the commercial polymer, PEDOT:PSS, we demonstrate dynamic, high-resolution color-tuning and high-diffraction-efficiency (~19%) beamsteering devices that operate at CMOS compatible voltages (~1.5V). Our devices can be realised as ultra-thin, sub-micron coatings, and provide a building block for a new generation of active opto-electronic devices amenable for integration with the human body, potentially enabling new applications in implantable light guiding and bio-imaging.

5:00 PM SB05.08.03 Multimodality Sense and Actuate Bioelectrical Interfaces Tzahi Cohen-Karni; Carnegie Mellon University, United States

My team’s efforts are focused on the development and engineering of nanomaterials-based flexible platforms to interrogate and affect the properties of tissue and cells. A few of the major challenges we strive to answer are: Can we make materials and platforms tailored to allow seamless and stable integration with cells and tissue as well as enable sensing and actuation? Can we develop scalable, low-cost, and low-energy systems based on networked nanomaterials to allow for high-precision, high-selectivity manipulation of cells? Can we engineer and integrate biocompatible and bioactive nanomaterials that can be used in various in vitro and in vivo applications? To this end, we are developing hybrid-nanomaterials that can be used in various input/output bioelectrical interfaces, i.e., bioelectrical platforms for chemical and physical sensing and actuation. The outstanding electrochemical properties of the synthesized hybrid-nanomaterials allow us to develop highly efficient catalysts, and electrical sensors and actuators. We demonstrated sensors capable of exploring brain chemistry and sensors/actuators that are deployed in a large volumetric muscle loss animal model. Finally, using the unique optical properties of nanocarbons in the form of graphene-based hybrid-nanomaterials and 2D nanocarbons (MXene), we have formed remote, non-geometric bioelectrical interfaces with excitable cells and modulated cellular and network activity with low needed energy and high precision. In summary, the exceptional synthetic control and flexible assembly of nanomaterials provide powerful tools for fundamental studies and applications in life science and potentially seamlessly merge nanomaterials-based platforms with cells, fusing nonliving and living systems together.

5:00 PM SB05.09.02 Biodegradable Gel Electrolyte for Self-Electrofied Implantable Biomedical Devices Gihoon Kim1,2; 1Korea University, Korea (the Republic of); 2BK21 Four Institute of Precision Public Health, Korea (the Republic of)

Gel electrolyte have attracted increasing attention as one of compartment of battery system due to their mechanical strength and high capacitance-to-volume ratio. However, the non-biodegradable gel electrolyte is still challenging to apply to various applications because of the harmfulness to environment and the toxicity to human. Here, we developed the biodegradable gel electrolyte by blending the polyvinyl alcohol (PVA) with polyethylene glycol (PEG) to enhance their mechanical, electrical, and electrochemical stability for implantable bioelectronic devices. We synthesized the different ratio of blended hydrogel (PEG/PVA = 1, 2.5, 5, 10, 20 %) by freezing-thawing method. The biodegradable gel electrolyte is achieved by immersing the blended hydrogel into ion-rich solution (i.e., Phosphate Buffered Saline (PBS) and ionic liquid etc.). The prepared gel electrolyte exhibits better mechanical strengths (tensile strength of ~30 kPa under 120 % of strain) and higher ionic conductivity (~50 mS/cm) compared to pure PVA hydrogel and PEG hydrogel. Although the liquid electrolyte induces the corrosion of biodegradable electrode (Mg, W, Mo etc.) surface leading to poor electrochemical performance, the prepared gel electrolyte can increase the anodic reaction up to ~3.7 V, which reduces the corrosion and hydrogen evolution reaction (HER) of biodegradable anode and cathode. In addition, the PEG/PVA blended hydrogel is degraded by 14 days at 37 °C, which can be applied to biodegradable bioelectronic devices. We anticipated that the biodegradable gel electrolyte can be applied for the biodegradable self-powered electrophotocells and biodegradable supercapacitor for implantable biomedical applications.

5:00 PM SB05.09.03 Design, Simulation and Fabrication of Novel Flat-Wire Braided Flow Diverter for Cerebral Aneurysm Yao-An Zhuang1, Lilian Lin1, Chen-Hsin Lin1, Ching-Chang Huang2 and Hao-Ming Hsiao1; 1National Taiwan University, Taiwan; 2National Taiwan University Hospital, Taiwan

Cerebral aneurysm is a weakened cerebral artery which causes localized ballooning of the blood vessel. As an aneurysm grows, it puts pressure on adjacent tissues and may eventually rupture, leading to severe events or even sudden death. Today the flow diverter, a stent-like mesh device, has gained increasing popularity for the endovascular treatment of cerebral aneurysms. The mechanism is to stop the blood flow into an aneurysm via the fine-mesh structure of the flow diverter to reduce the risk of rupture. It also serves as a scaffold for endothelialization, effectively sealing off an aneurysm from the body circulation. The paradigm shift in the treatment preference from traditional craniotomy reflects the growing confidence in the effectiveness of the flow diverter for managing cerebral aneurysms.

Braided flow diverter is currently used to treat cerebral aneurysms, with the braiding technology adopted to build stent-like mesh devices. Braiding is considered to be more cost-effective when compared to other stent fabrication techniques such as laser-cutting. When braiding, round wires extending from bobbins can be secured to the end of a mandrel under tension to form a braided device around it. In this paper, instead of using round wires, a novel flat-wire design with the wire dimension of 25 μm in thickness and 127 μm in width was investigated. This unique wire geometry possesses a higher aspect ratio that results in thinner struts and greater metal coverage (less opening). It is believed that thinner struts reduce the low wall shear stress zones and thus the risk of in-stent stenosis, a significant complication of narrowed arteries. Therefore, using flat wires could reduce the occurrence of in-stent stenosis, while increasing the metal coverage to cut down the blood supply to the aneurysm simultaneously.

A flat-wire braided flow diverter was investigated in this paper. Finite element analysis (FEA, ABACUS) and computational fluid dynamics (CFD, ANSYS) were conducted to evaluate the mechanical integrity and hemodynamic behavior under various conditions consistent with the current practice. CFD models were analyzed based on an ideal aneurysm assembly with a flat-wire braided flow diverter implanted to evaluate its therapeutic effects. Prototypes were fabricated in-house using a braiding machine with the capacity of up to 64 bobbins, followed by the validation of bench tests for proof of concept. FEA simulation results showed no material damage occurred during the manufacturing and deployment processes as the struts were within the safety range. CFD simulation results showed the flat-wire braided flow diverter stopped a significant portion of the blood flow into an aneurysm. The velocity streamlines helped visualize the effectiveness of the increased metal coverage. These conclusions suggest that the flat-wire braided flow diverter has a great potential to achieve the best possible clinical outcomes.

5:00 PM SB05.09.04 Porous, Antibacterial and Biocompatible Go/n-HAp/bacterial cellulose/β-glucan Biocomposite Scaffold for Bone Tissue Engineering Saqlain A. Shah1; 1Forman Christian College, Pakistan; 2University of Punjab, Pakistan

We developed a nanocomposite scaffold for bone tissue engineering (using bacterial cellulose (BC) and β-glucan (β-Gl)) via free radical polymerization and freeze-drying technique. Hydroxyapatite nanoparticles (n-HAp) and graphene oxide (GO) were added as reinforcement materials. The structural changes, surface morphology, porosity, and mechanical properties were investigated through spectroscopic and analytical techniques like Fourier transformation infrared (FT-IR), scanning electron microscope (SEM), Brunauer-Emmett-Teller (BET), and universal testing machine Instron. The scaffolds showed remarkable stability, aqueous degradation, sponginess morphology, porosity, and mechanical properties. Antibacterial activities were performed against gram -ive and gram +ive bacterial strains. The BgC-1.4 scaffold was found more antibacterial compared to BgC-1.3, BgC-1.2, and BgC-1.1. The cell culture and cytotoxicity were evaluated using the MTT/37-E1 cell line. More cell growth was observed onto BgC-1.4 due to its uniform interrelated pores distribution, surface roughness, better mechanical properties, considerable biochemical affinity towards cell adhesion, proliferation, and biocompatibility. These nanocomposite scaffolds can be potential biomaterials for fractured bones in orthopedic tissue engineering.
Comparison of Tensile Properties of Amniotic Membranes Sterilized with Different Techniques
Abbigail Poland, Molly Post, Olivia Logan, Isabella Sledge, Babak Safavieh and Mora Melican; Tides Medical, United States

The amniotic membrane has gained recognition as a promising biomaterial in the field of regenerative medicine. The market offers a diverse range of placental membrane products designed for various applications. When evaluating and characterizing the numerous amniotic products available, it becomes crucial to ensure that each product aligns with the specific user requirements, particularly concerning the mechanical characteristics for wound care applications. One effective method for testing this characteristic involves tensile testing. In this study, the Instron 5544 was used to test tensile strength of two different amniotic products. A standardized and optimized protocol was used to test two different amniotic products. A standardized and optimized procedure for conducting tensile tests on amniotic products has not been previously well-established. This study addresses these gaps by introducing a standardized method for the tensile testing of dehydrated amniotic membrane. Through this study, we compare the handling capabilities of Artacent Wound®, a dual layer amniotic scaffold, sterilized with electron beam (e-beam) sterilization, to Artacent Wound® sterilized using an alternative sterilization technique.

Multiple sterilization techniques, such as gamma irradiation, ethylene oxide (ETO) gas sterilization, e-beam, and several other approaches have been utilized to remove potential pathogens for products derived from human placentas. However, the sterilization method can lead to diverse impacts on the material's mechanical characteristics. To ensure that the mechanical properties are maintained with the alternative sterilization technique, the Artacent Wound® product is compared to the e-beam sterilized Artacent Wound® product.

Tensile tests were performed on two different Artacent Wound® products (one with e-beam sterilization and one with an alternative sterilization technique), and the products were tested for Failure Stress (MPa), Failure Strain (%), and Young’s Modulus (MPa). The tests were used to characterize and better understand the product’s mechanical properties and how the sterilization techniques impact these properties. By developing a method to test tensile strength for amniotic products, new products and new processing steps can be easily tested to determine the mechanical impacts to the product.

5:00 PM SB05.09.06
An Open-Source Platform for Clinical Autonomic Neuromodulation Therapies
Mona A. Mohamed1, Ali Soleimani1, Farbod Amirghasemi1, Ellis F. Meng1, Victor Pikov2, Raja Hirti1, Hangbo Zhao3 and Mari Mousavi1; 1University of Southern California, United States; 2Medpace Inc., United States; 3Med-Ally LLC, United States

The field of bioelectronic medicine is rapidly progressing, with emerging therapeutic approaches necessitating precise closed-loop control of neural activity in peripheral nerves like the vagus nerve, sacral nerve, pudendal nerve, enteric nervous system, and others. However, transitioning neuromodulation therapies for human clinical application poses significant challenges due to the high costs and lengthy development timelines required for implantable devices suitable for human use. Presently, many clinical research teams rely on off-the-shelf commercial devices for testing on both large animals and humans. These commercial devices are often tailored to specific applications and may not align with the requirements of novel therapies. Collaborations with large corporations are frequently complicated by potential conflicts of interest that hinder successful partnerships. Furthermore, existing devices often lack the capacity to record biomarkers from multiple sites, limiting their therapeutic potential. As a result, access to customizable neuromodulation technology stands as a substantial obstacle to scientific breakthroughs and the advancement of new treatments.

The CARSS Center, a collaborative venture involving the University of Southern California, Medpace Inc., and Med-Ally LLC, aims to address this challenge. They are creating an open-source system for closed-loop autonomic neuromodulation specifically designed for human clinical investigations. The CARSS system consists of an implantable pulse generator (IPG) equipped with Bluetooth capabilities and native support for running machine learning algorithms. Additionally, it includes a variety of leads for both stimulation and sensing purposes. The initial set of leads comprises a vagus nerve cuff and a sacral nerve linear array with combined stimulation and neural sensing capabilities, as well as electrocardiography, electromyography, and motion sensing leads for physiological monitoring. Furthermore, the system is designed to allow even non-expert users to run machine learning algorithms for clinical investigations.

5:00 PM SB05.09.07
A Cellulose Aerogel-Based Drug Delivery System using Punica Granatum Extracts - Invention to Innovation
Subharina Mahapatra1, Jyotirmayan De2 and Manjula Hebbale1; 1Bharati Vidyapeeth Dental College and Hospital, India; 2Indian Institute of Technology Bombay, India

Oral lichen planus is a widespread chronic mucocutaneous, autoimmune inflammatory disorder affecting the oral cavity. Oral lichen planus is usually associated with pain, burning sensation and irritation of the oral mucosa. Multiple therapeutic approaches including both topical and systemic corticosteroids have been used in the management. As a consequence of the reported adverse effects of corticosteroids, different natural plant extracts have been suggested. Pomegranate (punica granatum) have been identified for hundreds of years as a natural treatment modality for their numerous benefits for health. Topical punica granatum extracts gel in management of oral lichen plan has been tried as a topical medication and according to research it has anti-inflammatory property, which help to subside the symptoms of oral lichen planus but the disadvantage is that punica granatum extracts gel dissolve quickly inside the oral cavity by saliva, thus providing less application time. Prolonged application time of the medication is required for faster recovery.

As a result, drug (punica granatum extracts gel) -loaded cellulose aerogel have been introduced as a promising drug delivery carrier to deliver medications to the affected area by controlled release. They prolong the time of application as the medication slowly dissolves in saliva and is released to the particular applied area of irritation caused by oral lichen planus. Cellulose is used in this process, as cellulose is the perfect raw material for cellulose aerogel due to its easy availability, biodegradability, biocompatibility, and non-toxicity. It also offers a high surface area, a highly porous, interconnected fibre network, and the availability of various functional groups required for drug encapsulation.

Hence, a cellulose aerogel-based drug delivery system is developed from the punica granatum extracts gel in the management of oral lichen planus as an alternative treatment plan to prolong the application time and control release of the medication.

After development of the product, it has been applied in the oral lichen planus patients. Total thirty patients were divided into two groups, group a patient with topical corticosteroids and group b patients with drug (punica granatum extracts gel) -loaded cellulose aerogel. The results were better in group b patient, who were using drug (punica granatum extracts gel) -loaded cellulose aerogel.

5:00 PM SB05.09.08
Comparative Analysis of Sterilization Methods for Placenta-Based Products using an Animal Model
Molly Post, Olivia Logan, Denae Landry, Isabella Sledge and Mora Melican; Tides Medical, United States

Placenta-based products, known for their regenerative potential in various clinical applications, are either aseptically processed or require effective terminal sterilization methods to ensure safety and maintain their therapeutic properties. Providing an overview of a comparative analysis of healing rate in a full thickness animal model has been used to show the importance of evaluating the impact of sterilization on these materials in a biologically relevant context. The Sprague Dawley full thickness model is used to assess the in vivo response to sterilized placenta-based products, and to provide critical insights into immunogenicity, tissue integration, and the overall regenerative potential of these materials.

Several sterilization methods, including gamma irradiation, ethylene oxide (ETO) gas sterilization, electron beam (e-beam), and various other methods have been employed to eliminate potential pathogens from placenta-based products. However, the choice of sterilization method can have varying effects on the biological activity and safety. In this study, we discuss the utilization of an animal model to assess the effects of different sterilization techniques on the safety and efficacy of placenta-based products. The placenta-based product tested is Artacent Wound®, a dehydrated dual layer amniotic graft, sterilized with two different techniques. Furthermore, it addresses the importance of selecting appropriate animal models that closely mimic human physiology, ensuring that the findings are translatable to clinical applications. The animals are monitored for wound healing progress and adverse effects. In conclusion, employing relevant animal models allows for a more comprehensive evaluation of the impact of sterilization on these materials, bridging the gap between in vitro assessments and clinical applications.

5:00 PM SB05.09.09
Soft, Bioresorbable, Transparent Microelectrode Array Platform for Heart Disease Diagnosis and Treatment
Zhixuan Chen; The George Washington University, United States

Heart disease kills nearly 700,000 people in the United States each year, with an estimated annual cost of $219 billion. A key factor contributing to these alarming statistics is the lack of tools that can unravel complex pathophysiology, facilitate intraoperative or postoperative monitoring, and provide effective and timely clinical treatments.

Noble-metal-based microelectrode arrays (MEAs) have been widely used to probe the patterns of cardiac excitation waves and identify the regions causing arrhythmias, while electrical pacemakers and defibrillators are the cornerstone of therapy in clinical medicine to correct abnormal heart rhythm. However, they are problematic in detecting critical cardiac parameters such as intracellular calcium dynamics, metabolic activity, or target-specific cell types.
Optical mapping using voltage/calciug-sensitive dyes or intrinsic fluorescence can complement these electrical approaches by uncovering the roles of above-mentioned cellular parameters in both health and disease conditions. However, conventional opaque MEAs are not compatible with this as they block the passage of excitation illumination and fluorescence signals, and obscure the bio-signals by artifacts due to the photovoltaic effect. Furthermore, given the mechanical dynamic nature of hearts, higher requirements are placed on the flexibility of the interface devices. Therefore, developing such technology that can bridge electrophysiology and opto-physiology at cardiac interface is of significance but very challenging.

Soft transparent MEAs show great promise in tackling this challenge, as they allow light to transmit in both directions for simultaneous artifact-free optical and electrical investigation of cell/tissue from the same field of view and visualize the spatiotemporal distribution of cardiac activities with multiple parameters. Additionally, optically transparent MEAs are highly desired during clinical procedures to allow direct observation of areas of interest under the microscope for concurrent optical diagnostics/therapies (such as endoscopy) and guiding other procedures (such as catheters) on the hearts. However, all existing transparent MEAs are designed for chronic biointerfacing and require surgical removal when they malfunction or are no longer needed.

In comparison, biodegradable electronics provide unique opportunities to investigate, monitor, and treat short-lived cardiac complications, including postoperative arrhythmias and heart failure on the order of a few days to weeks following ischemic events or surgery, which account for at least one-third of postoperative deaths. Those devices can subsequently dissolve into benign products via natural metabolic mechanisms to avoid the complications, infection risks, and additional costs associated with surgical retrieval. However, soft transparent MEAs that exhibit biodegradable functionality remain unexplored.

Here, we report materials, device design, fabrication, characterization, and validation of the first fully biodegradable and transparent MEA platform. The developed fabrication strategy allows for controllable nanoscale transient patterns for the first time. The device enables multiparametric electrical and optical mapping of cardiac dynamics and on-demand site-specific stimulation to investigate and modulate cardiac physiology in rat and human heart models. In addition, the device can be used as a heart implant to perform the continuous process of arrhythmia detection, monitoring, and bipolar-pacing treatment in vivo over a clinically relevant period. The biodegradation dynamics and biocompatibility of the device are systematically investigated by histology and serology. The concept and design of this work lay the foundation for biodegradable cardiac technologies that advance postoperative monitoring and treatment of temporary patient pathologic conditions in certain clinical scenarios, such as myocardial infarction, ischemia, and transcatheter aortic valve replacement.

5:00 PM SB05.09.10 Structural and Biological Characteristics of a Novel Hydroxyapatite–Sodium Alginate-Based Biocomposite Material for Dental Implants Hussein S. Alrobie; Prince Sattam bin Abdulaziz University, Saudi Arabia

Materials intended for bone and dental implants must possess biocompatibility and good mechanical strength. To enhance these qualities, a novel hydroxyapatite–sodium alginate-based biocomposite was created by using wet precipitation technique. The XRD of the original and modified specimens closely matched the hydroxyapatite (HAp), and the presence of distinct HAp peaks in FTIR endorsed the successful synthesis of both HAp and modified hydroxyapatite–sodium alginate. The SEM images vividly exhibited porosity in the modified specimen, with a recorded density of 1.06 g/cm3. The peak microhardness value, 26.4 GPa, was attained in the optimized composition. As the dopant concentration increased, the antibacterial activity of the hydroxyapatite–sodium alginate-based biocomposite also increased. The absence of dopant ion leakage under physiological circumstances was confirmed by a 35-day examination of ion release in simulated body fluids. The results indicate that the developed composite holds substantial potential as a material suitable for teeth and bone implants, owing to its mechanical and biological characteristics.

5:00 PM SB05.09.13 Highly Conductive and Ultra-Thin Elastic Silver-Nanosheet Membrane for Neural Recording Sonwoo Jung1, 2, Minjeong Kim1, 2, Seungyeon Kim3, Tae-Wook Kim3, and Dae-Hyeong Kim1, 2, 3, 4, 5

Institute for Basic Science (IBS), Korea (the Republic of); 2Seoul National University, Korea (the Republic of); 3Jeonbuk National University, Korea (the Republic of)

Nanocomposites are gaining prominence as suitable materials for skin wearable and implantable electronics due to their tissue-like mechanical properties and adequate electrical properties. However, achieving both conformal adhesion and excellent electrical and mechanical properties is challenging, as thickness and conductivity are often in a trade-off relationship for most of the materials. To overcome the challenge, highly elastic and conductive nanocomposites have been developed by leveraging 1-dimensional nanowires. However, owing to the geometrical anisotropy of the nanowire, nanocomposites exhibited different properties depending on the directions. Here, we present a stretchable and laser-patternable nanomembrane using 2-dimensional(2D) silver nanosheets with isotropic and high electromechanical properties. The single layer of nanomembrane is ultrathin (~250 nm) and highly conductive (>80,000 S/cm) yet remains stretchable since the nanosheets dissipates the stress induced to the membrane. Furthermore, 2-dimensional nanosheets endow the membrane with isotropic mechanical and electrical performances in every direction. Based on float assembly fabrication, silver nanosheets were tightly gathered and partially embedded into the elastomer on the larger surface area of the silver nanosheet and constructed partial face-to-face contact. This face-to-face junction decreases the contact resistance of the nanomembrane, contributing to the high conductivity of the membrane. In addition, the silver nanosheet membrane was able to be manufactured with different dimensions and thicknesses by controlling fabrication variables, displaying distinct characteristics in electrical conductivity, stretchability, impedance, and modulus in each variable-controlled membrane. Moreover, through the bilayer stacking process, the contacts between silver nanosheets created extra percolation networks, resulting in a significant enhancement of conductivity, reaching up to 125,000 S/cm. By patterning the encapsulated nanomembrane with laser, we fabricated a stretchable electrode array making a conformal adhesion to the skin and nerves, demonstrating the future potential of the membrane for broad application both in wearable and implantable approaches.

5:00 PM SB05.09.14 Etching of Failed Polymeric Heart Valve Leaflets Reveals Cross-Tie Craze Microstructure Nirpa Khair3, Katie Vinterella2, Ethan Harrell1, Juliane Kindsfater1, Lakshmi P. Das2 and Susan James1, 3, 1Colorado State University, United States; 2Georgia Institute of Technology, United States

Rheumatic and calcific aortic valve disease presents a global public health concern, impacting millions of individuals across various age groups. The gold standard medical treatments recommend replacing the sick heart valve with xenograft-based bioprosthetic valves that are chemically fixed using glutaraldehyde, commonly sourced from bovine or porcine. Clinical investigations over more than two decades have validated the valves are prone to premature calcification and tearing, thereby limiting their durability. Moreover, challenges related to supply chains, inconsistent mechanical characteristics, and high costs have been constant issues for tissue valves. An innovative alternative approach involves enhancing polyethylene-based materials with hyaluronic acid (HA), a glycosaminoglycan naturally occurring in native heart valve leaflets. By incorporating small amounts of HA into a low-density linear polyethylene (LLDPE) thin film at the molecular level, a robust and hydrophilic biomaterial of the valves consistently tear and wear around highly stressed (from finite element analysis) commissure posts. Six of these worn posts were retrieved from failed valves and chemically etched. Low-voltage scanning electron microscopy (SEM) imaging was taken before and after chemical etching. The semicrystalline LLDPE polymer, with a crystallinity of 36% as determined by DSC, underwent chemical etching using a standard 2% w/v permanganate etching solution, followed by multistep washing. The SEM analysis of pristine LLDPE unveiled distinctive spherulitic structures consisting of well-organized lamellae with diameters of approximately 3 µm and lamellae thickness of 40-80 nm. The etching process effectively eliminated low-energy amorphous regions, revealing the spherical lamellae. A similar study was carried out on the worn and torn LLDPE valves.

The SEM images of the worn surfaces displayed signs of surface wear and aligned fibrils oriented perpendicular to the principal stress direction, akin to a phenomenon known as crazing. Following etching, some fibrils remained partially intact, while others exposed the crystals beneath them. These crystals within the fibrils lost their spherical superstructure, exhibiting thickened and fractured lamellae. The presence of these fibrils after etching suggested a state of hyper-crystallinity, a characteristic often observed in polyethylene-drawn filaments. In contrast, the worn surfaces that had tears displayed multiple irregularities at the torn surface. These included bumps, holes, a visually rough texture, and a lack of exposed crystals. Crystal disruptions were notably concentrated within 200-300 µm areas near the tear and wear, while the rest of the samples retained spherical morphology.

Remarkably, one of the worn samples unveiled the Kramer craze microstructure "cross-tie," composed of aligned and interconnected lamellae. The spacing between cross-tie lamellae ranges from 100-200 nm, and the thickness remained 40-80 nm. To the best of the author’s knowledge, the cross-tie structure has been only theorized with indirect evidence collected from lab-grown crazes. Direct evidence of cross-tie structure indicates crazing initiates the tears. Stress disentangles polymer strands, causing lamella fibrillation, but some do not disentangle. Instead, they pile up to bridge between fibrils. This study holds the potential to shed light on preventing polymer disentanglement, thereby mitigating crazing and improving heart valve durability.

5:00 PM SB05.09.15 Effects of Temperature on the Mechanical Properties of PEGDA and PDMS Copolymer Scaffold for Tissue Engineering Sam Lloyd-Harry1, Samaher Shaheen2, Ozgul Yasar-Inceoglu3

Here, we present a stretchable and laser-patternable nanomembrane using 2-dimensional(2D) silver nanosheets with isotropic and high electromechanical properties. The single layer of nanomembrane is ultrathin (~250 nm) and highly conductive (>80,000 S/cm) yet remains stretchable since the nanosheets dissipates the stress induced to the membrane. Furthermore, 2-dimensional nanosheets endow the membrane with isotropic mechanical and electrical performances in every direction. Based on float assembly fabrication, silver nanosheets were tightly gathered and partially embedded into the elastomer on the larger surface area of the silver nanosheet and constructed partial face-to-face contact. This face-to-face junction decreases the contact resistance of the nanomembrane, contributing to the high conductivity of the membrane. In addition, the silver nanosheet membrane was able to be manufactured with different dimensions and thicknesses by controlling fabrication variables, displaying distinct characteristics in electrical conductivity, stretchability, impedance, and modulus in each variable-controlled membrane. Moreover, through the bilayer stacking process, the contacts between silver nanosheets created extra percolation networks, resulting in a significant enhancement of conductivity, reaching up to 125,000 S/cm. By patterning the encapsulated nanomembrane with laser, we fabricated a stretchable electrode array making a conformal adhesion to the skin and nerves, demonstrating the future potential of the membrane for broad application both in wearable and implantable approaches.

5:00 PM SB05.09.14 Structural and Biological Characteristics of a Novel Hydroxyapatite–Sodium Alginate-Based Biocomposite Material for Dental Implants Hussein S. Alrobie; Prince Sattam bin Abdulaziz University, Saudi Arabia

Materials intended for bone and dental implants must possess biocompatibility and good mechanical strength. To enhance these qualities, a novel hydroxyapatite–sodium alginate-based biocomposite was created by using wet precipitation technique. The XRD of the original and modified specimens closely matched the hydroxyapatite (HAp), and the presence of distinct HAp peaks in FTIR endorsed the successful synthesis of both HAp and modified hydroxyapatite–sodium alginate. The SEM images vividly exhibited porosity in the modified specimen, with a recorded density of 1.06 g/cm3. The peak microhardness value, 26.4 GPa, was attained in the optimized composition. As the dopant concentration increased, the antibacterial activity of the hydroxyapatite–sodium alginate-based biocomposite also increased. The absence of dopant ion leakage under physiological circumstances was confirmed by a 35-day examination of ion release in simulated body fluids. The results indicate that the developed composite holds substantial potential as a material suitable for teeth and bone implants, owing to its mechanical and biological characteristics.
Tissue engineering is a growing field of materials research concerned with finding new materials and methods for the replacement or improvement of natural tissue structures. Previous studies have shown poly(ethylene glycol) diacrylate (PEGDA) to be a promising engineering tissue structure, or scaffold material. However, PEGDA scaffolds have been shown to lack sufficient mechanical properties that would be required for implantation in the human body. More research must be done to tune the mechanical properties of the scaffold. Many research institutions do not have access to all testing equipment needed to fully study the limitations of scaffold samples. Thus, the need for collaboration between institutions is often necessary. Numerous common testing methods require consistent environmental conditions to maintain the structure of scaffold to accurately collect data. The study of the limitations of environmental conditions is significant to avoid degradation of the structure and therefore keep the mechanical properties of scaffold samples. Experiments have shown PEGDA scaffolds to experience a decrease in strength and elasticity after refrigeration for 24 and 48 hours, but a restoration of mechanical properties was found after 72 hours. No studies have looked at mechanical properties beyond 72 hours of refrigeration. This study investigates the effects of temperature on the mechanical properties of UV cross-linked PEGDA and polydimethylsiloxane (PDMS) polymer scaffolds. Utilizing Fourier Transmission Infrared Spectroscopy, Scanning Electron Microscopy, X-ray Diffraction, and Raman Spectroscopy, the characterization of the copolymer scaffolds was performed. Compression testing was then performed on a Q5 50 Universal Testing Machine at a rate of 0.75 mm/min. These results were compared with that of refrigerated copolymer samples and plain PEGDA scaffold samples. Samples were refrigerated at 0 degrees Centigrade for 24, 48, 72, and 96 hours.

5:00 PM SB05.09.17
Degradation Effects on Mechanical Properties of Polyethylene Glycol Diacrylate (PEGDA) and Polydimethylsiloxane (PDMS) Copolymer Scaffolds for Tissue Engineering, Ozgul Yasar-Inceoglu1, Andre A. Fatehi1, Sam Lloyd-Harry1, Samahe Shafeen1 and Ozlem Yasar2; California State University Chico, United States; 2The City University of New York, New York, United States

The merging studies of innovative engineering and cell biology offers promising results for the repair and replacement of human tissues. The field of tissue engineering aims to address critical challenges in the medical field and to further advance research in the biomedical industry. Previous studies have shown engineered tissue scaffolds to degrade over time. Therefore, more research must be conducted on scaffold reliability and breakdown over time, to further understand the limitations of engineered materials inside the human body. This study examines the degradation effects on the mechanical properties of polyethylene glycol diacrylate (PEGDA) and polydimethylsiloxane (PDMS) copolymer scaffolds submerged in a Phosphate-Buffered Saline (PBS) solution. PBS has been shown to mimic the environment of the human body in previously published studies. The characterization of the copolymer scaffolds was executed by performing Raman Spectroscopy, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Fourier Transmission Infrared Spectroscopy (FTIR). Equilibrium Swelling testing was conducted by submerging samples in water over 15 minutes. Compression testing was conducted utilizing a Q5 50 Universal Testing Machine at a rate of 0.75 mm/min. The tests performed on the degraded copolymer samples were also conducted on non-degraded copolymer, degraded PEGDA, and non-degraded PDMS samples. The results of all samples were compared to understand the effects of degradation on the mechanical properties of copolymer scaffolds.

SESSION SB05.10: Engineered Materials for Organ Interfaces
Session Chairs: Philipp Gutruf and John Ho
Thursday Morning, April 25, 2024
Room 434, Level 4, Summit

10:00 AM *SB05.10.01
Engineering Conducting Polymer Hydrogels for Additive Manufacturing and Biointerfaces, Alexandra Rutz; Washington University in St. Louis, United States

Hydrogels are insoluble polymer networks swollen with water (>90% water by mass) and are used widely in biomedical applications for their similarities to native extracellular matrix. For bioelectronics, there are many efforts to build devices based on these materials to achieve tissue-matching stiffness and other tissue-inspired properties in order to improve the biointerface. For making electrodes and other device components based on semiconducting materials, conjugated polymers can be gelled into electronically conducting hydrogels. Such methods include simple mix-and-cast techniques, similar to other methods used widely in traditional (non-conducting) hydrogel processing. We have investigated conducting hydrogels based on the conjugated polymer poly(3,4-ethylenedioxythiophene) polyethylene sulfonate (PEDOT:PSS) fabricated by mixing in a gelling agent, ionic liquid. We have studied how the hydrogel precursor formulation and other fabrication variables of this method affect gel properties, such as swelling, conductivity, and elastic modulus. Further, we have evaluated the potential of these PEDOT-PSS hydrogels for biointerface applications and have found that these gels when processed appropriately are stable in vitro and support mammalian cell culture. Finally, we are developing these conducting polymer hydrogels for compatibility with additive manufacturing to grant structural control of these soft biologic interfaces. Such techniques provide manipulation of dimensions and microporosity, important for assembling these hydrogels into functional devices and optimizing tissue integration.

SESSION SB05.11: Central Nervous System Interfaces III
Session Chairs: Philipp Gutruf and John Ho
Thursday Morning, April 25, 2024
Room 434, Level 4, Summit

10:30 AM *SB05.11.01
Seeing the Sound: An Ultrasound-Mediated Intravascular Light Source enabled by Colloidal Mechanoluminescent Materials, Guosong Hong; Stanford University, United States

Light is used in a wide range of methods in biology and medicine, such as fluorescence imaging, optogenetics, photoactivatable gene editing, photothermal and photodynamic therapies to treat cancers, and photochemotherapy to inactivate viruses in vivo. A critical challenge of applying light in vivo, such as deep-brain optogenetic neuromodulation and photochemotherapy in deep organs, arises from the poor penetration of photons in biological tissue due to scattering and absorption. Therefore, delivering light deep into the body requires invasive procedures, such as the insertion of optical fibers and endoscopes, as well as surgical removal of overlying tissues. The very invasiveness of these procedures also precludes easy repositioning and volume adjustment of the illuminated region in the same subject. To address these challenges, our lab has developed an ultrasound-mediated intravascular light source, leveraging the deep-tissue penetration of focused ultrasound. We capitalized on mechanoluminescent nanotransducers (MLNTs), which are colloidal nanoparticles of mechanoluminescent materials synthesized via a biomimeral-inspired suppressed dissolution approach. These MLNTs can be delivered intravenously into blood circulation and emit light locally at the ultrasound focus. Owing to the deep penetration and fast temporal kinetics of ultrasound, we have demonstrated that this method can produce on-demand and dynamically programmable light emission patterns at elevated depths in different organs of live mice with millisecond precision. This ultrasound-mediated intravascular light source has allowed us to perform noninvasive “sono-optogenetic” neuromodulation in live mice, as well as brain-wide “scanning optogenetics” that activate different brain regions of the same mouse brain. Our development of the ultrasound-mediated intravascular light source has been published in PNAS (2019), Science (2020), Science Advances (2022), JACS (2023), and Nature Protocols (2023).

11:00 AM *SB05.11.02
Neural Interfaces to Human Organoids Designed for In Vitro and In Vivo Studies, Dayuuya Kuzum and Madison Wilson; University of California, San Diego, United States

Human cortical organoids, three-dimensional neuronal cultures, are emerging as powerful tools to study brain development and dysfunction. However, chronic monitoring of structural and functional maturation of organoids is challenging due to limitations of existing technologies. Here, we will present the state of the art in neural interfaces for human brain organoids. We will discuss electrical and optical methods of interrogating neuronal organoids in vitro and in vivo configurations. We will present multimodal data analysis for longitudinal monitoring of neuronal activity in the organoids and the surrounding neuronal circuits. We will highlight future applications of in vivo transplantation of human organoids for comprehensive evaluation of the development, maturation, and functional integration of neuronal networks.

11:30 AM *SB05.11.03
Flexible, Scalable, High Channel Count Stereo-Electrode for Recording in The Human Brain, Shadi A. Davely; Integrated Electronics and Biointerfaces Laboratory, United States

Over the past decade, stereoelectrodes placed in the content of deep brain electrodes commonly known as the stereoencephalography (SEEG) electrodes, are limited in their spatial resolution and ability to record from small populations of neurons, let alone individual neurons. Here, we will discuss a novel, customizable, thin-film (polyimide) human-grade flexible depth electrode with platinum nanorod contacts that is capable of
recording and stimulation at a depth of 10 cm in brain tissue, an electrode referred to as the UCSD microSEEG electrode. This 15μm thin, stylet-guided depth electrode is capable of recording local field potentials and single unit neuronal activity (action potentials), validated across species including humans. This device represents an advance in manufacturing and design approaches which extends the capabilities of a mainstay technology in clinical neurology.

**SESSION SB05.12: On-Demand Presentation**

**Thursday Morning, May 9, 2024**

**SB05-virtual**

10:30 AM SB05.12.01

Electromechanical Analysis of Silicon Nanomembrane Based Bendable MOS Capacitors with Ultrathin Nanolaminated Encapsulation

Chen Liu, Zhuofan Wang, Hongliang Lü, Yunming Zhang, Haonian Zhang, Shiyuan Cheng and Yi-Men Zhang; Xidian University, China

Flexible silicon nanomembrane (Si NM) based active implants as advanced biomedical electronics are essential for futuristic applications in sensing, healthcare, and human-machine interfaces. The development of thin-film encapsulation with excellent mechanical robustness and conformability is indispensable for ensuring the long-lived operation of Si NM based functional devices in a biological environment. Here, the electrical properties have been investigated on Si NM based metal-oxide-semiconductor capacitors (MOSCAPs) encapsulated with ultrathin Al2O3/alucone nanolaminates under mechanical strain conditions. As illustrated in the capacitance-voltage curves under mechanical-bending stress, the variation of the accumulation capacitance ($C_{acc}$) is observed to be lower than 1 % at both inward and outward bending radii of 85 mm and 38.5 mm compared with the planar condition for the encapsulated MOSCAP with a gate area of 0.02 mm$^2$, respectively. However, the corresponding reductions of $C_{acc}$ are approximately 2 % and 4 % for the bare device with the same gate area. Up to 4 % and 26 % reduction in the accumulation capacitance have been measured for the encapsulated MOSCAP with a gate area of 0.08 mm$^2$ at a bending radius of 85 mm under tensile stress and 38.5 mm under compressive stress, respectively. Furthermore, the relevant reductions of $C_{acc}$ are promoted to 9 % and 36 % for the bare device with the same gate dimension. Suppression of the gate leakage current has also been observed clearly for the encapsulated Si NM based MOSCAPs with an active area of 0.08 mm$^2$ compared with bare devices during bending, while the phenomenon could not be found for the devices with smaller gate areas. These findings demonstrate the great potential of nanolaminated films of Al2O3/alucone as the excellent encapsulation. It is also noted that a comprehensive study of the impact of the device gate area on the electromechanical properties will be beneficial to optimizing the scalable layout for achieving high mechanical reliable and high-performance flexible Si NM based MOSFETs to create the next-generation bioelectronic implants.

**SYMPOSIUM SB06**

Biohybrid Materials and Devices for Sensing, Robotics, Energy and Biomedicine

April 23 - May 9, 2024

**Symposium Organizers**

Neel Joshi, Northeastern University
Eleni Stavrinidou, Linköping University
Bozhi Tian, University of Chicago
Claudia Tortiglione, Istituto di Scienze Applicate e Sistemi Intelligenti

**Symposium Support**

Bronze
Cell Press

10:30 AM *SB06.01.01

Functional Neurological Restoration of Amputated Peripheral Nerve Using Biohybrid Regenerative Bioelectronics

Damiano Giuseppe Barone; University of Cambridge, United Kingdom

The development of neural interfaces with superior biocompatibility and improved tissue integration is vital for treating and restoring neurological functions in the nervous system. A critical factor is to increase the resolution for mapping neuronal inputs onto implants. For this purpose, we have developed a new category of neural interface comprising induced pluripotent stem cell (iPSC)–derived myocytes as biological targets for peripheral nerve inputs that are grafted onto a flexible electrode array. We show long-term survival and functional integration of a biohybrid device carrying human iPSC-derived cells with the forearm nerve bundle of freely moving rats, following 4 weeks of implantation. By improving the tissue-electronics interface with an intermediate cell layer, we have demonstrated enhanced resolution and electrical recording in vivo as a first step toward restorative therapies using regenerative bioelectronics.

11:00 AM SB06.01.02

Skin-Preparation-Free, Stretchable Microneedle Adhesive Patches for High-Fidelity Electrophysiological Sensing and Exoskeleton Robot Control

Hesseo Kim, Jihyun Lee, Ung Hoo, Dhileep K. Jayashankar, Karen-Christian C. Agno, Yeji Kim, Choong Yeon Kim, Youngjin Oh, Sang-Hyuk Byun, Bohyung Choi, Hwayeong Jeong, Woon-Hong Yeo, Zhuo
Bioadhesive and Immune-Compatible Polymer Bioelectronics
1:30 PM early monitoring of GI cancers.

S.B06.01.03
Hydrogel Interfaces for Merging Humans and Machines
Xuanhe Zhao
Massachusetts Institute of Technology, United States
The last few decades have witnessed unprecedented convergence between humans and machines that closely operate around the human body. Despite these advances, traditional machines made of hard, dry, and abiotic materials are substantially dissimilar to soft, wet and living biological tissues. This dissimilarity results in severe limitations for long-term, reliable and highly efficient interfacing between humans and machines. To bridge this gap, hydrogels have emerged as an ideal material candidate for interfacing between humans and machines owing to their mechanical and chemical similarities to biological tissues and the versatility and flexibility in designing their properties. In this talk, I will provide a comprehensive summary of functional modes, design principles, and current and future applications for hydrogel interfaces towards merging humans and machines.

S.B06.01.04
An Electroadhesive Hydrogel Interface for Prolonged Gastrointestinal Theranostics
Binbin Yang, Kewang Nan, Qing Zhu, Tom Khur, Hana Ro, Sophia Qin, Shubing Wang, Karen Jiang, Yonglin Chen, Guangyu Bao, Joshua Jenkins, Andrew Pettinari, Johannes Kuosmanen, Keiko Ishida, Niora Fabian, Jason L., Alison Hayward, Robert Langer, Giovanni Travero, Massachusetts Institute of Technology, United States; Brigham and Women’s Hospital, United States; Zhejiang University, China; Zhejiang Pharmaceutical University, China; McGill University, Canada
Establishing a robust and intimate mucosal interface that allows medical devices to remain for extended periods is valuable for theranostic purposes. However, achieving this goal has proven extremely challenging, particularly within the gastrointestinal (GI) tract. Here, we report the development of e-GLUE, an electroadhesive hydrogel interface for robust and prolonged mucosal retention following electrical activation. Notably, this novel mechanism can amplify the adhesion performance on the mucosa by up to 30-fold and extend in vivo GI retention of e-GLUE devices for up to 30 days. Strong mucosal adhesion occurs within one minute of electrical activation, despite the presence of luminal fluid, mucus exposure, and organ motility, thereby ensuring compatibility with complex in vivo environments. In swine studies, we demonstrate the utility of e-GLUE for instantaneous mucosal hemostasis, sustained local delivery of therapeutics, and device adhesion for up to 30 days. In vivo studies further show that e-GLUE can provide continuous mucosal adhesion over prolonged time periods.

S.B06.02.01
Bioadhesive and Immune-Compatible Polymer Bioelectronics
Shihong Wang
University of Chicago, United States
The use of bioelectronic devices for acquiring biological information and delivering therapeutic interventions relies on direct contact with soft bio-tissues. To ensure high-quality signal transductions, the interfaces between bioelectronic devices and bio-tissues must combine signal amplification with stable and conformable contact. Semiconductor-based devices (e.g., organic electrochemical transistors) have been developed as one of the most advanced technologies for high-performance bio-sensing. However, the rigid mechanical properties and the lack of tissue/skin adhesion from transistors largely prevent the formation of such intimate and long-term stable bio-interfaces. Also, immune-mediated foreign-body response (FBR) stands as the most widely existing challenge, which can lead to the growth of fibrotic tissue at the tissue-device interface. In this talk, I will introduce our material and device designs for introducing tissue-adhesive properties onto transistor-based biosensors. Then, to combat FBR, I will introduce a set of molecular design strategies for enhancing the immune compatibility of semiconducting polymers. I will also introduce the strategies and advantages of using these new biomimetic properties in bioelectrical and biochemical sensing.

S.B06.02.02
Biointerface Materials for Reliable and Conformable Integration of Electronics into Living Tissues
Anna-Maria Pappa
Khalifa University, United Arab Emirates
The development of micro-electronic devices that bridge the gap between traditional electronics with biological systems is highly desirable. The emergence of highly conjugated polymers has opened up exciting directions in biomedical research including point-of-care diagnostics. With the ultimate goal of fully integrated wearable sensors combined with IoT, and that of autonomous at-home diagnostic tests, organic bioelectronic technologies have been heavily explored the past decade resulting in novel device configurations. Multiplexing capability, ability to adopt to complex performance requirements in biological fluids, sensitivity, stability, literal flexibility and compatibility with large-area processes are only some of the merits of conjugated polymers for point of care diagnostics. This talk will summarize our recent efforts on developing biosensors for health monitoring, on rigid and flexible substrates leveraging the potential of conjugated polymers towards next generation point of care sensors.

S.B06.02.03
Organic Electronic Point-of-Care Devices as Drivers of Precision Medicine
Anna-Maria Pappa
Khalifa University, United Arab Emirates
The development of micro-electronic devices that bridge the gap between traditional electronics with biological systems is highly desirable. The emergence of highly conjugated polymers has opened up exciting directions in biomedical research including point-of-care diagnostics. With the ultimate goal of fully integrated wearable sensors combined with IoT, and that of autonomous at-home diagnostic tests, organic bioelectronic technologies have been heavily explored the past decade resulting in novel device configurations. Multiplexing capability, ability to adopt to complex performance requirements in biological fluids, sensitivity, stability, literal flexibility and compatibility with large-area processes are only some of the merits of conjugated polymers for point of care diagnostics. This talk will summarize our recent efforts on developing biosensors for health monitoring, on rigid and flexible substrates leveraging the potential of conjugated polymers towards next generation point of care sensors.

S.B06.02.04
Printable, Soft and Stretchable Conductor-Based Sensors for Human Body Interface
Tao Zhou
The Pennsylvania State University, United States
Soft and stretchable electronics have garnered significant attention owing to its wide range of applicability. The versatility of this technology has resulted in its utilization across multiple fields, such as soft robotics, skin-integrated electronics, biomedical devices, flexible displays, and human-machine interfaces. Here we present a hybrid material based on hydrogel and metal particles that simultaneously possesses high conductivity, stretchability, tissue-level modulus (~10 kPa), as well as 3D printability. This novel material was further applied to develop devices that can interact with the human body for motion sensor and EMG signal acquisition device, demonstrating huge potential for sensors and biomedical devices.

S.B06.02.05
Organic Semiconductors for Regenerative Medicine—Optical Modulation of the Cell Fate
Maria Rosa Antognazza
Istituto Italiano di Tecnologia, Italy
Use of light for selective and spatio-temporally resolved control of cell functions (photoceutics) is emerging as a valuable alternative to standard electrical and chemical methods. Here, we...
AI-Driven Cyborg Tissue Platform for Functional Maturation of Human Stem Cell-Derived Organoids

Inkyu Lee1, Abhijith Surendran2, Samantha Fleury3, Ian Gimino1, Cody Fell3, Alexander Curtiss2, Daniel J. Shiwarski1, Omar Refy1, Blaine Roithrock2, Seonghan Jo1, Tim Schwartzkopf1, Abijeet S. Mehta2, Yingqiao Wang1, Adam Sipe3, Sharon John1, Xudong J2, Georgios Nikiforidis3, Adam Feinberg2, Josh Halter3, Douglas J. Weber2, Omid Veiseh2, Jonathan Rivnay2 and Tzahi Cohen-Karni1

1Carnegie Mellon University, United States; 2Northwestern University, United States; 3Northwestern University, United States; 4Purdue University, United States; 5Tianjin University, China; 6The Pennsylvania State University, United States; 7Georgia Institute of Technology, United States

Implantable cell therapies have been investigated as an promising approach for tissue defects that require consistent therapy. However, oxygen insufficiency can be a key challenge. To address oxygen deficiency and support cells and tissues, exogenous oxygen delivery has been studied. While targeted gas circulation and decomposition of peroxides were employed for pancreatic islets and engineered therapeutic cells, however, they require bulky implants and transcutaneous supply lines, and are limited in oxygen production and its regulation.

Here, we report an electrocatalytic on-site oxygenation (ecO2) platform that enables controlled bioelectronic oxygen production in physiological environments to maintain cell viability and therapeutic functionality of human-induced pluripotent cells under hypoxic stress. Nanostructured iridium oxide serves as an electrocatalyst for oxygen evolution reaction in neutral pH. It enables a low oxygen evolution onset and generates stable oxygen generation without deleterious by-products over a 300 mV window of operation. ecO2 is capable of maintaining high cell loading (>60k cell/mm3) in hypoxia in vitro and in vivo. We demonstrate that the exogenous oxygen-generating device can be readily integrated into bioelectronics and accomplishes high loadings in miniaturized form factor. Our ecO2 platform can be deployed in broad bioengineering applications in cell therapies for chronic disease management.

5:00 PM SB06.03.01

Photosynthetic vs Photovoltaic Efficiency of Limnospira Indica, Perspective Cyanobacteria Strain for Space Mission Live Support Systems

Nikolay Ryzhkov1, Nora Colson2, Essraa Ahmed2, Paulius Pobedinsky2, Ken Haenen2, Paul Janssen and Artur Braun2

1Empa, Switzerland; 2Hasselt University, Belgium; 3SCK CEN, Belgium

Due to their excellent photosynthetic capability, which can be directly and efficiently applied in O2 generation, CO2 utilization, food and chemical production, as well as the photosynthetic production of fuels, cyanobacteria are being utilized by space agencies to establish life support systems in future space stations, planetary stations, and long-haul space missions [1]. In the harsh conditions of space, the use of live cyanobacteria is preferred over cellular components because cyanobacteria can adapt to and cope with stress, including ionizing radiation, enabling long-term autonomous operation.

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Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Hydrogel Variability in Drug Delivery: Balancing Mechanical Stress and Stimuli-Responsiveness

Hydrogels have garnered significant attention as eco-friendly, renewable soft materials in the context of achieving Sustainable Development Goals (SDGs). These hydrogels can be broadly categorized into two types based on the formation of the crosslinked gel network that holds water molecules: those held together by covalent bonds and those formed through non-covalent processes. Covalently bonded hydrogels exhibit robust mechanical properties, including tensile strength, viscosity, and elasticity, while non-covalent bond-based hydrogels offer the advantage of responsiveness to external stimuli. Specifically, hydrogels assembled through non-covalent molecular aggregates can be precisely tailored to achieve ordered structures and diverse functionalities, making them promising candidates for advanced intelligent drug delivery systems (DDS).

When hydrogels are employed in DDS applications, the preservation of their shape until they reach the target site, serving as carriers for model drugs, necessitates substantial mechanical functionalities, making them promising candidates for advanced intelligent drug delivery systems (DDS).

In conclusion, the ZIF-8@FePt nanorobots under RF stimulation herald a new era in drug delivery, merging materials science, nanotechnology, and medicine. While preliminary results are promising, comprehensive clinical trials are imperative for their transition from a theoretical model to a medical mainstream. This exploration marks a significant stride toward personalized, precision medicine, potentially revolutionizing healthcare paradigms.
Bimetallic nanoparticles (NPs) have been attention as attractive electrode materials owing to their unique and synergetic properties in many fields, especially in healthcare sensing platforms. Among them, Au-Pt bimetallic nano-clusters (NCs) are considered to be superior for their marked catalytic activity. We have confirmed this by comparing these bimetallic nanoclusters with dendritic Au (DenAu) NPs in glucose sensing applications. 

Since high standards for sensing devices are required, a highly selective and accurate detection with utmost selectivity are primary concerns, the demand for materials with exceptional catalytic activity has been raised. Furthermore, low power consumption and quick response time for glucose measurement are highly desirable. Herein, we have fabricated the sensor by co-depositing the Au-Pt NCs onto the patterned seed Au layer at optimal agitation rates and applied potential, it was characterized by its properties (interfacial impedance, cyclic voltamogram, and response to the various glucose concentrations) compared to DenAu. During electrochemical deposition, the optimal growth conditions for Au-Pt NPs and DenAu were -0.1 V for 1000 sec (stirring rate of 1000 rpm) and -0.07 V for 400 sec, respectively, which were relatively low potential as well as fast deposition time.

As a result, the sensor with Au-Pt NCs and DenAu showed remarkably high charge density yields of 309.21 μA/cm² and 73.74 μA/cm², respectively, while the sensor with plane Au electrode exhibited a charge density yield of 2.37 μA/cm². Moreover, they showed extremely enhanced interfacial impedance values of 1.3 Ω (Au-Pt NCS), and 5.6 Ω (DenAu) at 0.1 Hz compared to the Pt electrode with Ohmic contact 92.5 kΩ respectively. Although, both sensors are considered to be an optimal candidate for the highly catalytic glucose detection.

By virtue of the heightened catalytic activity of bimetallic NCs, our sensor with Au-Pt (NCs) could detect various concentrations of glucose at a wide range from 1 to 10000 μM without any use of a mediator. While considering the sensitivity and limit of detection (LOD), Au-Pt nano-clusters (NCs) exhibit exceptional sensitivity of 1715.46 μM M⁻¹cm² and a very low limit of detection of 1.5 μM, comparatively, DenAu shows 678μM M⁻¹cm² sensitivity and 6 μM limit of detection.

In the near future, the Au-Pt bimetallic nano-clusters (NCs) will be integrated into various sensing platforms (e.g., immuno-sensing, fuel-cell application, and electro-chronic system application, etc.), and their practical feasibility will be investigated.

5:00 PM SB06.03.12
Self-Assembly Sugar-Linked Nucleic Acid Nanoparticle for Nucleic Acid Medicine Delivery Noriko Miyamoto and Yukio Kitade; Aichi Institute of Technology, Japan

DNA- or RNA-based nucleic acid structures (NASs) have garnered significant interest as potential carriers for nucleic acid medicine delivery due to their ability to create unique sequence-based structures. However, for the biological application of NASs, it is still challenging to create a nanostructure that is stable and avoidance of recognition as an immunogenicity under physiological conditions.

We have developed a novel type of NAS called RION (reversibly ionic oligonucleotide-based nanoparticles including microRNAs) through a self-assembly process involving RNA-RNA hybridization and electrostatic interactions facilitated by chemically modified oppositely charged ion oligonucleic acids [Miyamoto N., et al., Advanced Therapeutics 2023, 6, 2200265]. In this research, we demonstrate the versatility of the chemical modification of RION, we designed a sugar derivative linked to RIONS. The sugar derivative-linked RION nanoparticles exhibit a spherical shape with a diameter of less than 100 nm, as observed in transmission electron microscopy images. Moreover, we found that sugar derivative-linked RION, when loaded with tumor suppressor microRNA, effectively inhibits the growth of human colorectal cancer cells (DLD-1 cells) in a dose-dependent manner. On the other hand, the sugar derivative-linked RION demonstrated transfection efficiency in a floating cancer cell line, a well-known difficult transfection with commercialized Lipofection regents. This report introduces RION technology as an innovative platform for delivering nucleic acid-based medicines, offering promising potential for applications in the field of cancer therapy and beyond.

5:00 PM SB06.03.13
Modifying Bio-Ingredients within an Integrated Food Printer using In-Situ Corona Discharge Non-Thermal-Plasma Approach: A Step Toward Creating Innovative Methods for Characterizing Engineered Food Materials and Biomedicine Kaiyu Vang1, Derek Xiong3, David Ryman1, Edbertho Leal-Quiros5, Saquib Ahmed1,2 and Sankha Banerjee1,4; 1California State University, Fresno, United States; 2University of California, Merced, United States; 3Buffalo State College, United States; 4University of California, Davis, United States

The present research is focused on pioneering new in-situ non-thermal plasma treatment methods for 3D printed bio-ingredients based on starch. Thanks to its natural abundance and cost-effectiveness, starch emerges as a highly pertinent raw material for substituting synthetic polymers in various applications. It enjoys a reputation for being non-toxic, biocompatible, and biodegradable, making it a secure choice for applications in the biomedical, food, and packaging sectors. Utilization of starch as a foundation for stabilizing, integrating, or releasing bioactive substances with applications as bioactive compounds incorporated within starch matrices in the pharmaceutical industry, with a particular emphasis on their use in orally disintegrating films. These methods aim to customize the attributes of the starch granule-surface proteins (SGSP). The study also involves assessing continuous and discontinuous gluten networks formed due to the interaction of SGSPs with quasi-static corona discharge plasma conditions. Additionally, the research investigates the bonding characteristics of starch-based bio-ingredients based on plasma current-voltage behavior. The surface of the cured starch-based samples will undergo profiling for characterization. The binding properties, gluten network formation, and porosity characteristics will be examined through electron microscopy for microstructural evaluation. Furthermore, advanced hybrid machine learning models will be developed in conjunction with analytical techniques and empirical models to create data-driven strategies for modifying both the surface and bulk properties of these materials.

5:00 PM SB06.03.16
An Open-Source Droplet Digital PCR (ddPCR) System for the Rapid and Accurate Detection of Bacteria from Environmental Water Samples Mason Brady, Jan M. Van Horn, Donald Ledvina, Albert Burkle, Paula Sanchez, Yiyun Li, Jerry Crawford, Micheal Grubb and Christie Chatterly; Fort Lewis College, United States

Droplet Digital PCR (ddPCR) is a method of rapid bacterial quantification in a liquid culture or solution. The development of an open source ddPCR system will allow this technology to become more affordable. The open-source ddPCR system utilizes reused optical components, including a Photomultiplier Tube (PMT) from a flow cytometer, aligned using optical fittings. The signals received from the PMT were passed through a circuit containing passive bandpass filters and amplifier stages. FITC fluorescent microspheres were used to test the potential of the ddPCR system. The system was characterized by its properties A/cm² and 73.74 μA/cm² sensitivity and 6 μM limit of detection. Since high standards like a broad range and a low limit of detection with utmost selectivity are primary concerns, the demand for materials with exceptional catalytic activity has been raised. The development of an open-source ddPCR system utilized reusable optical components, including a Photomultiplier Tube (PMT) from a flow cytometer, aligned using optical fittings. The signals received from the PMT were passed through a circuit containing passive bandpass filters and amplifier stages. FITC fluorescent microspheres were used to test the potential of the ddPCR system. The system was characterized by its properties A/cm² and 73.74 μA/cm² sensitivity and 6 μM limit of detection.

5:00 PM SB06.03.17
Potassium Hydroxide Etched Silicon Biomembrane Optimization and Characterization for Lung-on-a-Chip Applications Sahra G. Genc1, Leif Gislason2, Sally Thompson1, Sarah M. Schreiner3, Adrian Gestor4, Virginia Ferguson4 and Jeff Jessing1; 1Fort Lewis College, United States; 2STROBE NSF, United States; JILIA, University of Colorado Boulder, United States; 4University of Colorado Boulder, United States

Organ-on-a-chip technology is heavily studied as an alternative to animal and cell culture models. Most of these studies are primarily focusing on the biological aspects. There is a need to understand the mechanical and morphological properties and functionality of critical components of such devices. Our group is developing a Lung-on-a-Chip device based on a novel biomembrane formation method, with a thickness of approximately 1 µm. The membranes are fabricated through a process of chemical thinning p-type silicon wafers and electrochemical anodization to create the porous structure. Previously published results from our group on membranes that did not undergo the chemical thinning characterized with nanoindentation and scanning electron microscopy show a correlation between the porosity of the PSI samples with their reduced modulus and thickness. This current work focuses on the development and refinement of the technique used to etch ultrathin (less than ~5μm) silicon membranes using a potassium hydroxide (KOH) etchant. Further, we show the results of a small parametric study by varying the formation conditions during the KOH etch. The specific formation conditions that affect the resultant membrane surface quality are etch temperature, inclusion of a surfactant, and post-etch quench "rinse". The membranes mechanical and morphological traits are characterized using scanning electron microscopy, atomic force microscopy, and nanoindentation to discern the surface quality of the silicon biomembrane, considering parameters like roughness, defect density, and uniformity. These aspects are correlated to the different KOH process parameters to find the optimal approach, as well as its potential relationship with the membrane's morphological features. In general, the surface quality and membrane thickness uniformity improves with decreasing etch temperature, inclusion of propanol as a surfactant, and employing a multiple stage hot rinse following the KOH etch.
entirely out of hydrogel resulting in a fully soft joint. After printing and mechanically analyzing the joints by nanindentation measurements, the thermoresponsive actuation was evaluated by switching the ambient temperature between temperatures below and above the LCST of PNIPAM. In the future, the design of the soft joints may be improved to give more complex structures with sophisticated functionalities on the microscale.

5:00 PM SB06.03.21
3D Printing Conductive Hydrogels with Tunable Properties for Soft Robotics and Biosensing Trevor Kalkus, Tamara Unterreiner, Laura Wächter, Christina Schmitt and Christine Selhuber-Unkel; Heidelberg University, Germany

Soft electronics can serve a central role in the development of biosensors, wearable devices, and soft electronics. For these applications, flexible circuits with complex and organic geometries will be necessary. The 3D printing of conductive hydrogels offers a simple manufacturing method for creating such structures and provides opportunities for rapid iteration and modification. Because different applications may call for various hydrogel properties, we demonstrate the ability to tune ink viscosity, hydrogel stiffness, and hydrogel conductivity. These functional hydrogels are based on acrylamide, due its stability and ubiquity, and PEDOT-PSS, a commonly used conductive organic polymer, is embedded to provide conductivity. With thorough characterization, we highlight the advantages of designing conductive hydrogels in this way. Ultimately, we demonstrate the ability to print the components suitable for soft electronics. While this work provides a preliminary demonstration, future steps will focus on applying this method to create biosensors and soft robotics.

5:00 PM SB06.03.22
Electrochemical Sensing of Cytokines Utilizing Carbon Nanotube Fiber-Based Electrodes Megan N. Baker1,2, Allison Yoria2, Anna Ivanovskaya2, Razi haque2 and Samantha Santana2;
1The University of Texas at Austin, United States; 2Lawrence Livermore National Laboratory, United States

Aptamer based biosensors are a promising tool for further understanding various mechanisms underlying the body at a molecular level. Aptamers allow for indirect electrochemical sensing of chemical biomarkers and biomolecules. As a specific target molecule binds to the aptamer, there is a conformation change. Scientists have taken advantage of this conformation change and designed aptamers that bring the charged free end closer to the surface of an electrode, sensing an electrochemical change in response to the chemical concentration. However, the binding of aptamers to the surface of metal electrodes has shown to be very fragile, making the lifespan of such biosensors limited. For in vivo and even future clinical applications, the devices need to be stable both in and out of solution for long periods of time. We propose utilizing carbon nanotube fibers (CNT) to improve the adhesion of aptamers to the surface of electrodes. CNTs have great chemical stability, electrical properties, and high effective surface area making them ideal candidates for the substrate of the device. The chemical bond between carbon and the aptamers is more stable than that with gold, a biocompatible electrode material, allowing for a more stable device. To test this device design, we use aptamers that selectively bind to IL-6. The IL-6 aptamers are immobilized and attached to the CNT electrode using electrochemical conjugations. After successful attachment has been validated, the sensitivity of the device and limit of detection are evaluated and optimized. After optimization, the response time, lifetime, and biofouling response are analyzed. This is initially done in phosphate buffered saline (PBS) solution, but further testing in animal models is planned. The functionalized device can be used to decode immune status in blood using pro- and anti-inflammatory cytokines at physiologically relevant concentrations. This opens the door to being able to monitor and intervene in the immune system using bioelectronic interfaces, with the CNT sensor recording real-time immune system status and a future electrical interface with the nervous system modulating the immune system based on data from the sensor, a systems-level approach which has not been done before.

5:00 PM SB06.03.23
Continuous Whole Blood Dialysis Based on Regenerated Dialysate Utilizing TiO2 Nanowire Photo-Electrochemical Oxidation and Protective Forward Osmotic Membrane Guozheng Shao, Mineyuan Zhang, Hao Tang and Bruce Hinds; University of Washington, United States

While a traditional 4-hour dialysis treatment uses up to 120L of fresh dialysate per session, a full-scale bench-top system was developed to remove clinically relevant amounts of uremic toxins in whole blood using only 0.5L of commercial dialysate per 24-hour continuous dialysis process. Urea was removed by photoelectrochemical method through a UV/TiO2 nanowires array device connected to a Forward Osmosis (FO) membrane in a protected close loop, while other non-urea toxins were removed by Activated Carbon (AC) in the dialysate loop. Here we demonstrate a daily urea removal rate of 14.2g using 0.4m2 of hemodialyzer membrane and 2.3m2 FO membrane with 0.18m2 TiO2 nanowires array in Photoelectrochemical Oxidative Urea Removal (POUR) unit. Other non-urea toxins represented by creatinine and phenylacetic acid with a daily removal rate of nearly 7g were achieved by 70g of AC absorbent in the dialysate loop. Urea, creatinine and phenylacetic acid were constantly infused into the saline solution with the speed of 1.5g/24h, 5.6g/24h and 1.4g/24h to simulate actual human toxins level. Urea is continuously removed in a 0.15M NaCl saline solution by the photo-oxidation reaction occurring on TiO2 nanowire surface with the presence of UV source and applied bias to enhance the electron-hole pair separation within the single crystal TiO2 nanowire. The POUR loop was also protected from the potential oxidative species generated from the photooxidation of urea by inline AC absorber with real-time ORP and pH sensors, showing non-cytotoxicity to the blood loop. The FO membrane is also a key component to prevent small solute molecules from dialysate entering the POUR loop to lower its efficiency as well as forming harmful oxidative byproducts. Our results also showed a wide variety of treatment modes (ie. 4, 8, 12 hr daily times) by coupling different membrane components. More importantly, by eliminating the need for the external water source, our system offers possibilities of a variety of portable kidney dialysis treatment options for home, work and travel.

5:00 PM SB06.03.24
Characterization of Single and Dual-Consortium Microbial Systems in 3D-Printed Multi-Material Hydrogels LeAnn Le, Alshakim Nelson and Naraa Sadaba; University of Washington, United States

Engineered Living Materials (ELMs) capture the efficiency of cellular systems within polymeric matrices to provide bioelectric designs for production of commodities such as biofuels, vaccines, and the classic Seattle IPA. With extrusion-based 3D printing, we can print multi-material ELMs that afford controlled spatial organization of cell populations. With F127-bisurethane methacrylate (F127-BUM), an easily accessible triblock copolymer, we can synthesize bioinks with proper yield strain for extrusion-printing while also gaining robust biocompatibility and free diffusion of metabolites across the material. We maintain a basic understanding of F127-BUM structure but have limited knowledge of how the network interacts with cells. While these hydrogel constructs display robust metabolic function, prior studies have shown cells escaping into the surrounding media despite complete encapsulation, suggesting random migration through the material. However, in studies that culture two microbial species in adjacent F127 gels, higher-order spatial organization is observed as cell populations consisting of one species do not migrate into gel areas occupied by another cell species. In our studies, we propose an alternative 3D-printed core-shell cube structure that consists of a cell-laden inner core surrounded by a cell-free outer shell. This construct affords a model to study cell behavior of single and dual-cell consortiums in F127-BUM hydrogels as we seek to improve cell containment and preserve metabolic function in 3D printed hydrogel designs for bioproduction.

Using the core-shell cube structure, we demonstrated robust multi-domain functionality with Green Fluorescence Protein (GFP)-secreting E. coli and betaxanthin-producing S. cerevisiae. After six days, the multi-material constructs showed continuous GFP and betaxanthin production and diffusion into the media. Optical fluorescence microscopy showed GFP E. coli distribution focused on the core-shell interface while S. cerevisiae distribution is uniform throughout the core. Visual spatial separation between the core and the shell elements was maintained, cell escape after 48 h was observed using SEM as a result of microscopic inconsistencies in the printing process and cross-contamination of the extrusion nozzles during printing. By altering flow speed and the print design g-code, we improved cell containment.

To investigate impact of form factor on microbial behavior, we proposed a rectangular prism design with improved surface area-to-volume ratio to investigate the impact of geometric parameters on bioproduction and diffusion. We saw improvement in the GFP-system but observed little difference in our betaxanthin system. Additionally, we tested the performance of both core-shell constructs in co-culture systems by placing gels containing one cell population into free media containing a different microbial species. With the gel system, viability was maintained in both cell species for 6d.

Following the single consortia models, we expanded the core-shell design to contain a dual-microbial consortium. Inspired by symbiosis, this multi-domain hydrogel design contained a metabolically constitutive relationship consisting of engineered E. coli and S. cerevisiae strains. S. cerevisiae only produces betaxanthin in presence of L-DOPA.

During a six-day period, final betaxanthin production remained low as a result of the inner core consortia having limited access to oxygen as the outer shell consortia blocks nutrient access during overgrowth. As a result, we will adopt designs such as coaxial fibers or thinner dual-material biofilms to avoid limitations in oxygen and nutrient diffusion.

Overall, our investigation of multi-material F127-BUM hydrogels and their ability to afford a wide range of microbial systems and design possibilities establishes a necessary model to study the intricate relationship between hydrogel structure and cell behavior for bioproduction applications.

5:00 PM SB06.03.27
Micro-Vibrator Integrated Wet Adhesive Glycerogel Patch for Enhanced Transdermal Drug Delivery System Seo Yoon Kim1 and Byoung Soo Kim2; 1Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of); 2Korea Institute of Ceramic Engineering and Technology (KICT), Korea (the Republic of)
Transdermal drug delivery system (TDDS) is a painless method of delivering drugs by applying patches directly onto skin. Among the evolving variations of TDDS, hydrogel patches gaining prominence for its capacity to facilitate skin hydration and efficiently deliver pharmaceutical agents across the skin barrier. However, in order to facilitate commercialization, hydrogel-based patches need to effectively tackle three key challenges: (1) minimizing moisture evaporation, (2) enhancing adhesion in wet environments, and (3) precisely controlling the release dosage of the contained medication. Here, we introduce a novel glycerogel matrix that exhibits wet-adhesive properties, does not dry out, and possesses high toughness. This matrix is designed to facilitate prolonged skin contact and enhance the absorption of drugs. Next, the glycerogel matrix was combined with a micro-vibrator film in order to enhance medication penetration through the stimulation of skin microcirculation. The glycerogel matrix exhibits rapid adherence to various surfaces in a wet condition, with a time frame of less than 10 seconds. The strength of adhesion is influenced by the size and composition of the silica nanoparticles used for surface coating. We also confirmed the vibration-assisted drug release create a synergistic effect within the hydrogel, promoting efficient drug dispersion and enhancing skin penetration. This accelerates drug absorption and improves drug efficacy, resulting in faster drug release and shorter time to achieve therapeutic goals. We believe this synergistic integration of these components presents a novel paradigm in controlled drug release, allowing for precise modulation of therapeutic dosages.

Keywords: Tough hydrogels, bioadhesives, transdermal drug delivery, micro-vibration film, active drug delivery

5:00 PM SB06.03.28
Biocompatible WSe2 Nanosheet Antibiotics for the Therapy of Pathogenic Bacterial Infections Yoonhee So, Jun-Hyeong Lee, Jaewoo Lee, Sin Lee, Yejoo Yu, Yujin Choi and Jong-Ho Kim; Hanyang University, Korea (the Republic of)
Abuse of broad-spectrum antibiotics not only causes intestinal microbial imbalance but also emerges bacteria resistant to drugs. Therefore, it is an urgent task to develop narrow-spectrum antibiotics and new biocidal mechanisms to overcome the limitations of broad-spectrum antibiotics. Herein, we present ultrathin WSe2 and MoSe2 nanosheets exfoliated and functionalized with poly(acrylic acid) (PAA-WSe2 and PAA-MoSe2) in an aqueous solution as a narrow-spectrum antibiotic or a species-specific agent, respectively, for treatment of bacterial infection diseases. PAA-WSe2 nanosheets exhibited bactocidal activity only against gram-positive bacteria including multidrug-resistant S. aureus, whereas PAA-MoSe2 showed selective bactocidal activity against S. aureus only. Moreover, PAA-WSe2 accelerated the oxidation-reduction reaction mediated by lipoteichoic acid, a component of the cell membrane of gram-positive bacteria, producing Se4+ for antibacterial activity. Subsequently, the PAA-WSe2 nanosheets induced depeolarization and disruption of the bacteria-cytoplasmic membrane for the complete eradication of gram-positive bacteria. PAA-TMD nanosheets, including PAA-WSe2 and PAA-MoSe2 also exhibited outstanding biocompatibility against normal cells and hemocompatibility with red blood cells. Finally, PAA-WSe2 nanosheets effectively eradicated S. aureus infecting the wounds of mice, showing excellent therapeutic effects in vivo. These results suggest that PAA-WSe2 has been developed as a narrow-spectrum antibiotic used for various bacterial infections.

SESSION SB06.04: Living Materials I
Session Chairs: Eleni Stavrinidou and Claudia Tortiglione
Wednesday Morning, April 24, 2024
Room 427, Level 4, Summit

8:00 AM SB06.04.01
Microbial Encapsulation with Polyethylene-Glycol Based Hydrogel Materials for Protection Against Environmental Stress Factors Ryan Hansen, Niloufar Fattahi, Jeffrey Reed, Evan Heronemus, Priyasha Fernando and Prataparameswaran; Kansas State University, United States
Many emerging applications in microbial biotechnology require that microorganisms function under harsh or unfavorable environments. These environments may contain chemical toxins, reactive oxygen species, limited nutrients, extremes in pH and temperature, or exogenous microorganisms, among other stress factors. Microbial electrochemical cells (MECs), which use electroactive biofilms of anode respiring bacteria (ARB) for current production, are often limited by loss of ARB electrochemical activity due to these stress factors. This inhibits the use of novel MxC systems in applications related to water treatment, sub-surface remediation, remote sensing, and self-powered bio-batteries. In this work, we report the use of polyethylene-glycol (PEG) based hydrogel materials for encapsulation, stabilization, and toxin protection of ARB biofilms in a MxC system.

Hydrogels were formed using PEG divinyl sulfone and PEG tetraethal precursor molecules. These molecules couple together through base-catalyzed Michael addition reactions between thiol and vinyl sulfone end groups, generating highly crosslinked hydrogel networks with well-controlled, tunable mesh sizes. Precursor molecules were mixed together with anodic biofilms using an established dip coating procedure. The resulting hydrogels were resistant to acid or base hydrolysis over a range of pH values (pH = 3 to 10), appeared stable over ARB biofilms, and did not compromise biofilm viability over a 30-day trial period. The electrochemical activity of hydrogel-coated ARB biofilms was compared to uncoated ARB biofilms in a side-by-side manner, and it was found that the hydrogel coated anodes displayed higher current density under oligotrophic environments, higher current densities during exposure to high concentrations of ammonium toxin, and faster recovery after an ammonium shock. Hindered diffusion of ammonium ions through the hydrogel was identified as the cause for improved ARB performance during and after the ammonium shock.

These findings demonstrate the novel use of hydrogel materials to protect EAB from sharp chemical gradients that commonly occur during a chemical shock. Because hydrogel pore size can be modulated by controlling the molecular weights of the PEG precursor molecules, and catalytic functionality can be added to the hydrogel, these coatings can be further engineered to provide selective control of mass transport to functional microbres for their protection in a variety of applications. On-going work investigates enzymatic modification of these hydrogels to protect encapsulated bacterial cells from other chemical toxins for bioproduction and biomedicine applications.

8:15 AM SB06.04.02
Living Fabrications by the Engineered Bacteria Zhiquan Dai; Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, China
A key focus of synthetic biology is to utilize modular biological building blocks to assemble the cell-based circuits. Scientists have programmed the living organisms using these circuits to attain multiple delicate and well-defined functions. With the integration of tools or technologies from other disciplines, these rewired cells can achieve even more complex tasks. In this talk, we will present our recent work in versatile biommanufacturing of biogics and functional material fabrication by integrating the engineered cells and polymer physics and chemistry. By exploiting cell-material feedback, we are able to design a concise platform to achieve versatile production, analysis, and purification of diverse proteins and protein complexes, and also assembly of functional living materials. Our work demonstrates the use of the feedback between living cells and materials to engineer a modular and flexible platform with sophisticated yet well-defined programmed functions.

8:45 AM SB06.04.03
A Deep Insight into the Mechanism of Production of Living Conducting Materials Maria Lucharelli1, Giuseppina Tommasini2, Vittorio De Felicis1, Natalia Dell’Aversana1, Maria Antonietta Ferrara1, Giuseppe Coppola1, Francesca Di Maria3, Mattia Zangoli3, Maria Moros2, Angela Tino1 and Claudia Tortiglione1; 1Istituto di Scienze Applicate e Sistemi Intelligenti “E. Caianiello”, Consiglio Nazionale delle Ricerche, Italy; 2Istituto di Nanoscienzi Materiales de Aragón (INMA), Spain; 3Istituto per la Sintesi Organica e Fotoreattività, Consiglio Nazionale delle Ricerche, Italy
Living cells are able fabricate complex structure starting from simple building blocks, offering new paradigms to create new hybrid materials by combining synthetic and living features. We have previously shown the capability of the living tissue-like organism, the freshwater polyp Hydra vulgaris, to produce fluorescent and conductive interface embedded into the animal tissues, starting from thiophene-based compounds, demonstrating the feasibility to use these organisms as biofactories of novel biocompatible and deformable bioelectronic interfaces [1-2]. Here we show that the potential of biofiber production is broadly valid in other biological systems, and showed that it can be promoted by several human and murine cell lines and by other invertebrate in vivo models (such as the sea anemone Nematostella vectensis). The cell type and organism developmental stage influences the fiber shape, amount and optical properties. In order to understand the mechanism underlying the fiber biogenesis, on one side we performed a systematic chemical engineering approach to identify the structure/groups involved in the spontaneous fiber assembling. On the other, we performed several physical and chemical treatments to identify the cell machinery components involved in the biosynthetic process. Finally, by mean of advanced characterization methods and holographic imaging, we shed light on the mechanism of biofiber production and the fine structure, paving the way to new bioengineering concepts to fabricate novel living conducting materials.


Active Biointegrated Living Electronics for Multi-Dimensional Inflammation Management

10:45 AM
SB06.04.08

the size of the microcapsules, which further increases the applicability of this system. Laminin-111/collagenIV-mixed microcapsules undergo filamentation. Here, the E.coli turn into long filamentous bacteria and start shedding small bacteria from the end of the filaments. This time periods. We discovered two distinct behaviors of the same bacterial strain, depending on the type of protein used for generating the microcapsules. In the case of laminin-111 based phase to the outer release medium, placed above the droplets. Incubating this solution for approximately 20min at room temperature releases the established protein microcapsules into the layer positively charged ions are attracted to the negatively charged block-copolymer surfactant layer at the inner periphery of the droplet wall. This in turn attracts the negatively charged proteins. Consequently, engineering 3D ECM niche systems for controlled observation and manipulation of bacteria has become an important strategy, particularly in medical applications. In this research, we have established a novel droplet-based microfluidic approach for the controlled assembly of ECM-based protein microcapsules loaded with Escherichia coli (E.coli). Towards this end, water-in-oil emulsion droplets consisting of negatively charged block-copolymer surfactants are used as a template for the charge-mediated formation of a laminin- or laminin/collagen-based continuous layer on the inner droplet periphery. A double-inlet microfluidic flow-focusing device is implemented to encapsulate E. coli, proteins and divalent ions. The positively charged ions are attracted to the negatively charged block-copolymer surfactant layer at the inner periphery of the droplet wall. This in turn attracts the negatively charged proteins. After incubating the droplets at 37°C for at least 1h, the polymerized protein microcapsules are sequentially released into a physiological environment. Here, the droplets are covered with a layer of the release medium of choice and perfluoro-octanol is added dropwise from above. Perfluoro-octanol acts as a destabilizing surfactant, which allows the fusion of the inner phase with the outer release medium. The microcapsules are subsequently encapsulated E. coli. The extracellular components of the living hydrogels, prepared through thermal release of naturally occurring amylose polymer chains, are viscoelastic, capable of sustaining the bacteria with high viability, and facilitate transport microcapsules and seeding them on a glass coverslip allows for the analysis of bacterial behavior inside the droplets over longer time periods. We observed distinct behaviors of the same bacterial strain, depending on the type of protein used for generating the microcapsules. In the case of laminin-111 based microcapsules, bacteria colonies grow inside the microcapsules and simultaneously expand the microcapsule walls. The microcapsules can only withstand this growth up to a certain point, after that, the capsules break and release a large number of bacteria at once. This system can be used to a good extent, in the coencapsulated bacteria burst and hence generate a local source of infection. In contrast to the outbreak, E.coli incapsulated inside laminin-111/collagenV-mixed microcapsules undergo filamentation. Here, the E.coli turn into long filamentous bacteria and start shedding small bacteria from the end of the filaments. This behavior is widely distributed in various infectious diseases. This model can be used to conduct antibiotic studies on filamentous bacteria. These are just two examples to show the purpose of this system. With our new method it is possible to generate different kind of protein microcapsules and further the content is also not limited. Exchanging the aqueous phase allows for generation of various proteins, organisms and/or molecules being encapsulated inside water-in-oil droplets. Using microfluidics also allows us to tune the size of the microcapsules, which further increases the applicability of this system.

10:45 AM
SB06.04.08

Selective Hydrogel Membranes for Modular SynBio Processing Units

9:00 AM

SB06.04.04

Industrial microbiology has great potential in modernizing chemical manufacturing, particularly in the synthesis of high value products (HVPs) and precursors. To further mitigate issues within manufacturing regarding high energy consumption, environmental pollution, and slow response times to demand fluctuations, we can look to decentralized production and modular processing units. Hydrogels are 3D networks of crosslinked hydrophilic polymers that can retain large amounts of water without dissolution. Their rheological properties, cytocompatibility, and structural capabilities allow them a wide range of applications, including cell encapsulation, drug delivery, and membrane technologies. By encapsulating engineered microbes in hydrogel membranes, we can create engineered production units for multi-functional processes. Through rational material design characterization and computational modeling, we systematically verify the effectiveness of this concept in regulating metabolic fluxes, first in a 6-step reconstructed reaction and then in an 11-step one, respectively. As such, MetaLock is a generalizable strategy that is applicable to improving the productivity of a variety of synthetic pathways. We seek to underscore the importance of understanding detailed microbe-material interactions and to provide an outlook on leveraging MetaLock to accelerate the development of engineered living materials.

9:15 AM
SB06.04.05

Cellular Proliferation Driven Function in Engineered Living Materials

Taylor H. Ware; Texas A&M University, United States

Engineered living materials derive functionality from the characteristics of living and non-living components. We will describe two unique functions, growth and cell delivery, driven by the proliferation of embedded microorganisms within covalently crosslinked hydrogels. Living yeast–hydrogel and bacteria-hydrogel composites are capable of undergoing programmed shape change, where volume can increase by >5x. As the cells have higher modulus (~100x) than the gel, cell proliferation results in a macroscopic shape change of the composite. This growth can be used to create stimuli-responsive materials or to manufacture components with >95% biomass. When the proliferating cells reach a boundary of the material, these cells are released to the surrounding environment. We will describe systemic relationships that govern cell release. For example, the elastic modulus of the hydrogel can be tuned to set the rate of cell release over a range of four orders of magnitude. The use of these composites to deliver probiotic bacteria in a controlled fashion will be described.

9:45 AM BREAK
Biological Nanofibres from Electroactive Microorganisms Towards e-Biologies

Jean V. Manca, Koen Wouters, Robin Bonnié, Roland Valcke and Bart Cleuren; University of Hasselt, Belgium; 2 Aarhus University, Denmark

In nature, biological ‘nanofibers/nanowires’ in electroactive microorganisms such as Geobacter sulfurreducens, Shewanella oneidensis and the more recently discovered Cable Bacteria demonstrate remarkable electrical transport properties. These electroactive bacteria are receiving growing attention from diverse research fields, motivated by a fundamental interest in the underlying long-range transport mechanisms and in the potential future role in emerging domains such as bio-electronics, biodegradable electronics, and electronic biological materials (e-biologies). In the long-term these materials could open novel avenues for the growing problem of intrinsic electrical conductivity through the use of electrical probe measurements, with nanofiber conductivity values over 10 S/cm and an exceptionally long electron transport distance in the order of 1 cm. While nanometer-scale electron transport is known to occur in prokaryotes, chloroplasts and mitochondria, and micrometer-scale electrical currents are measured in the nanowire appendages of bacteria and archaea, the centimeter-scale electron transport by cable bacteria extends the known length scale of biological transport by several orders of magnitude.

To disclose the underlying electrical transport mechanisms occurring in Cable Bacteria several techniques are being introduced. Impedance spectroscopy provides an equivalent electrical circuit model, which indicate that dry Cable Bacteria filament functions as resistive biological wires. Recently, proof-of-principle biohybrid demonstrators have been prepared to investigate the electrical signal transmission possibilities in a broad frequency range. Temperature-dependent electrical characterization reveals that the conductivity can be described with an Arrhenius-type relation at a broad temperature range (-195°C to +59°C), indicative for hopping transport. Furthermore, when cable bacterium filaments are utilized as the channel in a field effect transistor, they show n-type transport with electron mobility values of ~0.1 cm²/Vs at room temperature and display a similar Arrhenius temperature dependence as the earlier mentioned conductivity. Overall, the obtained results so far demonstrate that the intrinsic electrical properties of the conductive fibres in Cable Bacteria are comparable to synthetic organic semiconductor materials, and so they offer promising perspectives for both fundamental studies of biological long-range electron transport as well as alternative organic electronic materials for the emerging field of bioelectronics, biohybrid electronics and for visionary technologies such as biodegradable electronics and other “More than Moore” technology platforms.

11:45 AM SB06.04.11 Spatially Resolved Charge Transfer Kinetics at the Quantum Dot-Microinterface Using Fluorescence Lifetime Imaging Microscopy

Mokshin Sur, Farzhal Salimi Jazi, J. C. Crowley, Youngchun Park, Bing Fu, Peng Chen, Warren R. Zipfel, Buz Barstow and Tobias Hanrath; Cornell University, United States

Micro-semiconductor biohybrids formed by integrating complex microbial enzymatic machinery with programmable optoelectronic properties of semiconducting quantum dots (QDs) have introduced compelling prospects for future photovoltaic solar-to-chemical transformations. Bringing these prospects to fruition requires a firm foundational understanding of charge transfer mechanisms at the micro- and bio-interface. One challenge is that the transfer of photocexcited carriers from a QD to a drive redox reactions in a proximate microbe involves a complex interplay of photochemical and physiochemical sub-processes, and the governing thermodynamic and kinetic factors are just beginning to emerge. The inherent heterogeneities of both the microbe and QD ensemble present a broad temporal range (10⁻⁴ to 10⁻⁹ s⁻¹) for different reaction rates. In this study, we leveraged advanced spectroscopic imaging tools (fluorescence lifetime imaging microscopy, FLIM) to interrogate charge transfer kinetics at the interface of a CdSe quantum dot (QD) film and Shewanella oneidensis microbes with sub-cellular spatial resolution. We focused on electron transport under fumarate-rich conditions and observed that both the intensity and lifetime of the QD’s photoluminescence decrease at on-cell and inter-cell positions relative to the off-cell background. These trends provide a map of electron transfer rates (in the range of 10⁸ to 10⁹ s⁻¹) from QDs to the cells for terminal reduction of fumarate. Our analysis of spatially resolved charge transfer rates reveals the role of cooperative effects in small groups of microbes, i.e., working together, small communities S. oneidensis exhibit faster charge transfer than isolated microbes. We attribute the cooperative effects to nanowire extrusions from S. oneidensis that facilitate charge uptake. Light driven electron transfer rates define the photo-chemical efficiency limits of photosynthetic semiconductor biohybrids, and this study provides important progress towards characterizing these electron transfer rates with enhanced spatial resolution.
mimicked this fascinating process developing artificial systems that allow converging light into electrical energy. In recent years, the possibility to couple abundant and sustainable photosynthetic biological catalysts with electrodes has called particular interest to harvest solar energy without the need of platinum group metals or other critical raw materials. However, bacterial cells did not evolve to exchange electrons with an external electron acceptor/donor, making the transfer of photoinduced electron to (and from) the electrode the most critical challenge to be overcome.

The talk will focus on the approaches that we are currently investigating to tailor the bacteria/electrode interface, specifically by (i) developing polydopamine-purple bacteria-based redox-adhesive matrices; (ii) modifying the cellular membrane of photosynthetic bacteria with inorganic nanoparticles; and (iii) developing bio-based electrode materials using polyhydroxybutyrate for enhanced bacteria colonization.

Application of the biohybrid materials obtained with these approaches for the development of sustainable biosensors and the production of energy carriers will be discussed, together with the challenges and outlook of this fascinating technology.

References

Acknowledgments
Matteo Grattieri would like to acknowledge the funding from Fondazione CON IL SUD, Grant "Brains to South 2018", Project No. 2018-PDR-00914.

4:00 PM SB06.05.05
An n-Type Conjugated Oligoelectrolyte Mimics Transmembrane Electron Transport Proteins for Enhanced Microbial Electrosynthesis
Glenn Ong1,2, Guillermo C. Bazan1, Ricardo J. Vázquez3, Samantha R. Mccuskey1 and Fernando L. Garcia1; 1National University of Singapore, Singapore; 2Indiana University Bloomington, United States

Interfacing bacteria as biocatalysts with an electrode provides the basis for emerging bioelectrochemical systems that enable sustainable energy interconversion between electrical and chemical energy. Electron transfer rates at the abiotic-biotic interface are, however, often limited by poor electrical contacts and the intrinsically insulating cell membranes. Herein, we report the first example of an n-type redox-active conjugated oligoelectrolyte, namely COE-NDI, which spontaneously intercalates into cell membranes and mimics the function of endogenous transmembrane electron transport proteins. The incorporation of COE-NDI into Shewanella oneidensis MR-1 cells amplifies current uptake from the electrode by 4-fold, resulting in the enhanced bio-electrooxidation of fumarate to succinate. Moreover, COE-NDI can serve as a "proton prosthetic" to rescue current uptake in non-electrogenic knockout mutants.

4:15 PM SB06.05.06
Bacterio-phage-Based Self-Propelled Catalytic Biohybrid Nanomotor
Xi Ding, Martha \(X_1^{2024}\) Ackerher and Elaine D. Haberer; University of California, Riverside, United States

Self-propelled biohybrid materials have potential applications in fields such as drug delivery to environmental remediation. Microorganisms, such as bacteriophage, provide untargeted parallelism and assembly. Their structure and surface, including exact shape and site-specific functional groups, are genetically encoded and known with atomic scale precision. Synthetic inorganic nanoparticles facilitate superdiffusive motion. Their interactions with chemical fuel or physical fields convert energy into locomotion. Of specific interest, here, are viruses with asymmetric capsid proteins, like the M13 bacteriophage, that can serve as programmable low-symmetry templates for autonomous biohybrid materials. The M13 has a high aspect ratio, a diameter of 6.5 nm and a length of 800 µm.

Fluorescently tagged and exposed to low concentrations of H2O2 to fuel self-propulsion. Using confocal fluorescence microscopy, nanomotor trajectory and motion were evaluated.

4:30 PM *SB06.05.07
In Situ Control of Cells and Multicellular Structures by Two-Photon Lithography
Christine Sellhuber-Unkel; Heidelberg University, Germany

In vivo, the tissue environment often provides strong confinement to cells and multicellular assemblies, particularly in cancer. Therefore it is highly important to mimic such confined environments, in order to investigate the impact of confinement on cellular systems. Here, we employed two-photon lithography, which allows to print directly into and next to multicellular assemblies. For example, we printed dome-shaped confinements with micrometer-sized openings to confine cancer spheroids in order to investigate the migration behavior of the cancer cells and also to study the effects of confinement on the spheroid. We have shown that confinement of the spheroids leads to a decreased cell migration speed and affects actin alignment and dynamics. Furthermore, in situ two-photon lithography provides a novel way of analyzing the behavior of specific regions of multicellular structures, by enabling the separation of multicellular structures from an aqueous environment.

In our study, we investigated the impact of confinement on cellular systems using two-photon lithography. We employed this technique to print directly into and next to multicellular assemblies, allowing us to study the effects of confinement on cellular behavior.

The Multifunctional Use of an Aqueous Battery for a High-Capacity Jellyfish Robot
Xu Liu, Shuo Jin, Yiqi Shao, Autumn Pratt, Duhan Zhang, Jacqueline Lo, Yong Joo, Lynden Archer and Robert Shepherd; Cornell University, United States

The batteries that power Untethered Underwater Vehicles (UUVs) serve a single purpose—to provide energy to electronics and motors; the more energy required, the bigger the robot must be to accommodate space for more batteries. This size dependency is further exacerbated by the high gravimetric density of batteries, requiring bigger hulls to displace water equaling the weight of the batteries. With the increased size, comes increased moments of inertia, reducing maneuverability. By choosing batteries that are primarily liquid (i.e. Redox Flow Batteries, RFBs), the increased weight can be distributed for improved capacity with reduced inertial moment; and, when also being used as hydraulic fluid, reduce the overall weight of the AUV. In this paper, we provide an RFB into the shape of a jellyfish, using two redox chemistries and architectures: (i) a secondary ZnBr2 battery with high power density, and (ii) a hybrid primary/secondary Zn2+ battery with high capacity. Our choice of a Jellyfish shape demonstrates a low inertial moment architecture, a hemisphere, facilitated by the easy shaping of fluid batteries. In our robot, the RFB electrolyte also provides hydraulic force transmission to control the shape of the jellyfish's bell, causing it to sink or swim. Finally, our choice of catholyte to fill the bell allows us to quickly recharge the battery by emptying the fluid and replacing it with pre-charged electrolyte (analogous to a gas station).

9:00 AM SB06.06.03
Communication with Plants Using Wearable Electrophysiology Sensors
Yifei Liu, Yi Jing Wong, Wenlong Li, Xin Jun Loh and XiaoDong Chen; 1Agency for Science, Technology and Research, Singapore; 2Nanyang Technological University, Singapore

Different parts and organs of a plant communicate using various forms of signals to optimize resource allocation and coordinate systemic responses to environmental stimuli for survival and growth. Investigating these communication processes is important to understanding plants' perception of environments and well-being as well as engineering approaches to improve plant health or induce desired behaviors. We aim to achieve this through electrophysiology, the study of electrical signals in plants, due to the simplicity of sensor design and rich biological insights buried in the signals.

In this talk, I will share my work on developing plant-interfacing materials for high-fidelity signal acquisition from plants having complex surface topography (e.g., hairy, rough, superhydrophobic), as well as achieving long-term stability during plant growth. The conformal adhesive attachment of the devices on plants makes them resistant to motion artifacts, and the noninvasive wearable form factor promises the potential for real-world deployment in farms and gardens.
Iron deficiency is a major global health concern, and dietary iron from plant consumption is a primary source for most people worldwide. However, the iron content in plants is heavily affected by various environmental and agronomic factors, including climate change such as rising temperature, water scarcity, and elevated atmospheric CO₂ level. Therefore, it is a pressing need to develop effective strategies to combat iron deficiency and ensure food security for the global population. Conventional analytical techniques to investigate the efficacy of foliar iron fertilization are not optimally suited to observe the nuances of foliar absorption, translocation, and iron speciation. This lack of information hampers the optimization of fertilization strategies and the development of more effective nutrient formulations.

In this work, we introduce a highly sensitive fluorescence iron nanosensor for elucidating the biochemistry of iron in plants, thereby enabling the formulation of precise fertilization strategies. This nanosensor can be easily incorporated into living plant species to monitor real-time iron uptake via both foliar and soil-based fertilizations. Our sensor, fabricated by conjugating a synthetic conjugated polymer onto single-walled carbon nanotubes, is designed to exhibit a unique orthogonal optical response that enables differentiation between Fe(II) and Fe(III).

Using hydroponically grown lettuce as a model for iron foliar application study, our sensor provides the means to monitor iron uptake, metabolism, and transport with high spatial and temporal resolution in the living plant. Our findings demonstrate that the plant’s mechanistic responses to the source of iron species depend on the chelation state rather than the oxidation state. Under conditions of iron deficiency or simulated abiotic stress, such as drought or salt stress, the diffusion and transport rate of iron species are also affected. We also observe a shared mechanistic response to chelated iron species across various plant species, hinting at the existence of conserved foliar iron homeostatic mechanisms.

With its ability to offer detailed insights into the dynamics of iron uptake and transport in real-time, we believe this sensor technology has the potential to revolutionize the study of iron uptake and distribution in plants. This advancement can lead to improved plant growth and yield through the development of more precise and efficient micronutrient management strategies.

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**Real-Time Monitoring of Iron Uptake and Transport in Plants with Optical Nanosensor**


**Singapore-MIT Alliance for Research and Technology, Singapore; Temasek Life Sciences Laboratory, Singapore; Massachusetts Institute of Technology, United States**

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**Microfluidic Microbial Fuel Cell Based Biosensors for Copper Ion and Formaldehyde in Water Monitoring**

**Hao Ren**

**ShanghaiTech University, China**

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**EcoRobotics—Bioinspired and Biohybrid Soft Robots for Environmental Monitoring and Preservation**

**Barbara Mazzolai**, **Fabian Meder**, **Emanuela Del Dottore**, and **Serena Armiento**

**Istituto Italiano di Tecnologia, Italy**

Meeting the global challenges of climate change represents one of the most important frontiers for science and sustainable technologies. With this ambition, our research activity envisions environmental responsibility, bioinspired systems that can grow, adapt, and are built with recyclable, or biodegradable, or biohybrid materials. We refer to them as ‘ecorobots’. These ecorobots are designed to imitate the adaptability of living organisms, allowing them to navigate and function effectively in complex and unpredictable environments. They are also designed to seamlessly integrate into natural ecosystems.

We primarily draw inspiration from soft invertebrates, such as cephalopods and earthworms, as well as plants, as they exhibit remarkable adaptive capabilities with smart, effective, and efficient strategies. Specifically, when studying plants, we can develop innovative ecorobots featuring structural-functional materials, distributed sensing and intelligence systems, and biohybrid energy-harvesting mechanisms. Much like their natural counterparts, these machines are envisioned to possess the ability to biodegrade at the end of their lifecycle, promoting sustainability. In this presentation, I will outline our approach to designing and developing ecorobots inspired by the characteristics of plants. Our primary objectives are twofold: first, to identify and extract the fundamental principles that underlie the biological functions of plants and translate them into technological solutions; and second, to advance our scientific understanding of the biological systems we draw inspiration from.

Our examples will include the following ecorobots: the Plantoid robot, the pioneering plant-root-inspired robot, equipped with artificial growing roots, distributed sensors, actuation mechanisms, and intelligence systems, designed for soil exploration and monitoring; the GrowBots, machines inspired by climbing plants that move by growing, tailored for various exploration
Molecular communication (MC), a bio-inspired technology, is emerging as an alternative way of communication by overcoming the limitations of conventional electromagnetic waves. As the demand for practical implementation of MC grows, physical components of MC (e.g., transmitter and receiver) have been fabricated through the integration of nano-/micro-technology. However, challenges such as slow speed of information molecule (IM) transmission, dispersion of IMs into the surrounding molecules, and interference between sequentially transmitted IMs persist in employing the transmitters. Furthermore, sequential delivery of multiple IMs with an adjustment of their time intervals to enhance the communication efficiency remains a significant challenge. Herein, we report a time-controlled delivery system that utilizes nanomotors as transmitters achieving precise multi-cargo delivery with desired time intervals. Nanomotors consisted of multi-metal nanorod (i.e., nickel head, gold bridge, silver flexible filament, and gold tail) are encapsulated with poly (N-isopropylacrylamide) (pNIPAm) based hydrogel, and nanomotors with various dimensions transport multi-cargo as IMs (e.g., Indigo carmine and Carminic acid) at different speeds under the same magnetic field. Consequently, nanomotors release IMs on-demand at desired locations upon near-infrared (NIR) irradiation, leading to IM delivery with high spatiotemporal density. Continuous linear sweep voltammetry (LSV) confirmed the sequential delivery of multiple IMs with time intervals of several minutes, indicating that nanomotors can transport IMs at higher transmission rate compared to diffusion-based methods. Furthermore, IM delivery using nanomotors exhibited higher signal intensity and reduced interosmary interference (ISI), which enables a continuous signal transmission with a lower error rate in communication. We believe our time-controlled multi-cargo delivery via nanomotors can serve as transmitters paving a way to realize practical MC systems, such as disease detection and monitoring. This will allow us to understand communications in biological/biometric systems or unexplored environments.

PEDOT:PSS Fiber-Based Highly Sensitive Strain Gauge Force Sensor for Biohybrid Robots Xinran Xie, Abhijith Surendran, Ruiling Wu and Jonathan Rivnay; Northwestern University, United States

Integrating biological components of contractile living muscle tissues with careful microstructure design, biohybrid robots have realized various biomimetic behaviors and functions such as swimming, walking, and object manipulation. However, the inherent vulnerability to the stimulation and increased dexterity of biohybrid robots require perception of their function and surroundings for tissue protection and accurate control. Currently, most biohybrid robots are stimulated to output large forces without considering their health status, causing short life and decreased performance. Therefore, biohybrid robots need to be equipped with sensors that can monitor muscle force and length similar to the Golgi tendon and muscle spindle in humans. The feedback signals would help with tuning stimulation parameters to better protect tissues from damage while generating stable and controllable force. This can be realized by incorporating a strain gauge force sensor within the muscle tissue to provide real-time strain and force information.

PEDOT:PSS fiber-based strain sensors remain elastic within 0-0.5% strain range, which is suitable for in vitro muscle strain monitoring. These fibers work like a resistive strain gauge and favorably combine electrical and mechanical properties, biocompatibility, stability, and commercial availability. Additionally, PEDOT:PSS fiber-based strain sensors are suitable for real-time monitoring and drug delivery systems featuring natural plant hooks; biohybrid energy harvesting systems; as well as solutions inspired by plant communication and emerging collective biological behaviors.

In the second part of this talk we discuss an integrated optogenetic and bioelectronic platform for stable and long-term modulation and monitoring of cardiomyocyte function. Optogenetic inputs were achieved through expression of a photoactivatable adenylyl cyclase (bPAC), that when exposed to blue light caused a dose-dependent and time-limited increase in intracellular cyclic AMP concentration and, subsequently, autonomous cardiomyocyte beat rate. Bioelectronic outputs from the MEA provided real-time readouts of cardiomyocyte behavior in response to optical modulation. Irradiation at 24 μW/mm² resulted in a ca. 17% increase in beat rate within 20-25 minutes of irradiation. Multiplexed readouts revealed that wavefront propagation rates throughout the monolayer remained constant between “on” and “off” states, demonstrating that optical modulation did not affect intercellular coupling. In addition, bPAC activation could be cycled through repeated “on” and “off” states via time-limited illumination or in a gradient fashion with 0.03-24 μW/mm² illumination. Cardiomyocytes could be modulated reproducibly over at least four days, demonstrating that bPAC expression as well as the bioelectronic interface were stable throughout that period.

Taken together, our studies demonstrate the feasibility of bioelectronic and optical techniques for monitoring and modulating cardiac function. We will discuss recent efforts in our lab toward 3D bioelectronics-embedded tissues and closed-loop feedback systems. We will also discuss potential clinical applications for cardiac regulation including arrhythmia diagnosis and intervention.

3D Printed GelMA/Hydroxyapatite Scaffold from Design to Biological Evaluation for Bone Tissue Engineering Fabiola Hernandez Rosas1, Ana Paola Salgado Alvarez1, José R. Alanis Gómez1, Manuel Jaime Rodriguez2 and Ximena Mejía Delgadillo1; 1Universidad Anahuac Querétaro, Mexico; 2Tecnológico de Monterrey, Mexico

Bone repair is a widely explored field in tissue engineering due to its significant impact on the human body’s structural integrity. Biomaterials based on calcium phosphate, such as hydroxyapatite (HA), have shown promise because of their ability to emulate the mineral composition and porous structure of bone. Additionally, the utilization of additive manufacturing has provided opportunities to create cellular scaffolds for bone grafts, allowing us to control properties like porosity, pore size, structural form, and mechanical characteristics. These designs are crafted using Computer-Aided Design (CAD) software. The primary objective of this project is to design, fabricate, characterize, and assess the bioactivity of 3D HA scaffolds for tissue engineering applications. To achieve this, hydroxyapatite was initially synthesized using the microwave-assisted hydrothermal method. Consequently, HA nanofibers acquired a hexagonal structure, enhancing their mechanical properties. Subsequently, the HA nanofibers underwent characterization through X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) to determine dimensions, morphology, topology, orientation, and crystalline structure. In addition, various 3D bone scaffolds with interconnected pores, facilitating permeability similar to trabecular bone morphology, were designed using Rhinoceros 3D CAD software with the Grasshopper extension. These scaffolds were produced using a 3D bioprinter with methacryloyl (GelMA) and laminin as bioink. Gelatin methacryloyl (GelMA) hydrogel with hydroxyapatite has shown its ability to promote osteogenesis and enhance osseointegration, as supported by both in vitro and in vivo studies. In this research, 3D Voronoi bioprinted scaffolds with GelMA/HA were designed and manufactured for in vitro biological evaluation using mesenchymal
Novel Virus-Templated Engineered Material for Photodynamic Treatments

Yu Sun1, Jesse Heacock1, Yan Li1,1, Jianggou Liu1,1, Chuchu Chen2 and Kaiyan Qiu2; 1Colorado State University, United States; 2Washington State University, United States

The development of novel wound-dressing materials has attracted significant research interests in recent years. With the advancement of nanofabrication, the application of nanoparticles (NPs) in drug delivery systems has become feasible. However, most existing work focuses on incorporation of metal, metal/semi-metal oxide, or organic particles into nanofiber scaffolds. There has been a lack of work on incorporation of drug-encapsulated polymeric particles into nanofiber scaffolds. In this study, gentamicin-encapsulated poly (lactic-co-glycolic acid) (PLGA) NPs were synthesized via a double emulsion solvent evaporation method. Electrospinning was used to incorporate gentamicin-encapsulated PLGA NPs into nanofiber scaffolds. Atom force microscopy (AFM), dynamic light scattering, scanning electron microscopy (SEM), ultraviolet-visible spectroscopy (UV-vis), and an agar diffusion method were utilized to characterize the morphologies, release profiles, and antibacterial activities of various gentamicin-loaded PLGA NPs incorporated nanofiber scaffolds. The results indicated the PLGA NPs had a spherical morphology with an average diameter of 130nm. Purification of PLGA NPs was essential to eliminate the residual polyvinyl alcohol (PVA) and to prevent particle agglomeration. The purified PLGA NPs were uniformly and individually incorporated into the polyurethane (PU) poly ethylene oxide (PEO) or PEO-only nanofiber scaffolds, but nearly none into the fiber alone. PEO served as a continuous phase in the PU:PEO mixture, which significantly improved the compatibility of PLGA NPs and PEO, resulting in a well-dispersed distribution of PLGA NPs in the monolithic nanofiber scaffolds. Excellent antibacterial performance against E. coli was found in both PU/PEO and PEO nanofiber scaffolds. This study of incorporating gentamicin-encapsulated PLGA NPs into nanofiber scaffolds provides insights for achieving successful incorporation of drugs-encapsulated polymeric NPs into fiber scaffolds. This promising microfabrication technology for delivery of therapeutic molecules with controlled release for biomedical applications.

3:00 PM SB06.08.04
Kirigami Electronics for Chronic Electrophysiological Recording of Human Neural Organoids
Bianxiao Cui; Stanford University, United States

Neurons transmit information via electrical signals. Recent advancement in neural organoids and assembloid technologies, derived from human stem cells, have offered a promising avenue for modeling aspects of nervous system development. To understand brain development and develop effective disease models, it is crucial to enable long-term, minimally invasive recordings from these three-dimensional systems. Current technologies, such as patch clamp, penetration, electrophysiology, planar electrode arrays, and substrate-attached flexible electrodes, do not, however, allow chronic recording of neural organoids in suspension, which is necessary to preserve their 3D architecture. Inspired by the art of kirigami, we developed flexible electronics that transition from a flat 2D pattern to a 3D basket-like configuration to accommodate the long-term culture of human neural organoids in suspension. This platform, named kirigami electronics (KiriE), integrates with and enables chronic recording of intact cortical organoids for 170 days while preserving their morphology, cytoarchitecture, and cell composition. KiriE detects disease-related hypertrophic phenotype. Furthermore, KiriE is compatible with simultaneous recordings from individual organoids in an assembloid and can capture activity in emerging cortico-striatal circuits. Moving forward, this flexible electronics system holds the potential to unveil disease phenotypes and reveal the activity patterns underlying the assembly of the nervous system.

3:30 PM SB06.08.05
Microstructures Printed via 2-Photon Polymerization (2PP) to Mechanically Stimulate 3D Multicellular Systems
Federico Colombos, Mohammadreza Taale, Gent Dautalab, Teresa Debatin, Philipp Kollenz, Maria Villiou, Fereydoon Taheri, Malin Schmidt and Christine Sellhuber-Unkel; University of Heidelberg, Germany

In nature, cells live immersed in an extracellular matrix with other cells, forming tissues and organs. These three-dimensional environments are essential for a wide array of vital biological processes. As a result, many research studies are now exploring the utilization of 3D multicellular systems such as spheroids, organoids, and organotypic cell cultures. These alternatives, when compared to conventional 2D cell culture methods, hold a significant advantage in closely resembling physiological conditions. Indeed, the mechanical forces acting upon cells can yield differing outcomes depending on whether the cells are in a 2D or 3D environment. Traditionally, most studies on mechanotransduction, especially in terms of the effects induced by mechanical stimulation, have been conducted on two-dimensional cultures. This approach, however, has provided only a limited understanding of the effects within a 3D culture. To address this limitation, we have developed a device for the mechanical stimulation of 3D multicellular systems using Two-Photon Polymerization (2PP). This device can be used to study the mechanical forces in the biological complexities of tissues at an exceptional micrometer-scale resolution. The design of the device allows the application of forces capable of stretching the encapsulated 3D multicellular systems with extreme precision, using a cantilever. Simultaneously, this system enables high-frequency imaging to assess the effects of stretching in vivo. Our findings have revealed that cyclic stretching over 30 minutes at a frequency of 0.5 Hz, and an average displacement of 0.22μm, leads to noteworthy alterations in the morphology and orientation of actin within the 3D multicellular system. Furthermore, this device can be easily customized to mechanically stimulate various types of multicellular systems, accommodating differences in shape and cell types.

4:30 PM SB06.08.06
Novel Virus-Templated Engineered Material for Photodynamic Treatments
Marika Iencharelli1,2, Paolo Emidio Costantini2, Vittorio De Felice1, Roberto Saponetti3, Angela Tino1, Francesca Di Maria1, Alberto Danieli1, Matteo Calvaresi1 and Claudia Tortiglione1; 1CNR-ISASI Consiglio Nazionale delle Ricerche, Italy; 2CNR-ISOF Consiglio Nazionale delle Ricerche, Via Piero Gobetti, Italy; 3Alma Mater Studiorum—Università di Bologna, Italy; 4Alma Mater Studiorum, Università di Bologna, Italy

Thiophene-based materials TMs, due to their excellent electron transport properties, optical properties, soft material nature, stability, solution processability, and water dispersibility, have demonstrated significant potential in photodynamic (PDF) therapies. To increase the cell uptake and the permeation of physiological barriers recent studies reported the use of proteins (human serum albumin, HSA) [1] or phages (M13 bacteriophage) [2] as natural carriers of different photosensitizers (rose Bengal, chlorin e6, oligothiophene EBC04), to induce cell death by apoptosis in a variety of cell lines. Here we propose a novel engineered living material for photodynamic therapy, i.e. a virus-templated platform, based on the M13 bacteriophage, engineered to display targeting ligands on its surface. By covering the surface of the M13 phage with oligothiophene molecule, a 1-D thiophene nanoplatfrom, M13EGFR(TNP) was synthetized and tested in vitro and in vivo. Cell culture experiments were carried out to validate the ability of the biohybrid material to maintain the EGFR-targeted tropism of the phage and to demonstrate the inability to infect normal mammalian cells. The assembloid-like animal model Hydra was employed to further confirm the possibility to use these engineered materials for photodynamic treatment and to screen for targeting properties. The transparency, softness and body simplicity together with the lack of ethical issue make Hydra a suitable model for this type of studies, enabling fast screening of cytotoxicity and identification of molecular pathways underlying necrosis or apoptosis pathways. Our work provides valuable insights into the potential of M13EGFR(TNP) for targeted photodynamic therapy, laying the groundwork for further exploration of this innovative living material in nanotheranostic applications.


4:00 PM SB06.08.07
Using Metamaterials and Cardiac Tissue Engineering to Engineer Robust and Contractile Cardiac Tissue Patches
Lewis S. Jones1, Hector Rodriguez1, Omer Dzemali2 and Robert Katzschmann1; 1ETH Zurich, Switzerland; 2Universitätsklinikum Zürich, Switzerland

Ventricular Septal Rupture (VSR) is a challenge in cardiac medicine with a high mortality rate of 45%-50%. Current treatment methods use bovine pericardial patches (BPPS), which are non-contractile, tend to calcify over time, and fail to integrate effectively with the myocardium. Therefore, patients do not tend to fully recover cardiac function. To address these limitations, we are engineering a cardiac-tissue patch that uses human stem cell-derived cardiomyocytes in hydrogel, reinforced with a metamaterial lattice. This approach allows us to tune the mechanical properties and contractility, while enabling stable implantation within the intraventricular space. Here, we will showcase our current results on metamaterial design and manufacturing, mechanical characterization (tunable stiffness and anisotropic ratio), and biological characterization (biocompatibility, cell maturation, and tissue contractility). In summary, we will show how metamaterials can be combined with engineered cardiac tissue to fabricate centimeter scale, three dimensional, and implantable cardiac tissues.
Pushing the Limit of Self-Assembly Ultrashort Peptides Minimum Gelation Concentration for Advanced Biomedical Applications

Abdulelah Alrashoudi, Manola Moretti and Charlotte A. Hauser; King Abdullah University of Science and Technology, Saudi Arabia

This novel approach demonstrates simple yet highly functional applications for the detections and quantification of bacteria, microorganisms or even viruses. Through the techniques of laser-induced nanomaterials and micropores, the manufacturing of microbes related sensing instruments would be immensely enhanced in terms of time efficiency as well as financial cost. With indications of such capabilities, it is assured that the future of microbial diagnosis will be optimized with next generation rapid sensors developed from laser evolved technologies, paving ways for further applications in fields of food safety, epidemiology and Point-Of-Care testing.

SESSION SB06.09: Poster Session II
Session Chairs: Elena Stavrinidou and Claudia Tortiglione
Thursday Afternoon, April 25, 2024
Flex Hall C, Level 2, Summit

Label-Free Laser-Induced Ni/AuNPs Micropore Reusable Electronic Sensor for Rapid Bacteria Detection and Quantification
Wing Yan Poon and Mitch Guijun Li; The Hong Kong University of Science and Technology, Hong Kong

The advancement of biosensors for microbes, especially of pathogenic bacteria has been an important research area aiming to develop rapid and accurate detection, with its crucialness to various applications in healthcare, food safety and environmental monitoring. Laser-induced nanoparticles have emerged as a viable solution to stimulate and identify electrochemical properties of bacteria. In this study, we propose a label-free laser-induced Ni/AuNPs reusable electronic sensor that enables fast and precise detection of pathogenic bacteria. The rapid bacteria sensor is achieved by two major innovative laser applications. The sensor is firstly fabricated by a laser-drilled micropore sized at approximately 1 μm on double sided laser-induced graphene (LIG) polyamide film. The size of the micropore is utilized to selective resistive pulse analysis which allows identifications across different pathogenic bacterial species along with machine learning. It is then followed by controlled potential amperometric analysis of different pathogenic bacteria using Ni/AuNPs modified LIG as electrode, providing quantitative details of bacteria present in the sample solution. The Ni/AuNPs modified LIG is efficiently manufactured by laser ablation of Ni-consisting crystal and Au thin film to laser-induced graphene. This novel bacteria sensor requires no additional coating of antibodies and non-reversible conjugations between bacteria and ligands, enabling its robust reusability on bacteria detection and quantification.

The rapid bacteria sensor has been achieved by two major innovative laser applications. The sensor is firstly fabricated by a laser-drilled micropore sized at approximately 1 μm on double sided laser-induced graphene (LIG) polyamide film. The size of the micropore is utilized to selective resistive pulse analysis which allows identifications across different pathogenic bacterial species along with machine learning. It is then followed by controlled potential amperometric analysis of different pathogenic bacteria using Ni/AuNPs modified LIG as electrode, providing quantitative details of bacteria present in the sample solution. The Ni/AuNPs modified LIG is efficiently manufactured by laser ablation of Ni-consisting crystal and Au thin film to laser-induced graphene. This novel bacteria sensor requires no additional coating of antibodies and non-reversible conjugations between bacteria and ligands, enabling its robust reusability on bacteria detection and quantification.
response mode but also offer mutual validation of detection results obtained through diverse modes. Recent efforts have been directed towards establishing analytical methods that incorporate multi-mode signal readout. Colorimetric assays employing antibodies have garnered significant attention due to their noticeable color change discernible by the naked eye, swift observation, cost-effectiveness, and ease of use for target molecules, whether they are small molecules, or even proteins. Colorimetric and Photothermal Dual-Mode Apta-Sensor for Selective Detection of Kanamycin Using Chitosan-Stabilized Platinum Nanozymes

Fucose, a naturally occurring sulfated polysaccharide derived from marine brown algae, has been explored as a promising therapeutic nanoparticle for cancer treatment. Effective strategies such as chemotherapeutic, photothermal therapy, and glucostarvation can create a conducive environment for successful cancer eradication. Harnessing the potential of functionalized fucoidan nanocarriers designed for the selective detection of KAN, relying on the KBA-derived enhancement of peroxidase activity in CS/PtNPs and its subsequent inhibition by KAN. The developed dual-mode colorimetric and photothermal aptasensor exhibited a linear detection range of 0.1–50 and 0.5–50 μM, with respective limits of detection (LOD) of 0.04 and 0.41 μM. Furthermore, the aptasensor effectively identified KAN concentrations in spiked milk samples, confirming its reproducibility and reliability in practical applications. Crucially, the proposed aptasensor eliminates the need for a washing step and demonstrates robust selectivity for KAN. These characteristics position the aptasensor as a versatile tool for the detection of small molecules with known aptamers.

Eventually, we achieve 1.2×104 Ω/cm² skin contact impedance and 30 dB signal-to-noise ratio (SNR) for the electrocardiogram (ECG) and electromyography (EMG). Furthermore, the carbon black sponge electrode demonstrates better wet condition stability compared to other coated sponge electrodes. We utilized this E-textile system for the patient study to collect uterine contraction signals and predict childbirth (Washington University Institutional Review Board, IRB 201612140). We strongly believe that this E-textile system will lead to a new opportunity for stable long-term electrophysiological signal collecting applications.

Addressing biological infections, kanamycin (KAN) finds extensive use in aquaculture, livestock husbandry, and agriculture. Nevertheless, the overuse of KAN leads to an excess of biological residues in the environment and food, resulting in potential nephrotoxicity, ototoxicity, and other harmful side effects for humans. Consequently, it becomes imperative to develop a rapid, selective, cost-effective, and sensitive detection system for KAN to safeguard human health and ensure food safety. Colorimetric assays employing antibodies have garnered significant attention due to their noticeable color change discernible by the naked eye, swift observation, cost-effectiveness, and ease of operation. Nonetheless, antibodies come with drawbacks such as high cost, sensitivity to storage conditions, and variability in quality from batch to batch, leading to decreased reproducibility. To address these challenges, we opted for aptamer molecules. These functional, single-stranded nucleic acids possess the ability to fold into specific 3-D structures, exhibiting high specificity for target molecules, whether they are small molecules, or even proteins. Nanozymes, nanomaterials exhibiting natural enzyme-like activities, have been recognized as viable substitutes to emulate natural enzymes such as horseradish peroxidase (HRP). This is attributed to their advantages of low cost, straightforward preparation, easy modification, excellent stability, and remarkable catalytic activity. Platinum nanoparticles (PtNPs), in particular, have found extensive use in bioanalytical applications due to their superior peroxidase-like activity, biocompatibility, and high chemical inertness. The choice of suitable stabilizing reagents is crucial in the synthesis of efficient nanozymes, as stabilizers significantly impact the physicochemical and biological properties of nanoparticles. In our study, chitosan (CS) was employed. The positively charged nature of CS facilitates the electrostatic binding of the negatively charged KAN binding aptamer (KBA) to chitosan-stabilized platinum nanoparticles (CS/PtNPs). Traditionally, immunosassays operate by detecting the target in a single mode. However, outcomes obtained through a single-mode signal readout can be susceptible to variations stemming from differences among operators, equipment disparities, and non-standard analytical protocols. In contrast, dual-mode sensing platforms not only possess the intrinsic characteristics of each response mode but also offer mutual validation of detection results obtained through diverse modes. Recent efforts have been directed towards establishing analytical methods that incorporate temperature changes as a signal, in addition to the colorimetric method, in immunosassays. Among various photothermal agents, oxidized TMB (TMB-ox) has emerged as a promising photothermal sensor due to its high photoconversion efficiency in near-infrared (NIR)-induced photothermal applications. TMB-ox exhibits distinct absorbance at UV-visible (652 nm) and NIR (808 nm) wavelengths, making it suitable for use as a probe in both colorimetric and photothermal detection.

This work, CS/PtNPs, were used to construct a dual-mode colorimetric and photothermal aptasensor designed for the selective detection of KAN, relying on the KBA-derived enhancement of peroxidase activity in CS/PtNPs and its subsequent inhibition by KAN. The developed dual-mode colorimetric and photothermal aptasensor exhibited a linear detection range of 0.1–50 and 0.5–50 μM, with respective limits of detection (LOD) of 0.04 and 0.41 μM. Furthermore, the aptasensor effectively identified KAN concentrations in spiked milk samples, confirming its reproducibility and reliability in practical applications. Crucially, the proposed aptasensor eliminates the need for a washing step and demonstrates robust selectivity for KAN. These characteristics position the aptasensor as a versatile tool for the detection of small molecules with known aptamers.

Fucoidan Incorporating Fucoidan/Chitosan for Co-Encapsulation of TMB, Glucose Oxidase and Prussian Blue: Applications in Chemotherapy, Photothermal Therapy and Glucostarvation Treatment Nanocarrier Incorporating Fucoidan/Chitosan for Co-Encapsulation of TMB, Glucose Oxidase and Prussian Blue: Applications in Chemotherapy, Photothermal Therapy and Glucostarvation Treatment

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Nanozymes, nanomaterials exhibiting natural enzyme-like activities, have been recognized as viable substitutes to emulate natural enzymes such as horseradish peroxidase (HRP). This is attributed to their advantages of low cost, straightforward preparation, easy modification, excellent stability, and remarkable catalytic activity. Platinum nanoparticles (PtNPs), in particular, have found extensive use in bioanalytical applications due to their superior peroxidase-like activity, biocompatibility, and high chemical inertness. The choice of suitable stabilizing reagents is crucial in the synthesis of efficient nanozymes, as stabilizers significantly impact the physicochemical and biological properties of nanoparticles. In our study, chitosan (CS) was employed. The positively charged nature of CS facilitates the electrostatic binding of the negatively charged KAN binding aptamer (KBA) to chitosan-stabilized platinum nanoparticles (CS/PtNPs). Traditionally, immunosassays operate by detecting the target in a single mode. However, outcomes obtained through a single-mode signal readout can be susceptible to variations stemming from differences among operators, equipment disparities, and non-standard analytical protocols. In contrast, dual-mode sensing platforms not only possess the intrinsic characteristics of each response mode but also offer mutual validation of detection results obtained through diverse modes. Recent efforts have been directed towards establishing analytical methods that incorporate temperature changes as a signal, in addition to the colorimetric method, in immunosassays. Among various photothermal agents, oxidized TMB (TMB-ox) has emerged as a promising photothermal sensor due to its high photoconversion efficiency in near-infrared (NIR)-induced photothermal applications. TMB-ox exhibits distinct absorbance at UV-visible (652 nm) and NIR (808 nm) wavelengths, making it suitable for use as a probe in both colorimetric and photothermal detection.

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Nanocarrier Incorporating Fucoidan/Chitosan for Co-Encapsulation of TMB, Glucose Oxidase and Prussian Blue: Applications in Chemotherapy, Photothermal Therapy and Glucostarvation Treatment

Fucoidan, a naturally occurring sulfated polysaccharide derived from marine brown algae, has been explored as a promising therapeutic nanoparticle for cancer treatment. Effective strategies such as chemotherapeutic, photothermal therapy, and glucostarvation can create a conducive environment for successful cancer eradication. Harnessing the potential of functionalized fucoidan nanocarriers in combination with chitosan, acting as a nanocarrier, presents an opportunity for biological activation, particularly in abnormally acidic extracellular environments. In this study, we developed a fucoidan (Fu)-chitosan (CS) nanocarrier through a self-assembly technique and encapsulated it with 3,3′-tetramethylbenzidine (TMB), prussian blue (P), and glucose oxidase (GOX) (Fu/CS/PtNPs). The synthetic multi-stimuli-responsive Fu/CS/PtNPs nanoparticles were characterized using dynamic light scattering (DLS), zeta potential, UV absorption, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) analyses. DLS analysis indicated an average particle size of 440 nm, consistent with the spherical morphological structures observed in TEM results. Moreover, the positive zeta potential of 22.9 mV affirmed the stability of the synthesized particles.

For the electrophysiological signals, the sponge electrode can drastically increase the contact area between skin and electrode in water and gel condition. In addition, it also keeps the water or gel from entering the sponge, which is important to overcome the hydrophilicity of PDMS and carbon black, and maximize the absorption of water or gel into the sponge electrode. Layer-by-layer (LBL) coating is utilized with poly-L-lysine.

Eventually, we achieve 1.2×10^4 Ω·cm² skin contact impedance and 30 dB signal-to-noise ratio (SNR) for the electrocardiogram (ECG) and electromyography (EMG). Furthermore, the carbon black sponge electrode demonstrates better wet condition stability compared to other coated sponge electrodes. We utilized this E-textile system for the patient study to collect uterine contraction signals and predict childbirth (Washington University Institutional Review Board, IRB 201612140). We strongly believe that this E-textile system will lead to a new opportunity for stable long-term electrophysiological signal collecting applications.
The flow cytometry study provides evidence supporting the cytotoxic effects of 0.77 μg/mL Fu/CS@TPGox under laser conditions, yielding the highest rate of apoptosis (84.5%) compared to glucose starvation and chemodynamic treatment (60%). The utilization of three anti-cancer strategies—chemotherapy, photothermal treatment, and glucose starvation—is evident in the findings, showcasing Fu/CS@TPGox’s substantial anti-cancer impact at low concentrations. This research holds the potential to contribute to the development of more effective anticancer therapies for cancer treatment. A comprehensive investigation of these novel methods will be conducted to assess their in vivo efficacy and toxicity in comparison to other anti-cancer drugs in the future.

**Keywords:** Fucoyan, Chitosan, Photothermal therapy, Chemodynamic therapy, Glucose starvation

**5:00 PM SB06.09.10**

**A Conformal Second Skin for Long-Term Electrophysiology Monitoring of Plants**  Yi Jing Wong1,2, Xiaodong Chen1 and Xian Jun Loh2; 1Nanyang Technological University, Singapore; 2Agency for Science, Technology and Research, Singapore

Electrophysiological (EP) signals are important plant health indicators as they are pivotal in the growth development and plants’ response to environmental stimuli or stresses. Long-term plant health monitoring through analysis of EP signals has become increasingly important with the growing risk of global agriculture instability. However, the long-term attachment of wearable electrodes has always been hindered due to hydrogel dehydration or poor conformability with plant surfaces.

In this presentation, I will share my work on the development of a long-term coupling layer to achieve stable monitoring of plant EP signals. The high conformality of the coupling layer allows the non-invasive recording of EP signals for a month with superior signal-to-noise ratio and minimal drift. This work investigates the coupling mechanism and demonstrates potential applications, with the objective of laying the foundation for use of wearables in understanding plants’ long-term responses to environmental changes.

**5:00 PM SB06.09.11**

**A Fibrous Matrix Immobilized with Milk Exosomes for Improved Wound Healing**  Hoai-Thuong Duc Bui1, Gaeun You2, Hyeoksoo You1 and Hyejung Mok2; 1Kangwon National University, Korea (the republic of); 2Konkuk University, Korea (the republic of)

This study aims to provide an advanced therapy for wound recovery by immobilizing pasteurized bovine milk-derived exosomes (mEXO) onto a polydopamine (PDA)-coated hyaluronic acid (HA)-based electrospun nanofibrous matrix (mEXO@PMAT) using a straightforward dip-coating technique. The goal of this study is to create a wound-healing biomaterial that is composed of mEXO-immobilized mesh. mEXOs that have been purified and measured at approximately 82 nanometers contain a number of microRNAs (miRNAs) that are associated with collagen synthesis, cell proliferation, and anti-inflammatory properties. These miRNAs include let-7b, mir-184, and mir-181a. These miRNAs are responsible for eliciting increased mRNA expression of keratin5, keratin14, and collagen1 in human keratinoocytes (HaCaTs) and fibroblasts (HDF). During the course of fourteen days, the mEXOs that have been immobilized onto the PDA-coated meshes are progressively freed from the meshes without experiencing a burst-out effect. In the cells that have been treated with HaCaTs and HDF, the degree of in vitro cell migration is greatly increased in the cells that have been treated with mEXO@PMAT. This is in comparison to the cells that have been treated with unmodified or PDA-coated meshes. A further benefit of the mEXO@PMAT is that it facilitates substantially quicker wound closure in vivo without causing any noticeable toxicity. Therefore, the prolonged liberation of bioactive mEXO from the meshes has the potential to significantly promote cell proliferation in vitro and accelerate wound closure in vivo. This has the potential to be utilized by mEXO@PMAT as a promising biomaterial for wound healing.

**5:00 PM SB06.09.13**

**TD-DFTB Investigation and Deposition of Au onto Ag Nanocubes for Enhanced Stability and Sensing**  Ayomide D. Oluwafemi, Tim Kowalczyk and Ying Bao; Western Washington University, United States

Silver nanocubes are appealing to scientists and significant in technology due to their optical, electric, and chemical properties. However, there are limitations to chemically modifying silver nanocubes and they are susceptible to oxidation leading to the loss of their shape, stability, and quality. A solution is to deposit a metal like gold on silver nanocubes that is resistant to oxidation and chemically modificable. This prevents silver nanocube deterioration, ensuring their stability and modification potential. Unfortunately controlling the synthetic parameters that shape gold-coated silver nanocubes is difficile. The galvanic replacement reaction between gold and silver can erode, hollow, or disintegrate silver nanocubes. We conducted several tests to create a viable and reproducible gold-coated silver nanocube synthesis process. This research employed both thermodynamic and kinetic control to prevent galvanic replacement reaction by decreasing the gold precursor’s reduction potential with potassium iodide and adjusting the pH to regulate the reduction power of the reducing agent. We also evaluated various experimental settings and parameters vital to the synthesis. The refractive index sensing potential of gold-coated silver nanocubes was assessed and chemically treated with MUTAB ((11-Mercaptoundecyl)-N, N, N-trimethylammonium bromide). The Time dependent density theory functional (TD-DFTB) computational methodology was used to better understand the synthetic process and the atomic parameters vital to the synthesis. The refractive index sensing potential of gold-coated silver nanocubes was assessed and chemically treated with MUTAB ((11-Mercaptoundecyl)-N, N, N-trimethylammonium bromide). The Time dependent density theory functional (TD-DFTB) computational methodology was used to better understand the synthetic process and the atomic system, focusing on gold and silver electronic interactions and the effects of iodide (I), Chlorine (Cl), and Sulphite ions (SO3)2- on the galvanic replacement reaction, nanostructure geometry and stability. Overall, this study expands on gold-coated silver nanocube research. It gives more insights on how gold-coated silver nanocubes are synthesized, maintains their shape, improves stability, and functionality.

**5:00 PM SB06.09.15**

**Thermodynamically Stable Nanotubular mRNA Carriers made of Self-Adjusting Peptide Building Blocks**  Youjin Jung; Yonsei University, Korea (the republic of)

While mRNA delivery technology holds significant promise, storage and safety-related problems still exist, which arise from the inherently low thermodynamic stability of conventional mRNA carriers. The existing mRNA carriers have generally spherical structures. Considering the filamentous nature of mRNA and the exceptional thermodynamic stability associated with nanotubes among nano-assemblies, we could dynamically enhance the thermodynamic stability by developing mRNA carriers in the form of nanotubes. Through cooperative interactions, mRNAs and peptides were fabricated into rigid nanotubes that resemble tobacco mosaic virus. The fluctuating and irregular mRNA strand was coated by a single layer of peptide building blocks. The crucial factor in developing the mRNA nanotube lies in designing self-adjusting supramolecular building blocks (SABs). SABs contain -helical coiled coils, that incorporate two contrasting properties, namely dynamic flexibility and stiffness, within a single molecule. mRNA nanotubes with bound ligands for targeting exhibited high uptake efficiencies and the tunable transfection efficiencies in mammalian cells. Consequently, mRNA nanotubes will provide underlying technology in advancing the development of more stable and safe mRNA vaccines and therapeutics.

SESSION SB06.10: Biosensing

Session Chairs: Matteo Grattieri and Tedrick Thomas Salim Lew

Friday Morning, April 26, 2024

Room 427, Level 4, Summit

8:15 AM SB06.10.01

**Genetically Encoded Nanoparticles Synthesized Intracellularly**  Or Shemesh1,2, Krishnashis Chatterjee3, Pururav Ramakrishna2 and Amanda Lin2; 1The Hebrew University of Jerusalem, Israel; 2The University of Pittsburgh, United States

Despite major advances in detection and therapy, multiple cancers are still aggressive and incurable. Metal nanoparticles are being tested and used for tumor imaging, radiotherapy, and hyperthermia. However, using nanoparticles in living specimens is impeded because they often fail to reach the target cell or desired subcellular organelle, causing insufficient efficacy and safety concerns. Sophisticated chemical coatings and targeting aids such as vesicles and antibodies designed to address these pitfalls, provide only a partial solution, as they either increase off-target activity or hinder the clinical function of the nanoparticles. To solve this, we had the nanoparticles of interest made by the tumor cells, using their own genetic machinery. We expressed genes in the same cell type that would encapsulate the nanoparticles and synthesize the nanomaterial. While the cell itself can synthesize these nanoparticles, our approach involves the genetic code of the cell itself. This allows for the production of nanoparticles that are specifically designed for the cell's environment, potentially improving their efficacy and reducing toxicity.

8:30 AM SB06.10.03

**Nanopillar Devices for Single Molecule Sensing in The Clinic**  Alain Woehrling, Junrong Li, Selvakumar Edwardranga, Christopher Howard, Richard Lob and Matt Trau; The University of Chicago

Nanopillar devices offer a unique approach to single-molecule sensing, enabling the detection of individual molecules with high sensitivity and specificity. These devices utilize the unique optical properties of nanopillars to enhance the signal-to-noise ratio and allow for the detection of molecules at extremely low concentrations. The compact design and high sensitivity of nanopillar-based devices make them ideal for integration into clinical diagnostic tools. These advancements in nanopillar technology are paving the way for more precise and effective molecular diagnostics in a clinical setting.
The precise and early detection of biomarkers serves as molecular evidence for managing emerging diseases, enabling timely interventions, and potentially saving lives. Nanomaterials and nanostructures, with their unique physico-chemical properties, can be harnessed to develop innovative sensing systems for multiplex biomarker detection, generating patient-specific molecular profiles from a single blood sample. At the Centre for Personalised Nanomedicine at UQ, our focus is on developing translational nanotechnologies. We explore nanomaterials and nanostructures to design highly sensitive and multiplex sensing systems for profiling circulating biomarkers in the clinic. In this presentation, we will highlight our recent adventures into single molecule sensing and show how these sensing systems can provide a new window into complex diseases. We will introduce a nanopillar sensing device with single molecule sensitivity for monitoring the human immune system [1], cancer [2, 3] and postacute sequelae of COVID-19 (unpublished). Furthermore, we exemplify the design of novel biohybrid nanoprobes for sensing of emerging infectious diseases [4].

References

8:45 AM SB06.10.04
Rapid miRNA Detection Enhanced by Exponential Hybridization Chain Reaction in Graphene Field-Effect Transistors Zhaoli Gao and Ting Huang; Department of Biomedical Engineering and Shun Hing Institute of Advanced Engineering, The Chinese University of Hong Kong, Hong Kong

Point-of-care nucleic acid testing with speed, accuracy, and precision is crucial for early detection and timely treatment of diseases. Electronic biosensors that utilize target recycling and hybridization chain reaction (THRCR) in combination with graphene field-effect transistors (GFETs) show great promise for highly sensitive diagnostics of nucleic acid, reaching the limit of detection down to 100 aM. However, a challenge arises from its linear kinetics, which results in prolonged sensing times for lower concentration oligonucleotides, e.g., approximately 15 hours for 100 aM oligonucleotides. Here, we report a 30-fold reduction in sensing time, from 15 hours to a mere 30 minutes, for detecting 100 aM miRNA, which is achieved by developing an exponential amplification reaction pathway, synergistically compatible with GFETs. This enables the target miRNA to exponentially trigger TRHCR, leading to long-nicked double-stranded polymers that can be detected by GFET through chemical gating. Consequently, our approach facilitates the detection of 22 mer miRNA at concentrations as low as 100 aM in human serum samples, achieving a time frame congruent with point-of-care testing and superior specificity against single-base mismatched interfering oligonucleotides. Our work paves the way towards highly precise, efficient, and label-free nucleic acid testing, thus facilitating early-stage detection of cancer and other diseases at the point of care.

9:00 AM *SB06.10.05
Superstrong Electronic Hydrogel Actuators (ECO) Max M. Hamedi; KTH, Sweden

Superstrong Electronic Hydrogel Actuators (ECO)

Intelligent systems combine sensing, actuation, and computation to achieve complex tasks and functions. Soft electrically controlled multifunctional materials, especially hydrogels, are the most promising materials for such systems as they are as adaptable as biological systems yet compatible with advanced systems through electronics. We describe an electroactive hydrogel fabricated from cellulose nanofibrils from trees, and conductive nanomaterials, like CNTs or 2D MXenes. These nanoparticles self-assemble into an anisotropic composite networks with an open mesoporous structure that can hold lots of water and be highly permeable to substances in their surroundings. The anisotropy of the network allows high expansion in one direction while maintaining very high strength and high electric conductivity in the other. The electrochemical charge/discharge of the conductors in the hydrogels controls the internal salt concentration and consequently their osmotic swelling. This allows direct electrically controlled actuation where around 700 water molecules expand/contract the structure for each ion/electron pair inserted/de-inserted at only ±1 volt, resulting in up to 300% electroosmotic expansion, and with very high pressures reaching 1 MPa.

This mode of electronic actuation has not been shown before. We call these electroosmotic (ECO) actuators. Our ECO hydrogel actuators have emergent properties not present in any previously known soft material. ECO actuators represent a new form of smart soft material, opening possibilities not achievable with other materials systems: as they enable monolithic integration of sensors and many other functions into the same composite, for example using 3D printing techniques.

References

9:30 AM BREAK

10:00 AM SB06.10.06
A Breakthrough in Nanotechnology-Enhanced Glucose Sensors Yuxu-Hao Hsiao, Rajan D. Chakravarthy, Yu-Hsiang Hsiao and Hsin-Chieh Lin; National Yang Ming Chiao Tung University, Taiwan

According to the International Diabetes Federation (IDF), 537 million adults worldwide suffered from diabetes in 2021, and it is expected that by 2045, one out of every eight adults will have diabetes. As a result, monitoring blood glucose concentrations is essential.

Recent breakthroughs in materials science have led to the creation of nanomachines, mimicking the catalytic functions of natural enzymes, typically comprising metals, metal oxide or metal-organic frameworks (MOFs), offering benefits of stability, precision, and rapid reaction rates for blood glucose measurement. Nanomachines, though versatile, tend to lack the specificity of natural enzymes, limiting their practicality, and some may exhibit low biocompatibility.

Hence, we created enzyme nanoparticles, fusing nanomaterial attributes with enzyme benefits to preserve natural enzyme advantages and compensate for nanozyme limitations like reduced catalytic activity, specificity, and biocompatibility, tailored for utilization in glucose sensors.

The findings illustrate that by incorporating organic enzyme-based nanoparticles, the electrode can attain outstanding glucose detection capabilities through the utilization of nanotechnology, enabling reduced enzyme dosage, heightened reaction efficiency, and enhanced stability, thus presenting a promising prospect for the future development of a novel blood glucose sensor.

10:15 AM SB06.10.07
MXene-Based 3D-Nanomaterials Printed Wearable System: A Self-Powered Solution for Continuous Physiological Biosignal Monitoring Rahim Esfandyarpour and Shinguirai Chakong; University of California, Irvine, United States

The development of sustainable, self-powered wearable sensing systems capable of recording physiological biosignals is pivotal for personalized health monitoring, but such devices have remained elusive. In this study, we introduce a novel, self-powered, MXene-based 3D-nanomaterials printed flexible wearable system tailored for continuous, real-time physiological biosignals monitoring. This integrated system combines power-efficient triboelectric nanogenerators (TENG), highly sensitive pressure sensors, and multifunctional circuitry. MXene, a two-dimensional (2D) transition material known for its unique electronegative, conductive characteristics, and triboelectric properties, serves as the foundation of our device and is ideally suited for 3D-printing. We paired MXene with a skin-mimicking Styrene-ethylene-butylene-styrene (SEBS) substrate, which boasts a positive triboelectric characteristic and exceptional stretchability. Our wearable, MXene-based, self-powered physiological sensing system delivers an output power of ~816.0 mW m−2 for its TENGs, with a sensor sensitivity of ~6.03 kPa, a low detection limit of ~9 Pa, and a rapid response time of ~90 ms. This makes it possible to continuously monitor the radial artery pulse (RAP) waveform in real-time, without reliance on external power sources. Furthermore, the system's capabilities extend to on-demand RAP monitoring and wireless data and power transmission via near-field communication. This development represents one of the inaugural wearable systems for real-time physiological biosignal monitoring, fully powered by human motion, showcasing its tremendous promise in the field.
In addition to the medical phantoms, the alginate-based hydrogel can be further functionalized with nanoparticles for cardiovascular and musculoskeletal disease treatment. By incorporation of vegan, food safe and biodegradable, which is highly suitable for surgery practice that is destructive. These advantages also make it the perfect material system for fabricating patient-specific the individual organ and tissue within one material system. The used materials are cheap and easy to obtain even in resource-constrained or developing countries. Moreover, they are 100% phantom can be measured under CT and US, after which the students or surgeons can be trained to identify the tumor from the CT and US images and then practice removing the tumor. Another type of phantom is the so-called multipurpose phantom, which integrates multiple imaging modalities and allows for surgery practice within a single construct. For example, these phantoms exhibit limited suitability for hands-on surgical training. Surgical practice inherently involves destructive procedures, thereby precluding the subcellular resolution evaluations. While progress has been made in the development of wearable sensors and continuous health monitoring, these devices can only monitor a limited set of physical signals and suffer from poor operational stability in biofluids. To meet the demand for reliable long-term continuous monitoring and objective stress assessment, we developed a consolidated artificial intelligence-reinforced electronic skin (CARES) platform that deconvolutes the biological mechanism behind stress responses. Integrated with miniaturized iontophoresis module, microfluidic channels and system-level engineering, the platform is capable of monitoring three key vital signs as well as six molecular biomarkers in human sweat. To enable continuous long-term daily monitoring, we developed a general material strategy for biochemical sensors by introducing analogous composite materials into the sensor interface that achieves an unprecedented long-term sweat biomarker analysis of over 100 hours with high stability. The high performance of CARES platform was evaluated through continuous multimodal physiochemical monitoring over 24-hour real-life activities, and can differentiate physiological and psychological stressors, as well as quantification of psychological stress responses with a high accuracy and confidence level. Such fully-integrated CARES platform can be adapted to monitor a broad spectrum of disease diagnosis and pave the way for numerous practical wearable applications such as intelligent healthcare and personalized medicine.

Phantoms are specialized models designed to mimic the properties of human tissue or body structures for use in various medical and healthcare applications. These phantoms are usually made for single application. For example, calibration phantoms usually contain materials with known density, size, or other physical properties e.g., polyethylene, acrylic, and polycarbonate, which can be used in computed tomography (CT), magnetic resonance imaging (MRI), and ultrasound (US) to calibrate the imaging equipment, ensure accurate measurements, and detect potential issues or deviations. They are not applicable for utilization in surgery training. Phantom models are usually made from soft materials like silicones, utilized for educational and skill development purposes. They replicate anatomical structures and allow medical students and professionals to learn basic surgical techniques, honing advanced skills, and improving the dexterity and coordination. However, these phantoms exhibit limited suitability for hands-on surgical training. Surgical practice inherently involves destructive procedures, thereby precluding the subsequent reutilization of the phantoms. Materials like silicones owing to their resistance to natural degradation processes, exhibit persistence in the environment over an extended period, thereby constraining its applicability in the context of surgical training. These commercial phantoms have relatively high cost, which limits their use, especially in developing countries. Another type of phantom is the so-called multipurpose phantom, which integrates multiple imaging modalities and allows for surgery practice within a single construct. For example, these phantoms can be measured under CT and US, after which the students or surgeons can be trained to identify the tumor from the CT and US images and then practice removing the tumor. However, the cost of making such phantoms is usually extremely high due to the materials and complicated fabricating process. In this work, we have developed a facile material system based on alginate and vegetable fat for fabricating the multipurpose phantom. The mechanical, US and CT properties of the materials can be tuned independently to achieve the desired properties of the individual organ and tissue within one material system. The used materials are cheap and easy to obtain even in resource-constrained or developing countries. Moreover, they are 100% vegan, food safe and biodegradable, which is highly suitable for surgery practice that is destructive. These advantages also make it the perfect material system for fabricating patient-specific phantoms for difficult surgery planning and practicing.

In addition to the medical phantoms, the alginate-based hydrogel can be further functionalized with nanoparticles for cardiovascular and musculoskeletal disease treatment. By incorporation of nanoparticles, the injectability or printability of the hydrogels can be modified and the release of the bioactive substances can be achieved under controlled conditions.

DNA-Based Immunostimulatory Hydrogel Loaded with Nanoparticle-Detained Toxins as a Toxoid Vaccine against Bacterial Infection Zhongyuan Guo, Ronnie H. Fang and Liangfang Zhang; University of California San Diego, United States

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Ultrashort peptides that self-assemble into hydrogel matrices can provide mechanical and adhesion cues by a slight change in their sequence. Here we report two examples of specific sequence designs for tissue engineering and coral restoration applications.

Cells' interactions with their microenvironment influence their morphological features and regulate crucial cellular functions including proliferation, differentiation, metabolism, and gene expression. Most biological data available are based on in vitro two-dimensional (2D) cellular models, which fail to recapitulate the three-dimensional (3D) in vivo systems. This can be attributed to the lack of cell–matrix interaction and the limitless access to nutrients and oxygen, in contrast to in vivo systems. Despite the emergence of a plethora of 3D matrices to address this challenge, there are few reports offering a proper characterization of these matrices or studying how the cell–matrix interaction influences cellular metabolism in correlation with gene expression. In this study, two tetrameric ultrashort self-assembling peptide sequences, FF1K and F11K, were used to create in vitro 3D models using well-described human dermal fibroblast cells. The peptide sequences are derived from naturally occurring amino acids that are capable of self-assembling into stable hydrogels without UV or chemical cross-linking. Our results showed that 2D cultured fibroblasts exhibited distinct metabolic and transcriptomic profiles compared to 3D cultured cells. The observed changes in the metabolomic and transcriptomic profiles were closely interconnected and influenced several important metabolic pathways including the TCA cycle, glycolysis, MAPK signaling cascades, and hemostasis. Data provided here may lead to clearer insights into the influence of the surrounding microenvironment on human dermal fibroblast metabolic patterns and molecular mechanisms, underscoring the importance of utilizing efficient 3D in vitro models to study such complex mechanisms.

Coral reef survival is threatened globally. One way to restore this delicate ecosystem is to enhance coral growth by the controlled propagation of coral fragments. To be sustainable, this technique requires the use of biocompatible underwater adhesives. Hydrogels based on rationally designed ultrashort self-assembling peptides (USP) are of great interest for various biological and environmental applications, due to their biocompatibility and tunable mechanical properties. Implementing superior adhesion properties to the USP hydrogel compounds is crucial in both water and high ionic strength solutions and is relevant in medical and marine environmental applications such as coral regeneration. Some marine animals secrete large quantities of the aminoacids dopa and lysine to enhance their adhesion to wet surfaces. Therefore, the addition of catechol moieties (Do) within the USP sequence containing lysine (IIZK) should improve the adhesive properties of USP hydrogels. However, it is challenging to place the catechol moiety (Do) within the USP sequence at an optimal position without compromising the hydrogel self-assembly process and mechanical properties. Here, we demonstrate that, among three USP hydrogels, DoIIZK is the least adhesive and that the adhesiveness of the IIZDoK hydrogel is compromised by its poor mechanical properties. The best adhesion outcome was achieved using the IIZKD hydrogel, the only one to show equally sound adhesive and mechanical properties. A mechanistic understanding of this outcome is presented here. This property was confirmed by the successful gluing of coral fragments by means of IIZKDDo hydrogel that are still thriving after more than three years since the deployment. The development of biocompatible underwater glue suggests that it could be advantageously implemented for other applications, such as surgical interventions.

**Keynote Speaker**

**Invited Paper**

10:30 AM SB06.05.03

**Living Material Architecture as the Reciprocal Interactions Between Materials and Embedded Cells**

*Salman Karim* and Nakhiah Goulbourne; University of Michigan, United States

The interface between biomaterials and synthetic biology leads to engineered living materials that have superior properties such as tunability, programmability, growth, self-healing, disturbance sensing, and adaptation to their surroundings, etc. This three-dimensional interaction between cells and hydrogels made from synthetic polymers or nature-derived biopolymers gives rise to a smart, complex, dynamic, and stimulus-responsive system which opens up a new frontier for tissue engineering, regenerative medicine, self-healing materials, and sustainable building materials. However, the engineering of living materials is still in its infancy as the control of the properties including mechanical properties such as elasticity, stiffness, plasticity; swelling behaviour, microscale architecture, biological signalling, response sensitivity, stability, and deformation etc, is not well understood. Additionally, advancements in the 3-D printing, manufacturing, and assembly of material architecture are required to engineer functional materials. Our focus is on the engineering of load-bearing structures by cell embedding during scaffold fabrication using 3-D bioprinting in a spatially organised manner. An attempt has been made to engineer living materials of distinctive chemical and physical living structures by developing algae-laden hydrogel motifs to gain mechanistic insights into their morphology, pattern formation, and stability. The encapsulation of microalgae *Chlamydomonas reinhardtii* in 3D hydrogel scaffolds with predesigned geometries was carried out to examine different parameters such as material composition and its effect on bioprinting structures, mechanical properties of hydrogel such as swelling and stability in culture, pattern geometry, cell survival during the plotting, cell viability and growth by measuring oxygen release and chlorophyll, spatial distribution of cells within the matrix, and build structure stability. Further, the relationship between printing parameters and plotting material composition will be tested. Overall, the purpose of this study is to identify the mechanism of failure in 3-D living materials by identifying the role of algae-hydrogel interactions during the growth, stability, and deformation of *Chlamydomonas reinhardtii* in a hydrogel medium. The results from this study will facilitate the transition from microscale to macroscale living architecture.

**SYMPOSIUM SB07**

**Lipid Materials—Theory, Fundamentals and Applications**

April 23 - April 25, 2024

**Symposium Organizers**

Shelley Claridge, Purdue University

Aurelia Honerkamp-Smith, Lehigh University

Elizabeth Kelley, NIST

Cecilia Leal, University of Illinois, Urbana-Champaign

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* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION SB07.01: Fundamental Properties of Lipid Materials and Membranes

Session Chairs: Elizabeth Kelley and Cecilia Leal

Tuesday Morning, April 23, 2024

Room 439, Level 4, Summit
Ionizable lipid-containing nanoparticles (LNPs) have enabled the delivery of RNA for a range of therapeutic applications. In order to optimize safe, targeted and effective LNP-based RNA delivery platforms, an understanding of the role of composition and pH in their structural properties and self-assembly is crucial, yet there have been few computational studies of such phenomena. Here we present a coarse-grained dissipative particle dynamics model of ionizable lipid and mRNA-containing LNPs. Our model allows access to the large length- and time-scales necessary for LNP self-assembly, and is automatically mapped and parameterized with reference to all-atom structures and simulations of the corresponding components at compositions typical of LNPs used for mRNA delivery. Our simulations reveal insights into the dynamics of self-assembly of such mRNA-encapsulating LNPs, as well as the subsequent pH change-driven release of mRNA.

**10:45 AM **SB07.01.03

**Dynamics of Fluid Bilayer Membranes: Insights from GUV Flickering and Electrodeformation**

Peta M. Vlahovska: Northwestern University, United States

A lipid bilayer is the main component of the membranes that envelope cells and cellular organelles. While the fluidity of the bilayer is known to control lateral mobility of embedded biomolecules, its importance in membrane shape transformations is less appreciated. In this talk, I will discuss the significant role played by membrane viscosity in the bending dynamics of highly-curved structures such as liposomes and sub-cellular organelles. We extend the model of Seifert and Langer [Europhys. Lett. 1993] for the dynamics of a planar viscous bilayer to a quasi-spherical vesicle. The theory predicts a slower relaxation rate, \( \alpha \approx 4 \), for a spherical harmonic mode \( q \), a drastic change from the classic result \( \alpha \approx 3 \). Flickering spectroscopy, which is the analysis of experimentally recorded dynamically-driven shape fluctuations of giant vesicles (GUVs), confirm the theoretical results in the case of phospholipid/cholesterol mixtures and, for the first time, demonstrate that membrane viscosity slows down bilayer undulation dynamics giving the appearance of an effectively stiffer membrane. For scattering techniques such as Neutron Spin Echo, the theory predicts an anomalous diffusion exponent of 1/2 governing the Dynamic Structure Factor instead of the commonly used 2/3 [Zilman and Granek, Phys. Rev. Lett. (1996)]. Furthermore, we extend the theory to viscoelastic membranes motivated by the flickering dynamics of block-copolymer vesicles and recent electrodeformation experiments that show a two-time scale response, consistent with Kelvin-Voigt viscoelastic material, in the transient ellipsoidal deformation induced by an applied uniform AC electric field of DMPC vesicles near the melting transition.

This research was supported by NIGMS award IR01GM140461

**11:15 AM SB07.01.04**

**Impact of Structurally Active Lipids on Lipid Nanoparticle Delivery Processes**

Lining Zheng and Cecilia Leal; University of Illinois, United States

RNA therapeutics have the potential to treat many diseases that are not targetable by small molecules. One of the biggest challenges in RNA therapy is RNA delivery. Lipid nanoparticles(LNPs) is one of the most successful RNA delivery systems to date, however the delivery efficiency of LNP systems is still hindered by inefficient endosomal escape. How LNPs impact the endosomal escape process is still poorly understood. In this work, we explore how structurally active lipids that can form bicontinuous cubic and inverse hexagonal phases impact the properties of active model endosomal membranes, to better understand the change of endosomes when lipids from LNPs diffuse into the endosomal membrane. We formed giant unilamellar vesicles (GUVs) with different molar percentages of structurally active lipids, and with fluctuation analysis showed that the bending modulus of the membrane reduces with the increase in structurally active lipid content. The presence of membrane protein can greatly impact endosomal membrane properties, so GUVs with V-ATPase, a membrane protein that is essential to the endosomal escape process, were also formed to model active endosomal membranes.

**SESSION SB07.02: Phase Separation in Lipid Materials and Membranes**

Tuesday Afternoon, April 23, 2024

Room 439, Level 4, Summit

**1:45 PM **SB07.02.01

**Liquid-Liquid Phase Separation in Membranes is a Product of Universal Material Properties and Specific Biological Outcomes**

Sarah Kelley; University of Washington – Seattle, United States

Many lipid membranes reversibly phase separate to form large (micron-scale) liquid domains. These systems vary widely, from simple membranes composed of only three lipid types to complex membranes of living yeast cells or giant plasma membrane vesicles. Independent of the source of the phase-separating membrane, the size, shape, and behavior of the resulting liquid domains is governed by the membrane’s material properties and the physical conditions under which it is held. For example, small domains in fluidic vesicles grow larger as membrane tension increases and as temperature decreases. Similarly, the temperature at which a membrane undergoes liquid-liquid phase separation is influenced by its lipid composition and the surfaces it touches. In simple membranes, these experimental conditions are imposed by researchers. In contrast, yeast cells actively regulate their lipid composition to achieve a particular biological outcome, namely, to maintain an offset between their growth temperature and their membrane transition temperature.

**2:15 PM **SB07.02.02

**Monolayer Domain Shapes - Equilibrium or Kinetically Controlled?**

Joseph A. Zasadzinski1; Cain Valtierez-Gaytan1, Zachary McAllister1 and Benjamin Stottrup2; University of Minnesota, United States; 1Augsburg University, United States

Lateral phase separation of lipid monolayers and bilayers into domains of different composition or local order is the basis of the “raft” hypothesis of cell membrane organization in which sub-micron domains, or rafts, of different local composition or order nucleate and grow from a continuous phase within the cell membrane. These physical and chemical inhomogeneities within the membrane provide sites for multiple different proteins to localize and carry out complex cell functions. Phase separation and domain formation is also important to the dynamic spreading and surface tension lowering ability of native and clinical lung surfactants (LS) used to treat neonatal respiratory distress syndrome (NRDS) in premature infants. The relative simplicity of two-dimensional lipid monolayer films makes them ideal systems to study the fundamental issues that govern lateral phase separation, the evolution of domain microstructure, and the effects of this microstructure on interfacial dynamics. Here we show that a myriad of domain morphologies that occur during monolayer compression are the result of the classic Mullins-Sekerka growth instability (1) that occurs during crystallization from a multicomponent melt. On compression of dipalmitoylphosphatidylcholine-hexadecanol (DPPC-HD) monolayers with 1-5 mol% cholesterol, originally circular domain develop finger-like growth patterns as the surface pressure is increased. The finger widths and number vary with compression rate and each well with semi-quantitative agreement with the predictions of the Mullins-Sekerka theory. The Mullins-Sekerka theory postulates a diffusion front instability that predicts that the finger widths are set by a balance between line tension, crystallization rate, and the local variation in chemical potential between crystal and melt. The fingers are purely kinetically driven but eventually evolve into an extended stripe domains whose width depend only on surface pressure and temperature. The stripe width in independent of the route by which the morphology is approached, suggesting thermodynamic equilibrium. These observations help explain the wide variety of domain shapes observed in lipid monolayers that depend on compression rate and monolayer history.

**2:45 PM SB07.02.03**

**Tiny Forces from Flow Transport Membrane Proteins on Cell Surfaces**

Aurelia Honerkamp-Smith; Lehigh University, United States

Many cells sense and respond to flow in their environment, and flow responses regulate important physiological processes such as blood pressure. A paradox in cardiovascular flow sensing is that shear forces applied by blood flow are extremely small, and it is currently unknown how cells detect them. We propose a mechanical solution to this problem: lipid-anchored membrane proteins can be rearranged even by tiny shear forces. We have previously shown that avidin linked to biotinylated lipids in supported membranes forms micron-scale concentration gradients in response to flow and then sensors shear forces. We observe that in both living cells and glass-supported lipid bilayers, proteins move downstream when flow is on, forming a concentration gradient, and that the gradient disappears when the flow is turned off. This gradient is sensitive to flow magnitude and direction and disappears when flow stops. We estimate protein diffusion constants and hydrodynamic forces by observing the gradient dynamics. Our recent work demonstrates the sensitivity of our method for measuring these forces, allowing us to correlate hydrodynamic force with the folded shape of lipid-anchored proteins, distinguish membrane drag on different lipid anchors, and demonstrate that similar protein transport can occur on the surface of living cells. Our results support the hypothesis that lateral transport of membrane proteins may contribute to flow sensing.
Lipid bilayers are the universal structure of all cell membranes and depend on the propensity of specific phospholipid classes to form fluid lamellar phases. However, no biological membranes are composed entirely of bilayer-forming lipids, instead balancing species with low and high intrinsic curvatures. I will describe how this dynamic plays out in organisms that have adapted to hydrostatic pressure, which increases by 1 atmosphere every 10m in the water column. Small angle x-ray scattering of lipid suspensions from deep sea comb jellies (ctenophores) collected at depths up to 4km revealed a remarkable ability to access non-lamellar lipid phases, which are inhibited by pressure. Lipidomic analysis across a wide range of species identified phospholipids with large, negative spontaneous curvature as a depth-specific adaptation across the phyllum. High pressure molecular dynamics of lipid-derived bilayers supports this adaptation. Using engineered bacterial strains, we found that lipid spontaneous curvature can modulate pressure tolerance. Based on these results, we propose a homeocurvature adaptation model for cell membranes, in which the effect of pressure on lipid shape can contribute to both fitness and specialization in the deep oceans.

4:00 PM SB07.02.05
Nanoscale Molecular Organization in Polymer-Lipid Hybrid Systems using Cryo-Electron Microscopy Analysis of Nanoparticles (NPs) Nurila Kambar and Cecilia Leal; University of Illinois at Urbana-Champaign, United States

Membranes play an essential role in diverse engineering fields such as biomedicine, energy generation and water treatment. Thus, development of new types of membranes with tailored properties has been an active area of research. Two-component hybrid materials where phospholipid (PL) membrane stacks are hybridized with synthetic block copolymers (BCP) are of great interest due to their ability to combine the unique properties of two different materials. Hybrid membranes can demonstrate a wide range of self-assembled structures and properties that can be tailored to specific applications. The nanoscale arrangement of hybrid membranes into distinct lateral domains with varying structures and compositions is considered crucial for membrane functionality. The precise understanding of this organization has been challenging, primarily due to the absence of direct methods for probing nanoscale membrane features. Utilizing machine learning for the domain analysis of hybrid multilamellar nano-sized vesicles in cryo-TEM images, we are able to precisely generate detailed high-resolution 2D thickness maps of the membranes. These maps provide insights into the distribution of polymer-rich, lipid-rich, and well-mixed domains within the vesicles. Despite the optical microscopy indicating homogeneous mixing in the hybrid membranes, we reveal the coexistence of two distinct membrane structures within homogeneously mixed lipid-polymer hybrid vesicles. In this study, we highlight the significance of our semi-automated technique for directly imaging nanodomains in both biomimetic and biological membranes.

5:00 PM SB07.02.06
Lipid Structural and Dynamic Organization of Lipid Nanoparticles via Static and Time-Resolved Small-Angle Scattering Shayna Hilburg and Lilo D. Pozzo; University of Washington, United States

Lipid nanoparticles have revolutionized human health outcomes, as evidenced by the mRNA vaccines used to combat COVID-19. Despite the success of these self-assembled nucleic acid therapeutics, the physicochemical fundamental properties of the non-viral delivery vectors must be better understood to be more easily tuned and optimized. In this work, we use small-angle X-ray (SAXS) and neutron scattering (SANS) to study the organization of lipid nanoparticles. Specifically, we investigate how the environmental changes lipids nanoparticles experience during storage and delivery and the fundamental properties of macromolecular cargo impact particle structure and dynamics. The effects of lipid charge state and nucleic acid properties are studied through static SAXS and SANS measurements as well as time-resolved SANS, which provides insight into the molecular exchange. Such information demonstrates what drives degradation in storage, what parameters can be changed to improve component dissociation allowing more efficient endosomal escape, and how nucleic acid properties can impact lipid formulation selection.

6:00 PM SB07.02.07
How an Extra Terminal Group on Fatty Acids Leads to The Formation of Nanostructured Langmuir Films? Adam Squires; University of Bath, United Kingdom

Assemblies of fatty acid (FA) monolayers are induced by the presence of a single terminal methyl group that increases the total curvature of the molecular monolayer. Using nanostatic Langmuir monolayers, we observe that the horizontal length of the monolayer is increased by a factor of 5 when two terminal methyl groups are introduced. We observe the spontaneous curvature of the monolayer to be -0.3 for both of these 19MEA molecules. Thus, the spontaneous curvature is decreased by half in the presence of two terminal methyl groups.

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Pegylation of drug nanocarriers, and of lipid-based vectors in particular, is a common strategy to grant them stealth properties and promote their prolonged circulation in the bloodstream. Pegylation has numerous applications in drug delivery.

The development of acid degradable linkers that rapidly hydrolyze at endosomal pHs is a central problem in the field of drug delivery. Acid degradable linkages are challenging to develop because of their instability. In this report we present a new acid-degradable linker based on an azide-acetal, which rapidly hydrolyzes at endosomal pHs but has exceptional stability at pH 7.4. The azide-acetal linkage hydrolyzes via a two-step mechanism that requires reduction and acid hydrolysis and has a unique combination of stability and rapid triggerable hydrolysis. The azide-acetal has a hydrolysis half-life of days at pH 7.4 and can be conveniently synthesized and incorporated into delivery vectors, however after in situ reduction with DTT it hydrolyzes with a half-life of minutes at pH 6.0. We used the azide-acetal linker to synthesize acid degradable nanoparticles that demonstrate that these new lipids are significantly better at delivering mRNA to mice than traditional lipids. Lipid nanoparticles containing acid degradable linkages transfected multiple non-liver organs after an intravenous injection and efficiently transfected brain tissue after an intracranial injection. The azide-acetal linkage has the potential to solve the instability problems associated with acid degradable linkers and has numerous applications in drug delivery.

**2:00 PM SB07.04.02**

**Preformed Vessel-Mediated Delivery of Messenger RNA for Retinal Gene Therapy**

Gaurav Sahay; Oregon State University, United States

Quantitative nucleic acid encapsulation by lipid-based nanoparticles (LNPs) is often thought to be one of the main prerequisites for successful cargo delivery, as the lipid environment protects mRNA from degradation by external nucleases and assists in initiating delivery processes. However, here we report the delivery of mRNA via preformed vesicle approach (PFV-LNPs) that defies this precondition. PFV-LNPs possess superficial mRNA localization that proved exceptionally beneficial in delivering mRNA to the back of the eye. Successful delivery of GFP mRNA to retinal pigment epithelium and photoreceptors was observed in mice, non-human primates, and human retinal organs. This approach was generally beneficial as indicated by improved EGFP transfection with PFV-LNPs containing binding lipids. We posit that the PFV architecture may be beneficial to transfect local targets like the back of the eye. We will also discuss the impact of surface modifications for LNP mediated gene editing.

**2:30 PM BREAK**

**3:30 PM SB07.04.03**

**Stimuli-Responsive Liposomes for Triggered Cargo Release and Activated Cell Delivery**

Michael Best and Jinchao Lou; University of Tennessee Knoxville, United States

Liposomal nanocarriers are effective for the encapsulation and delivery of a wide range of therapeutic cargo in a manner that improves drug pharmacokinetic properties. However, liposome therapeutic properties could be advanced by enhancing control over cell delivery as well as cargo release. This presentation will describe the development of stimuli-responsive liposomes designed to achieve both of these goals. One approach employs synthetic lipid switches engineered to modulate lipid membrane properties upon contact with disease-associated conditions, such as through programmed chemical reactions and/or conformational changes. In particular, we will focus on encapsulated cargo release triggered by the binding of chemical agents/molecules that are commonly upregulated in diseased cells. A second strategy involves chemically triggering of cell entry. In this design, liposomes are masked as neutral carriers until they encounter stimuli that generate cationic lipids, thereby activating cell entry. The presentation will include the design and synthesis of stimuli-responsive lipid switches, analysis of selectivity of cargo release in the presence of different stimuli, investigation of changes to liposome membrane properties, and evaluation of cellular delivery properties triggered by disease-associated stimuli.

**4:00 PM SB07.04.04**

**Poly(N-Vinyl Amide)-Lipid Conjugates as Poly(Ethylene Glycol) Alternatives for The Modification of Lipid-Based Nanocarriers**

Antoine Debuigne, Manon Berger, François Toussaint, Sanaa Ben Djema, Christine Jerome, Anna Lechanteur, Denis Mottet and Geraldine Piel; University of Liege, Belgium

Pegylation of drug nanocarriers, and of lipid-based vectors, is a common strategy to grant them stealth properties and promote their prolonged circulation in the bloodstream. However, PEG is also associated with the accelerated blood clearance (ABC) effect, leading to the fast elimination of the medicine from the body, and to the PEG dilemma, which consists in uptake issues due to the presence of the polymer layer around the carrier. For these reasons, the search for PEG alternatives in drug delivery systems is timely. This work explores the potential of poly(N-vinyl amide) linkages, including poly(N-vinyl pyrrolidone) (PNVP), as PEG alternatives for the development of non-toxic, efficient and less immunogenic lipid-based carriers, in particular siRNA-loaded lipoplexes and lipid nanoparticles dedicated to gene therapy. For this purpose, novel poly(N-vinyl amide)-lipid conjugates were synthesized by reversible deactivation radical polymerization. This strategy allowed to control the molar mass of the hydrophilic polymer sequence and to functionalize its extremity with lipids, such as 1,2-distearoyl-sn-glycero-3-phosphoethanolamine (DSPE), to ensure their anchoring at the surface of the lipid carriers. The surface active properties of these poly(N-vinyl amide)-lipid conjugates and their interaction with phospholipid bilayers were studied by Langmuir film balance and quartz crystal microbalance with dissipation monitoring (QCM-D). The anchoring of the poly(N-vinyl amide)-lipid conjugates on the surface of siRNA-loaded lipid nanocarriers and their ability to prevent protein adsorption were demonstrated by dynamic light scattering, zeta potential and nanoparticles tracking analyses. In vitro and in vivo studies demonstrated the non-toxicity, stealth properties and transfection efficiency of the accordingly modified siRNA-loaded lipid nanocarriers. Importantly, compared to their pegylated counterparts, lipid nanocarriers decorated by poly(N-vinyl amide) showed lower immunogenicity in particular after the second injection which constitutes a key step to the development of safer lipid-based carriers. 


Funding: LIPEGALT-ARC project (Concerted Research Action program), National Fund for the Scientific Research FNRS.

**4:15 PM SB07.04.05**

**Biodegradable Polymer-Lipid Nanoparticles for Effective In Vivo mRNA Delivery**

Yivan Yanu and James Hedrick; Bioprocessing Technology Institute, Agency for Science, Technology and Research (A*STAR), Singapore; IBM Almaden Research Center, United States

Currently, only 2 mRNA Covid-19 vaccines from Moderna and Pfizer-BioNtech have been approved by the US FDA for human use. Both vaccines utilize SARS-CoV-2 mRNA as the antigen and lipids as the carrier. The lipids consist of 3 different types of lipids (PEG-lipid conjugate, ionizable lipid and helper lipid) and cholesterol. The ionizable lipid condenses mRNA into lipid nanoparticles (LNPs) through electrostatic interaction and self-assembly. The mRNA-loaded LNPs stimulate the immune cells for prophylactic response against the SARS-CoV-2 virus. The use of PEG-lipid (ALC-0159) makes theLNPs unstable in vivo, leading to delivery of mRNA primarily after the liver i.v. injection of mRNA LNPs. In this study, we synthesize amphiphilic block copolymers of PEG and biodegradable polycarbonate with varying chain length and urea moiety to replace PEG-lipid conjugate. Urea functional groups are used to form hydrogen-
In this study, we have pioneered the development of Ang2-conjugated cubosomes, an approach aimed at enhancing BBB penetration and improving the uptake of glioblastoma cells. Our interest because of their inherent benefits, including biocompatibility, facile surface functionalization for targeted drug delivery, and improved solubility for poorly soluble drugs. These on healthy tissues. Additionally, delivering drugs from the bloodstream to the brain is hindered by the presence of the blood-brain barrier (BBB). Lipid nanoparticles have gained substantial for patients. Various treatment methods, such as surgery, radiotherapy, and chemotherapy, have been developed to address brain diseases; however, they often come with significant side effects Glioblastoma multiforme is an exceptionally aggressive form of brain cancer known for its high malignancy and resistance to traditional treatments, leading to a bleak prognosis. Therefore, developing a new way of loading technology in exosome is in urgent need. We expect these functional groups on the polymer backbone to attribute interesting behavior to the LNPs. In this regard, our mannose-polymer stabilized LNPs showed spleen-targeted delivery of luciferase mRNA in comparison to PEG-stabilized LNPs.

**Conclusion:**
- A comprehensive analysis of these developed nanoparticles was conducted to assess their particle size, surface charge, and internal structures through dynamic light scattering and scontron Nath. Moreover, the design enabled the simultaneous investigation of the cubosomes’ ability to cross the BBB and enter U87 cells. To further evaluate the anticancer effectiveness of CDDP/TMZ-loaded cubosomes, in vitro cytotoxicity studies on U87 glioblastoma cells was conducted.

**Results:**
- These developed lipid cubosomes exhibited a particle size of approximately 300 nm, possessed an internally ordered inverse primitive cubic phase, achieved a high conjugation efficiency of Ang2 on the particle surface, and displayed an encapsulation efficiency exceeding 70% for both CDDP and TMZ. We employed various in vitro BBB models, including hCMEC/D3 cells in one channel (representing the blood channel) and U87 glioblastoma cells in an adjacent, interconnected channel (representing the brain channel). This design enabled the simultaneous investigation of the cubosomes' ability to cross the BBB and enter U87 cells. To further evaluate the anticancer effectiveness of CDDP/TMZ-loaded cubosomes, in vitro cytotoxicity studies on U87 glioblastoma cells was conducted.

These findings suggest that the Ang2-functionalized cubosomes hold great promise for improving BBB penetration and enhancing the delivery of therapeutics to glioblastoma.

**References:**
- Kwanoh Kim
- Hojun Kim
- Korea Institute of Science and Technology, Korea (the Republic of)

**Conclusion:**
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**Aims:**
- In this study, we have pioneered the development of Ang2-conjugated cubosomes, an approach aimed at enhancing BBB penetration and improving the uptake of glioblastoma cells. Our previous research successfully yielded a range of amphiphilic block copolymers, synthesized through RAFT polymerization, which included polyethylene glycol (PEG), poly(2- dimethylamino)ethyl methacrylate (PDMAEMA), and poly(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl acrylate) (PTBA). These polymers served as energy-efficient stabilizers for monoolein cubosomes with pH nad H2O2 responsiveness. In this study, we selected PEG14-b-PDMAEMA17-b-PTBA9-Araft polymer to craft Ang2-conjugated monoolein-based cubosomes, loaded with the anti-cancer drugs cisplatin (CDDP) and temozolomide (TMZ), which are known for their poor solubility.

**Methods:**
- A comprehensive analysis of these developed nanoparticles was conducted to assess their particle size, surface charge, and internal structures through dynamic light scattering and scontron Nath. Furthermore, their potential to enhance BBB penetration was evaluated using three in vitro models: a Transwell BBB model based on the hCMEC/D3 human brain endothelial cell line, a 3D hCMEC/D3 spheroid model, and an innovative microfluidic BBB-GM on-a-chip model. This microfluidic model featured a unique setup with hCMEC/D3 cells in one channel (representing the blood channel) and U87 glioblastoma cells in an adjacent, interconnected channel (representing the brain channel). This design enabled the simultaneous investigation of the cubosomes' ability to cross the BBB and enter U87 cells. To further evaluate the anticancer effectiveness of CDDP/TMZ-loaded cubosomes, in vitro cytotoxicity studies on U87 glioblastoma cells was conducted.

**Results:**
- These developed lipid cubosomes exhibited a particle size of approximately 300 nm, possessed an internally ordered inverse primitive cubic phase, achieved a high conjugation efficiency of Ang2 on the particle surface, and displayed an encapsulation efficiency exceeding 70% for both CDDP and TMZ. We employed various in vitro BBB models, including hCMEC/D3 cell Transwell assays, 3D spheroid cultures, and microfluidic BBB/GM on-a-chip models, to evaluate the effectiveness of these cubosomes in crossing the BBB. The results demonstrated that Ang2-functionalized cubosomes exhibited superior BBB penetration. Furthermore, these modified cubosomes exhibited significantly increased uptake by U87 glioma cells, with a notable three-fold enhancement observed in the BBB-GM on-a-chip model compared to unmodified cubosomes. Moreover, CDDP-loaded Ang2-functionalized cubosomes exhibited a heightened toxic effect on U87 glioma spheroids.

**Conclusion:**
- These findings suggest that the Ang2-functionalized cubosomes hold great promise for improving BBB penetration and enhancing the delivery of therapeutics to glioblastoma.
Airborne dust particulates are a major constituent of total atmospheric pollution affecting global environmental and human health that must be urgently mitigated. Particulate matter (PM) with diameter <10 μm is deeply inhaled into the lungs, causing significant human health risks particularly for cardiovascular and respiratory health. PM is also environmentally harmful, affecting global biogeochemical cycles, polluting water bodies and air masses, and impacting global climate. Control of fugitive dust emissions is a major operational challenge to various industries including construction, agriculture, transportation, energy, and mining. Previous dust suppressant materials have included amphiphilic synthetic polymers as water additives, which interact with dust particles after water evaporation due to their amphiphilic properties and encourage particle agglomeration, thus suppressing dust generation. However, these synthetic polymers and other conventional dust suppressant materials have short-term effectiveness, are corrosive to machinery, and increase toxicity concerns to both humans and the environment.

Herein, bioinspired glycolipids are being investigated as alternative dust suppressants to conventional amphiphilic polymers. Glycolipids are naturally-occurring molecules consisting of sugar and lipid moieties, thus making them amphiphilic molecules with both hydrophobic and hydrophilic properties. While glycolipids can be extracted from bacterial membranes, there are issues with batch size and ill-defined and inconsistent mixtures, causing further problems for quality control. By synthetically manufacturing glycolipids, quality control issues are mitigated, and the processing provides the ability to modify their molecular structures and physiochemical properties.

We have investigated the relationship between dust suppression performance and molecular structures of glycolipids by varying (1) sugar head type, (2) sugar head number, (3) lipid tail length and (4) lipid tail number. Static and dynamic characterization methods have revealed that specific sugar heads, lipid tail lengths, and number of sugar heads/lipid tails influence the self-assembled structures of glycolipids and their interactions with dust particles, resulting in enhancing or diminishing of dust suppression capabilities. Specifically, glycolipids with single rhombohedral and yxlose sugar head demonstrated up to 90% better dust suppression performance compared to the water control, and both types also produced further enhanced dust suppression properties as their lipid tail lengths increased. Furthermore, those glycolipids with double lipid tails demonstrated excellent dust suppression performance > 95% better than the water control, indicating that the addition of a second lipid tail may enhance the wetting interaction of the glycolipids with small particles. This was further investigated through ATR-FTIR, DLS and SEM, and specific details will be discussed. Additionally, thermal characterization via DSC shows that several glycolipid types undergo a phase change to liquid at approximately 50°C and maintain the liquid phase at normal temperature. Our previous work with liquid amphiphilic polymers has shown that they are highly effective dust suppressants because their liquid phase facilitates more efficient physical interactions between the polymer and small particles, and this glycolipide phase change mechanism appears to follow a similar mechanism to those previously observed.

This work presents that bioinspired glycolipids are promising dust suppressant materials, and the ability to tune their molecular structures allows us to further enhance their dust suppression performance. Our findings are expected to facilitate the development of highly-efficient glycolipid structures to effectively reduce airborne dust levels contributing to enhanced human health and environmental safety.

SESSION SB07.06: Lipid Materials and Membranes in Living Systems
Session Chairs: Aurelia Honerkamp-Smith and Cecilia Leal
Thursday Morning, April 25, 2024
Room 439, Level 4, Summit

9:00 AM *SB07.06.01 How to Build a Synthetic Virus without a Living Host for Vaccination Susan Daniel1, Neha Karnat2, Hector Aguilar-Carreno1, Ekaterina Selivanovitch1, Vivian Hu3 and Shahrzad Ezzatpour1; 1Cornell University, United States; 2Northwestern University, United States

There are 1.6 million mammalian and waterfowl viruses (Bull.WHO, 2018; 96:292). Even though only a miniscule set of these are known to infect humans, the potential that additional zoonotic viruses exist is high. Moreover, the natural evolution of viruses is rapid and hard to predict. Our best defense against viral illness is to train our immune system to recognize a threat before we are exposed to it. While vaccines address this need, we are largely ill-prepared to design, manufacture, and distribute vaccines rapidly during a pandemic outbreak. To stay abreast of viral threats, we must transform our approach to vaccine science and engineering. mRNA vaccines are one approach, as are “virus-like particle” (VLP) vaccines. Our team takes another approach; we use synthetic biology and engineering to build a proteo-lipid nanoparticle vaccine that is easy to synthesize, tunable in antigen(s) presentation, nonvirulent, and eliminates cell production currently required to generate both VLP vaccines or the expression of the antigen from mRNA lipoparticles. We have achieved the successful cell-free synthesis of Nipah virus viral coat proteins embedded into lipid vesicles using our synthetic biology approach and show that the nanoparticles we created elicit neutralizing antibodies in mice. We have also successfully synthesized into lipid vesicles the full transmembrane Spike protein from coronavirus and hemagglutinin from influenza into lipid nanoparticles using cell-free approaches. This synthetic approach enables molecular-level modification that can be guided by computational and data-driven design approaches, leading to a modular approach to vaccine optimization. New insights into fundamental mechanisms of immune response will be enabled by unprecedented homogeneity of the particle structure possible with this approach.

9:30 AM *SB07.06.02 Probing The Physical Properties of Therapeutic Carriers that Modulate Uptake by Clathrin-Mediated Endocytosis Grant Ashby and Jeanne C. Stachowiak; The University of Texas at Austin, United States

Cell surface receptors facilitate signaling and nutrient uptake. These processes are dynamic, requiring receptors to be actively recycled by endocytosis. Due to their differential expression in disease states, receptors are often the target of drug-carrier particles, which are adorned with ligands that bind specifically to receptors. These targeted particles are taken into the cell by multiple routes of internalization, where the best-characterized pathway is clathrin-mediated endocytosis. Most studies of particle uptake have utilized bulk assays, rather than observing individual endocytic events. As a result, the detailed mechanisms of particle uptake remain obscure. To address this gap, we have employed a live-cell imaging approach to study the uptake of individual liposomes as they interact with clathrin-coated structures. By tracking individual internalization events, we find that the size of liposomes, rather than the density of the ligands on their surfaces, primarily determines their probability of uptake. Interestingly, targeting has the greatest impact on endocytosis of liposomes of intermediate diameters, with the smallest and largest liposomes being internalized or excluded, respectively, regardless of whether they are targeted. These findings, which highlight a previously unexplored limitation of targeted delivery, can be used to design more effective drug carriers. Our ongoing work is examining the coupling between multiple physical parameters – size, targeting, rigidity, surface charge – during individual particle uptake events, toward a better understanding of the design space for effective particle-based delivery of therapeutics to cells.

10:00 AM BREAK

10:30 AM *SB07.06.03 Smart Blood: Red Blood Cell based Drug Carriers Maikel Rheinstadter; McMaster University, Canada

Airborne dust particulates are a major constituent of total atmospheric pollution affecting global environmental and human health that must be urgently mitigated. Particulate matter (PM) with diameter <10 μm is deeply inhaled into the lungs, causing significant human health risks particularly for cardiovascular and respiratory health. PM is also environmentally harmful, affecting global biogeochemical cycles, polluting water bodies and air masses, and impacting global climate. Control of fugitive dust emissions is a major operational challenge to various industries including construction, agriculture, transportation, energy, and mining. Previous dust suppressant materials have included amphiphilic synthetic polymers as water additives, which interact with dust particles after water evaporation due to their amphiphilic properties and encourage particle agglomeration, thus suppressing dust generation. However, these synthetic polymers and other conventional dust suppressant materials have short-term effectiveness, are corrosive to machinery, and increase toxicity concerns to both humans and the environment.

Herein, bioinspired glycolipids are being investigated as alternative dust suppressants to conventional amphiphilic polymers. Glycolipids are naturally-occurring molecules consisting of sugar and lipid moieties, thus making them amphiphilic molecules with both hydrophobic and hydrophilic properties. While glycolipids can be extracted from bacterial membranes, there are issues with batch size and ill-defined and inconsistent mixtures, causing further problems for quality control. By synthetically manufacturing glycolipids, quality control issues are mitigated, and the processing provides the ability to modify their molecular structures and physiochemical properties.

We have investigated the relationship between dust suppression performance and molecular structures of glycolipids by varying (1) sugar head type, (2) sugar head number, (3) lipid tail length and (4) lipid tail number. Static and dynamic characterization methods have revealed that specific sugar heads, lipid tail lengths, and number of sugar heads/lipid tails influence the self-assembled structures of glycolipids and their interactions with dust particles, resulting in enhancing or diminishing of dust suppression capabilities. Specifically, glycolipids with single rhombohedral and yxlose sugar head demonstrated up to 90% better dust suppression performance compared to the water control, and both types also produced further enhanced dust suppression properties as their lipid tail lengths increased. Furthermore, those glycolipids with double lipid tails demonstrated excellent dust suppression performance > 95% better than the water control, indicating that the addition of a second lipid tail may enhance the wetting interaction of the glycolipids with small particles. This was further investigated through ATR-FTIR, DLS and SEM, and specific details will be discussed. Additionally, thermal characterization via DSC shows that several glycolipid types undergo a phase change to liquid at approximately 50°C and maintain the liquid phase at normal temperature. Our previous work with liquid amphiphilic polymers has shown that they are highly effective dust suppressants because their liquid phase facilitates more efficient physical interactions between the polymer and small particles, and this glycolipide phase change mechanism appears to follow a similar mechanism to those previously observed.

This work presents that bioinspired glycolipids are promising dust suppressant materials, and the ability to tune their molecular structures allows us to further enhance their dust suppression performance. Our findings are expected to facilitate the development of highly-efficient glycolipid structures to effectively reduce airborne dust levels contributing to enhanced human health and environmental safety.

SB07.06.06
Erythro-PmBs: A Selective Polymyxin B Delivery System using Antibody-Conjugated Hybrid Erythrocyte Liposomes

Hannah Krivic, Sebastian Himbert and Maikl Rheinstadter;
McMaster University, Canada

Due to the growing worldwide antibiotic resistance crisis, many currently available antibiotics have become ineffective as bacteria develop resistance mechanisms. Only a limited number of potent antibiotics can successfully suppress microbial growth; however, these are often considered a last resort due to their toxicity. We have developed a novel PmB delivery system by conjugating hybrid erythrocyte liposomes with antibacterial antibodies to combine high loading efficiency with targeted delivery. The retention of PmB is enhanced through the incorporation of the negatively charged lipid, DMPS, into the red blood cell's cytoplasmic membrane through electrostatic interactions. Molecular dynamics (MD) simulations reveal an optimal fraction of DMPS in the hybrid erythrocyte membranes that allows for complete anchorage of PmB by inserting their acyl tail into the hydrophobic membrane core. Anti-Escherichia coli antibodies are attached to these hybrid erythrocyte liposomes using DSPE-PEG maleimide linkers. Our studies demonstrate that these erythro-PmBs have a loading efficiency of approximately 90% and effectively deliver PmB to E. coli, with minimum inhibitory concentration (MIC) values comparable to those of free PmB. However, the MIC values for Klebsiella aerogenes significantly exceeded the resistance breakpoint, indicating that the inclusion of anti-E. coli antibodies enables erythro-PmBs to selectively transport antibiotics to specific targets. MD simulations further suggest a fusion or lipid exchange mechanism between erythro-PmBs and the outer membrane of E. coli.


How Anisotropic Surface Chemistry Changes The Nano-Biomembrane Interaction: From Janus Nanoparticles to Viruses

Yan Yu; Indiana University-Bloomington, United States

The non-uniform surface chemistry is ubiquitous for both naturally occurring and engineered nanoparticles. Microbes, such as viruses, are known to have anisotropic presentation of proteins on their surfaces. Engineered nanoparticles are often designed to have homogeneous surface chemistries to enable novel applications. How does the anisotropic chemistry of nanoparticles impact their interactions with biological membranes and cells? More importantly, can we take advantage of the anisotropic surface chemistry to reverse-engineer nano-bio interactions? In this talk, I will present my group’s recent research progress toward addressing those questions. On the one hand, using engineered “two-faced” Janus nanoparticles with different surface chemistries on two hemispheres, we demonstrated that spatially separating charges and hydrophobicity on the nanoparticles renders them more potent in perforating lipid membranes and thereby in killing a broad range of bacteria. On the other hand, using non-enveloped viruses, we found that the partial hydrophobicity on the viral capsid enables the viruses to deform and penetrate the lipid membrane, leading to their infection of host cells. Our studies from both living and non-living worlds provide direct evidence that the spatial distribution of surface functionalities, rather than just its overall surface chemistry, on a nanoparticle, plays a crucial role in determining its interaction with biomembranes.

Multicellular Lipid Compartmentalization with Environmentally Responsive Release.

Richard Archer, Tsuyoshi Inaba and Shin-Ichiro M. Nomura;
Tohoku University, Japan

Smart drug release systems have gained attention as a method of using existing medicines in a more effective manner. However, topically applied medicines still rely on uncontrolled diffusion for delivery. Here we propose the use of multicellular lipid compartments (MCLCs) to encapsulate, regulate and control the release of encapsulated drugs. MCLC systems are lipid-based, semi-permeable bilayer vesicles that are typically between 20-200 µm and delivered by continuous lipids as microparticles or microcapsules. The lipid membranes show high stability over months of observations and have semi-permeable properties, allowing water and other small molecules across while retaining larger target molecules. MCLC systems are easily formed on milliliter scales within seconds from desired aqueous solutions by simple application of “lipid-inks”. These lipid-inks are formed from a mixture of natural phospholipids, commercial surfactants, and oils. We show that phospholipids play a crucial role in driving the distinctive cellular morphologies while the surfactants help increase the stability of the system. To create properties for real-world applications, we encapsulate MCLC systems within polysaccharide hydrogels to improve their stability and enable their use as practical, tangible devices.

Using these MCLC-hydrogels we demonstrate the release of the encapsulated contents into external aqueous environments using membrane solubilization strategies. Release rates from the membrane are shown to be related to compartmentalization conditions due to sequential membrane breakdown. Additionally, we show membrane breakdown can be triggered and enhanced by introducing toxic species, leading to environmentally sensitive release conditions. The compartmentalization strategy also allows for heterogeneous cellular mixing, creating single MCLC systems consisting of multiple different types of separated drugs, and multiple release conditions leading to multi-step or sustained delivery outputs. We believe this work could lead to medical patches for smart and customizable trans-dermal drug delivery. Their environmental sensitivity could lead to smart-release capabilities capable of modulating drug release depending on skin conditions, further increasing their effectiveness by introducing conditional delivery.

Beyond drug delivery, we also hope to develop MCLC systems into simple cell models, communicating permeable networks and bio-inspired soft-robots.

SYMPOSIUM SB08

Advanced Biomaterials and Bioelectronics for Neural Interfacing
April 22 - April 25, 2024

Symposium Organizers
Guosong Hong, Stanford University
Seongjun Park, Korea Advanced Institute of Science and Technology
Alina Rwei, TU Delft
Huiliang Wang, The University of Texas at Austin

Symposium Support
In this talk, I will present our recent progress in related areas. High-Density Flexible Neural Electrode and Application in Neurological Disease Monitoring

I will present our efforts in ultraflexible neural electrodes and recent progress in scaling-up their channel count and density. I will also discuss using these electrodes for recording and stimulation in animal models.

Microelectrode Arrays for Electrophysiology of Astrocyte Lineage Cells

Here, we demonstrated a multi-shank high-throughput 120-channel flexible neural electrode based on polyimide thin polymer substrate, which consists of 6 shanks. The thickness of the electrode is 4 micrometers, and the width of the electrode is only 100 micrometers. At the same time, we used tungsten wire with a diameter of 20 microns as an auxiliary implant shuttle to minimize brain damage. In addition, we designed a reliable and controllable plug-in shuttle device to perform implantation of electrode and retraction of shuttle which can not only completes high-density implantation of multi-shank electrodes, but also able to operate at different approaching and retraction speed. We demonstrated that the prepared high-density flexible electrodes can be implanted in multiple brain regions and deep brain regions and it demonstrated stable in vivo action potential signal detection for up to 6 months. At the same time, immunological tissue section also showed that the prepared high-density neural electrodes cause lower acute immune responses and long-term immune responses. With this technology, long-term brain-computer interfaces based on high-density neural electrodes can be realized in the near future, will benefit to patients with serious brain diseases.

Nonfibrotic Bioelectronic Interfaces with Diverse Organs

Implanted biomaterials and devices face compromised functionality and efficacy in the long term due to foreign body reactions and subsequent formation of fibrous capsules at the implant-tissue interfaces. Here, we demonstrate that an adhesive implant-tissue interface can mitigate fibrous capsule formation in diverse animal models, including mice, rats, humanized mice, and porcine models, by minimizing the establishment of the inflammatory microenvironment and subsequent infiltration of inflammatory cells at the implant-tissue interface. Histological analysis shows that the adhesive implant-tissue interface does not form observable fibrous capsules on diverse organs, including the abdominal wall, colon, stomach, lung, peripheral nerves, and heart, over 12 weeks in vivo. In vitro protein adsorption, multiplex Luminex assays, quantitative PCR, immunofluorescence analysis, and RNA sequencing are additionally performed to validate the hypothesis. We further demonstrate long-term bi-directional electrical communication enabled by implantable electrodes with an adhesive interface over 12 weeks in a rat model in vivo. This finding may offer a promising strategy for long-term anti-fibrotic implant-tissue interfaces.

Microelectrode Arrays for Electrophysiology of Astrocyte Lineage Cells

Astrocytes, a type of glial cell present in the central nervous system, play a crucial role in brain information processing together with neurons. These cells prominently exhibit Ca2+ excitations and are also characterised by electrophysiological activities that derive from voltage-gated ion channels on their membranes. However, there are few tools specifically optimised to detect their
A Multimodal Neural Probe for Seizure Signals Monitoring and Optical Stimulation Treatment to Epilepsy

Na Xiao1,2,3, Tao Zou1,2, Ruohong Weng3, Chung Tin3 and Paddy K. L. Chan1,2
1. The University of Hong Kong, China; 2. Advanced Biomedical Instrumentation Centre, China; 3. The City University of Hong Kong, China

Epilepsy is a central nervous system disorder which affects more than 65 million people worldwide. Seizures are often accompanied by abnormal discharges of a large number of neurons overall the brain, causing periods of unusual behavior, sensations, loss of awareness and even death. Electrical stimulation to deep brain regions has been demonstrated to be effective methods of seizure control for patients with drug-resistant seizures. However, the neural probes used in clinical applications for monitoring the neural signal or delivering electrical stimulation have significant disadvantages in the poor conformability, risk of tissue damage, long-term stability issue and ete. Soft-material based electrode array has emerged as a promising alternative to metal probes for their small size, biocompatibility, and more importantly, their flexibility and conformability.

Here we demonstrated a soft multimodal device that contains 16-channel depth electrodes and 16-channel ECoG electrodes. The electrodes were fabricated with gold as conductive layer and polyurethane-C as the supporting layer, coated with PEDOT:PSS and pHEMA to reduce the impedance and enhance the bio-compatibility. By using a 50 um diameter thin optical fiber as shunt, the depth electrodes were implanted to the focal region of seizure, meanwhile, the ECoG electrodes were placed on the surface of the brain cortex of a half-hemisphere. This design allows us to monitor the LFP signals from the seizure source region, such as hippocampus, and spreading ECoG signals from the brain surface, simultaneously. The optical fiber shunted was also served for delivering light stimulation to the source region. Data analysis results show that when we input both of the ECoG and LFP signals recorded with our device into a seizure detection computer model, the detection accuracy is high then only use one of them. The correlation coefficient and phase locking value analysis between the LFP channels and ECoG channels further demonstrated the functional connections between the seizure focal region and different spreading regions. We also found that the optical stimulation delivered to the hippocampus region of AAV-ChR2-infused animals effectively suppressed the seizures signals at both LFP and ECoG levels.

A Multimodal Neural Probe for Seizure Signals Monitoring and Optical Stimulation Treatment to Epilepsy

Na Xiao1,2,3, Tao Zou1,2, Ruohong Weng3, Chung Tin3 and Paddy K. L. Chan1,2
1. The University of Hong Kong, China; 2. Advanced Biomedical Instrumentation Centre, China; 3. The City University of Hong Kong, China

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Session SB08.05: Bioelectronic Interface III
Session Chairs: Seongju Park and Alina Rwei
Wednesday Morning, April 24, 2024
Room 433, Level 4, Summit

5:00 PM SB08.05.05
A Highly Stretchable and Conductive PEDOT:PSS/PEG-Coated Au Nanoparticle Nanomembrane for a Low-Impedance Biointerface
Yoonja Lee1,2 and Dae-Hyung Kim1,2,1; Seoul National University, Korea (the Republic of); 2Center for Nanoparticle Research, Institute for Basic Science, Korea (the Republic of)

PB08.05.05: Bioelectronic Interface III

A biointerface, which denotes the interface between human biological systems and devices, plays an important role in the field of wearable and implantable electronics since mechanical mismatch leads to low signal-to-noise ratio, delamination of devices, and even tissue damage. However, achieving a conformal contact between the device and the tissue remains challenging due to its difficulty in simultaneously satisfying high stretchability, high conductivity, low impedance, and biocompatibility. Herein, we present a novel material of coating an Au nanoparticle nanomembrane (Au NP NM) with a mixture of polyelectrolyte-doped polyelectrolyte-sulfonate (PEDOT:PSS) and polyethylene glycol (PEG) to fabricate a biointerface with ultrathin thickness, low impedance, high elasticity, and metal-like conductivity. AU NP NM, made of the float assembly with gold nanoparticles partially embedded on a styrene-ethylene-butylene-styrene (SEBS) substrate, forms a conductive percolation pathway that remains intact even in 200% tensile stretching. Then, the interaction between PEDOT:PSS/PEG and Au NP NM creates optimal contact, which improves the conductivity and durability while stretching (400%). Therefore, the coating of PEDOT:PSS/PEG does not disturb the Au percolation pathway rather, it reinforces its connectivity, thus improving stretchability, resulting in a biointerface with high charge storage capacity and high conductivity. This material could be incorporated into brain interfaces to facilitate efficient stimulation and monitoring of electrophysiological signals.

5:00 PM SB08.05.06
Materials Strategies to Fabricate Metal-Like Stretchable Nanocomposites Using Locally-Bundled Nanowires for Wearable Devices
Hyunjin Lee1,2 and Dae-Hyung Kim1,2,1; Seoul National University, Korea (the Republic of); 2Institute for Basic Science (IBS), Korea (the Republic of)

Stretchable conductive nanocomposites are a key focus in the field of wearable bioelectronics. Achieving a balance between metal-like conductivity (over 100,000 S/cm) and significant stretchability (more than 100%) for advanced skin-compatible devices remains a formidable task. This paper introduces a method for creating such a nanocomposite, employing locally clustered silver nanowires, which are stabilized using a combination of 1-propanethiols and 1-decanethiols. The process involves solidifying the nanocomposite through solvent evaporation in a highly humid environment, which clusters and stabilizes the nanowires within the organic solution. This local bundling reduces contact resistance and preserves the percolation network, enhancing conductivity. The use of both 1-propanethiol and 1-decanethiol further enhances this effect. Consequently, a nanocomposite is produced with exceptional conductivity (approximately 122,120 S/cm) and stretchability (around 200%). These outstanding electrical and mechanical properties are vital for various skin-like electronic applications. The paper showcases the application of this material in a wearable thermo-stimulation device.

5:00 PM SB08.05.07
Investigating Biocompatibility of PEDOT-based Biopolymers for Enhanced Integration into Neuronal Networks
Nevena Stajkovic1,2, Isabela Berndt Paro1,1, Janic Tökö1,1, Valeria Criscuolo1,2,1, Francesca Santoro1,2,1, Institute of Biological Information Processing – Bioelectronics, IBI-3, Forschungszentrum Jülich GmbH, Germany; 2Faculty of Electrical Engineering and IT, RWTH, Aachen, Germany, Germany

In the neuroelectronics field, neuromorphic devices based on organic electrochemical transistors (OECTs) are important, as they emulate neuronal features such as short- and long-term synaptic plasticity and adaptivity1 because of the characteristic mixed ionic-electronic conduction mechanism of conjugated polymers like poly(3,4-ethylidene dioxythiophene) – PEDOT:PSS. Depending on the application, aside from PSS, PEDOT can be doped with negatively charged counterions such as hexafluorophosphate (PF6-) or perchlorate (ClO4-).2,3 Moreover, functionalization of PEDOT:PSS with azobenzene group via click chemistry produces photo-responsive azo-PEDOT:PSS biopolymers.4 To achieve full integration of OECT-based neuromorphic devices into neuronal networks, the interface between biological cells and biopolymers is critical.5 The surface geometry, biomaterial roughness, and its chemical composition can affect the neuron-material interfaces, neuron morphology, and network development. Developing new biomaterials with improved features in terms of stability and conductivity is in demand to achieve seamless integration and broaden the biological applications of OECTs considering also the potential role of different counterions in triggering neuronal outgrowth at the cell-chip interface.

In this work, the interfaces of cells and semiconductor PEDOT-based biopolymers—PEDOT:PSS, PEDOT:PF6, PEDOT:ClO4, and modified PEDOT:crosslinking PEDOT:crosslinking PEDOT—are investigated. The PEDOTcrosslinking PEDOT:crosslinking PEDOT:PSS, PF6, and ClO4, and modified PEDOT:crosslinking ClO4 are investigated. The PEDOTcrosslinking ClO4 is interesting owing to its ability to bind Na+, which can mimic sodium channels that are abundantly expressed in the nervous system. The interfaces of cells and PEDOT:PSS, N2, PEDOT:PF6, and N2-PEDOT:ClO4, which can be functionalized into photo-responsive azo-PEDOT, are also studied. The biocompatibility of the biopolymers is investigated by assessing the viability and morphology of HT22 neuronal cells on each material. To assess the HT22 survival rate and cytotoxicity, standard in vitro assays (Live/Dead, MTT, and cellular ROS) are used. Cell morphology is assessed by labeling the actin cytoskeleton. The focused ion beam/scanning electron microscopy (FIB/SEM) is used to gain a deeper insight into cell-biomaterial interfaces. Currently, biocompatibility assays and FIB/SEM are being carried out to investigate primary neuron-biomaterial interfaces. Also, neuron overgrowth on biopolymers is being studied by measuring the spreading of axons and dendrites.

The results of this study are of importance since they will provide a characterization of new semiconductive biomaterials with potential applications in the neuro- and optoelectronics fields.
The interaction between electrogenic cells and external devices is indispensable for tasks like cell recording and stimulation. In particular, the physical cell-chip coupling has a crucial impact on the electrical conduction mechanism. A deepened comprehension of how cells interact with artificial materials is of utmost importance in the quest for effective interfaces. The process of cells adhering to and spreading on pseudo 3D micro-structures, is a well-coordinated mechanism that hinges on cell adhesion and the cell's capacity to adapt its cytoskeletal architecture to conform to vertically aligned structures[1, 2]. This scenario highlights a knowledge gap in our understanding of how to modulate neural network development and how cell membranes conform to protruding vertical electrodes, particularly for creating an effective 3D representation of the cell to be integrated into the cell-electrode equivalent circuit for recording and stimulation modeling. On this purpose a biomimetic dendritic electrode[3] has been fabricated by using the two-photon polymerization lithography[4].

Firstly, three structures' geometry have been identified: thin that can initiate contacts with presynaptic terminals and are therefore essential in the initial stages of spinogenesis; the mushroom shape as a result of the plastic and dynamic reshaping of the neuronal circuits during synaptic development and the stubby. The experimental approach involved the primary cortical neurons. In our work, we have demonstrated the mechanical interactions occurring at focal adhesion sites. These interactions oversee the continuous remodeling and adjustment of cells on the material's surface and have the capacity to generate localized traction forces on the substrate. Neurons can utilize these forces to facilitate directed movement through contact guidance. Additionally, this mechanism promotes the engulfment event by facilitating membrane invagination, leading to the precise localization of transmembrane proteins, including integrins. This localization helps induce a specific cytoskeletal arrangement. Furthermore, our results indicate how microelectrodes can impact directionality and influence the remodeling of the neural network, particularly affecting the growth cone phase, shifting from pausing to a resting state. Importantly, we’ve demonstrated that the growth cone rate changes in response to different pitch configurations. Significantly, our research has revealed that biomimetic topographical cues can swiftly impact membrane adhesion proteins and enhance the efficiency, as demonstrated through the 3D reconstruction integrated into an electrical equivalent model. With an eye toward future applications in controlling signal dissipation, this work has the potential to enhance the recording of electrogenic cells.


9:30 AM BREAK

SESSION SB08.07: Optical and Non-Invasive Stimulation
Session Chairs: Guosong Hong and Huiliang Wang
Wednesday Morning, April 24, 2024
Room 433, Level 4, Summit

10:15 AM SB08.07.01 Optoelectronic Interfaces: From Random-Access Photostimulation to Neuromodulation Bozhi Tang University of Chicago, United States

The development of new neural interfaces necessitates innovative materials and advanced device concepts. Our lab has introduced a monolithic system designed for optoelectronic interfaces that effectively interact with neural and cardiac systems. Utilizing semiconductor-enabled biomodulation interfaces, we have enhanced the capabilities of random-access photostimulation. The devices demonstrate significant translational potential for medical applications, ranging from cardiac system modulation to peripheral nerve stimulation. In this talk, I will also introduce a new electrochemical system for neuromodulation. Our lab's future focus will be on refining the performance and reliability of the random access systems. We aim to expand the range of medical applications, improve device efficiency, and ensure seamless integration into clinical practices.

10:45 AM SB08.07.02 Implantable Photocurable and Microwave Neural Interface Chen Yang Boston University, United States

High precision neuromodulation is a powerful tool for fundamental studies in neuroscience and potential treatments for neurological disorders. Here we report new developments in implantable non-genetic photocurable and microwave neural interfaces for high precision neuromodulation in retina and brain. First, we will discuss our design of biocompatible soft photoacoustic retina prosthesis. We confirmed successful blind retina stimulation through a PDMS-based photoacoustic film safely with a spatial resolution of 50 microns ex vivo and in vivo. These results show the potential of using photoacoustic signal to drive activity in photoreceptor-damaged retinas. Second, we will report an implantable miniaturized multifunctional fiber integrating with electrodes for simultaneous stimulation and recording in brain in vivo. Successful electrophysiology recording upon photoacoustic stimulation has been demonstrated in mouse brain acutely as well as up to 1 mon after implantation of the stimulator. Such devices open up potential for improved closed-loop stimulation in deep brain stimulation without the interference between the conventional electrical stimulation and recording. Lastly, we will discuss a miniaturized millimeter size microwave antenna as a wireless implantable neural interface to inhibit neural activities in vitro, ex vivo and in vivo. Suppression of seizure activities in brain in an epileptic rodent model has been achieved using low intensity microwave together with the implanted microwave antenna 6-10 time less than the FDA microwave threshold.

11:15 AM SB08.07.03 Flexible and Biocompatible Photocurable Photoacoustic Film for Vision Restoration at Ultrahigh Spatial Resolution Yueming Li1, Audrey Leong2, Hélène Moulet3, Jean-Damien Louise2, Serge Picaud2 and Chen Yang1, 2Boston University, United States; 3Sorbonne Université, France; 4Xoruss, France

Retinal degenerative diseases represent a major factor leading to irreversible blindness. Despite extensive research efforts, a definitive curative treatment remains elusive. The development of retinal prostheses, encompassing bionic and photovoltaic devices, has aimed to address this unmet clinical need. However, these technologies face inherent issues such as crosstalk from current leakage impacting spatial resolution, limitations in electrode numbers limiting the visual angle, and difficulties related to internal strain during fabrication. To address these challenges, we introduce a novel solution utilizing a uniform and flexible photoacoustic film composed of candle soot and polydimethylsiloxane for high-precision retinal stimulation as a subretinal implant. This approach leverages on the advantages of light patterning flexibility to overcome the limitations of unit spacing, electrode numbers, and internal strain observed in other devices. Our experiments demonstrate that this photoacoustic film effectively stimulates the retinas of blind rats ex vivo, achieving a spatial resolution of 50 µm. Moreover, upon implantation in rats, this flexible photoacoustic film exhibits superior biocompatibility. Significantly, the photoacoustic stimulation induced visual responses that were recorded in the rat brain's visual cortex. These findings hold promise for the restoration of vision in individuals suffering from age-related macular degeneration and retinal dystrophy, offering a potential solution with improved spatial resolution and better biocompatibility.

11:30 AM SB08.07.04 Fabrication, Characterization and In Vivo Validation of Flexible Optical Cortical Probe Amélie Albon1, Emma Butt2, Keith Mathieson2 and Charles Rezaei-Mazinani1, 2EMSE, France; 3University of Strathclyde, United Kingdom

Mechanically-flexible neurotechnologies based on soft and biocompatible organic materials have significant advances for neuroscience applications. However, integrating active electronic components into polymeric-based neurotechnologies is still a challenge. This is particularly important for optogenetic applications where, despite important advances in light delivery technologies (such as optical fiber or inorganic µLED-based optoprobe) they mostly rely on rigid substrates. This is a key obstacle to their successful integration with neural tissue. In this work, we focus on the development of a novel optical cortical-probe (optoprobe), seamlessly integrating high performance inorganic µLEDs for optogenetic stimulation, along with organic electrodes for electrical recording. This optoprobe offers a plastic and conformable interface with the cortex. Here, we present our fabrication method for the integration of 4 µLEDs (100x100 µm, 4.5 µm) and 4 PEDOT:PSS based electrodes (50x50 µm) and fully characterize the optoprobe for optogenetic stimulation and electrical recording. This includes analysis of the electrical crosstalk between the drive currents for the µLEDs and the electrical recording component (sensitive to 10s of microvolts). Driving the µLEDs can also increase the optoprobe’s temperature profile and influence the long-term stability of the optoprobe – both of these effects have been studied in accelerated testing. Furthermore, we show validation of the optoprobe performance in mouse auditory cortex in vivo. Integrating electrodes and µLEDs on a common transparent substrate has the potential to improve stimulation control by facilitating real-time
Byunghun Lee, Geoffrey Beach and Polina Anikeeva; Massachusetts Institute of Technology, United States

noticeable discrepancies observed in the current literature with this theory; it has been observed quite often that superparamagnetic nanoparticles have significant heating, but have no hysteresis on a cellular scale due to better local heating.

Magnetic nanoparticles (MNPs), used as alternating magnetic field (AMF) transducers, are currently actively being researched as a non-invasive way of manipulating biological systems. The SB08.08.01

applications, including drug delivery, cell signaling and imaging.

We exploit the magnetothermal approach to control calcium signaling in cells within deep organs and with a minimally invasive scheme. While the common approach of magnetothermal stimulation exploits MNPs in the form of ferrofluid, my lab recently pioneered a new design of a three-dimensional nanocomposite that can examine cell signaling under thermal effects in microenvironment that is suitable for cell organization and functionalities. We introduce a novel concept for the field of bioelectronic medicine with new materials design and in-depth nanocomposite characterization. One intriguing target of the magnetothermal approach is the heat sensitive ion channel, the transient receptor potential vanilloid 1 (TRPV1), the capsaicin receptor. TRPV1 is a non-selective cation channel that is calcium-permeable and can be activated by heat with temperature threshold above 42 Celsius. Previous studies have demonstrated the expression of TRPV1 in various peripheral organs as well as sensory neurons. We use this model to demonstrate our approach of cells activation in three-dimensional magnetic nanocomposites.

SESSION SB08.09: Ultrasound/Mechanical Stimulation
Session Chairs: Guosong Hong and Seongjun Park
Wednesday Afternoon, April 24, 2024
Room 433, Level 4, Summit

Iron oxide magnetic nanoparticles (MNPs) with diameter of 20-25 nm dissipate heat when exposed to weak alternating magnetic fields (AMFs) with amplitudes <50 mT and frequencies of 100-600 kHz. This heat can be exploited to activate cells that have thermally sensitive ion channels on their membrane via magnetothermal modulation. AMF has a high penetration rate with no deleterious effects, and therefore suitable for the activation of cells within deep organs in the body. Iron oxide nanoparticles are biocompatible and being utilized in different biomedical applications, including drug delivery, cell signaling and imaging.

2:15 PM SB08.08.03
Controlling Neuronal Cell Signaling within Three-Dimensional Magnetic Nanocomposites Dekel Rosenfeld; Tel Aviv University, Israel
Piezoelectric Currents: Mechanistic Degeneration of Hydrogels Induces Ionic Currents that Stimulate Nerves John D. Madden1 and Yuta Dobashi2; 1University of British Columbia, Canada; 2University of Toronto, Canada

The nervous system operates at tens of millivolts and employs ionic currents. Similar voltages and ionic currents are generated when hydrogels are compressed. This opens the possibility of stimulating the nervous system directly using the electrical energy produced when ionically conductive materials are deformed. To demonstrate this effect, a finger was firmly tapped on a slab of polyacrylamide hydrogel containing 1.5 M of sodium chloride solution. The resulting current was fed into PEDOT-coated Pt-Ir electrodes wrapped around a rodent peripheral nerve. The mechanical input produced currents of 10 μA at voltages of less than 100 mV. Hhindlimb twitches were produced. This 'self-powered' sensing interfaces with nerves without any signal conditioning or amplification. We dub the underlying mechanisms "piezionic", in loose analogy to piezolectrics. A pressure gradient applied to the hydrogel produces a flow of electrolyte and ions within it. Some ions displace faster than others as they translate through the nanopores of the hydrogel, likely due to differences in size between anions and cations. Similar effects are seen in other ionically conducting polymers including conjugated polymers and ionically conductive membranes. Response times can be quite fast (≈30 ms) when thin gels are used, which create large pressure gradients around the indentation area, and fast transport. The piezionic effect creates the possibility of a fully ionic artificial mechanonreceptor that can interface with the nervous system - though long distance, high density signal conduction may be best achieved using thin metal wires.

4:00 PM #SB08.09.02
Flexible Transducers for Ultrasound Neuromodulation
Sang-Mok Lee, Taemin Lee, Suenghyon Nam and Hyunjo J. Lee; KAIST, Korea (the Republic of)

Wearable ultrasound patches possess the potential to transform conventional medical ultrasound applications by enabling hands-free, prolonged, and uninterrupted diagnostic and therapeutic procedures. However, current flexible ultrasound transducers often lack the ability to govern their curvature and are limited in terms of production throughput and design flexibility. In this work, we present a method for fabricating flexible ultrasound transducers with controllable curvature, utilizing high-yield silicon microfabrication and employing flex-to-rigid structures. The transducer's curvature is modulated through Joule heating, utilizing a low-melting-point metal alloy. The transducer demonstrates remarkable electrical and acoustical performance at central frequencies of 1.5 MHz and 3.4 MHz when immersed. We deployed this flexible transducer to induce neuromodulation of immune responses within an internal organ, illustrating the potential for continuous therapeutic interventions via a wearable ultrasound patch.

4:30 PM #SB08.09.03
Deep Brain Stimulation by Blood–Brain-Barrier-Crossing Piezoelectric Nanoparticles Generating Current and Nitric Oxide under Focused Ultrasound
Won Jong Kim; POSTECH, Korea (the Republic of)

Noninvasive E-Textile System for Long-Term Multimodal Electrophysiological Monitoring in Sports and Clinical Healthcare
Junyi Zhao and Chuan Wang; Washington University in St. Louis, United States

Textile-based electronic systems have emerged as a promising platform for creating noninvasive and comfortable human-machine interfaces across various domains, including sensing, display, and communication, which aligns with the contemporary drive for enhanced miniaturization and multifunctionality. This work presents a novel E-textile system comprising in-plane electrode layout and bioinspired conductive microfibers. This configuration allows for gel-free and motion-artifact-tolerant recording of multiple physiological signals, including electrocardiography and electromyography, capturing muscle activity triggered by motor neurons. More specifically, the base layout features a screen-printed array of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), with PEDOT:PSS-coated fluffy microfibers stacked on top. The vertically oriented hairy microfiber conductors ensure exceptional conformal and robust skin contact, while the dispersed microfiber electrodes substantially increase the effective contact area, significantly reducing the contact impedance between the electrode and skin. This feature enables comfortable all-day wear under dry conditions without the need for ionic gels. To ensure the durability and functionality of the textile in harsh conditions, a self-assembled monolayer (SAM) of trichloro(1H,1H,2H,2H-perfluorooctyl) silane is vaporized as a superhydrophobic coating. This treatment preserves the natural texture of the textile while maintaining the intrinsic conductivity of the electrodes. Additionally, portable miniaturized circuitry was meticulously designed and manufactured to enable multi-channel recording, signal processing, and wireless communications.

These advancements facilitate the seamless integration of the E-textile system into everyday life, broadening its potential applications. This study explores the application of E-textile systems in real-life scenarios, including strenuous exercise and clinical studies. We commence by demonstrating the robustness and stability of the E-textile system during professional cycling training sessions. Remarkably, the recorded signals remained clear and free from motion artifacts, even in the presence of intense sweating, maintaining a signal-to-noise ratio of approximately 30 dB. Real-time monitoring facilitated on-the-spot data analysis, including heart rate and muscle output. Next, we tested the waterproof capability of the system by integrating it into an E-textile-equipped swimsuit. Throughout the professional swimming training, the fully submerged E-swimsuit consistently delivered reliable electrocardiography recordings, demonstrating its resilience and suitability for aquatic environments. Even when encountering water flows, the E-swimssuit showcased robust performance, making it ideal for water sports. Finally, the textile-based E-patch with electrode arrays was employed in clinical studies to monitor maternal/fetal health. Multiple pregnant subjects were involved for capturing multichannel maternal-electrocardiography and uterine-electromyography signals. The recorded multichannel uterine-electromyography signals were further processed to generate noninvasive and high spatiotemporal resolution three-dimensional (3D) electromyometrical images with a fast frame rate. This groundbreaking achievement offers unique insights into neural activities within the uterus, aiding in the diagnosis of abnormal obstetrics symptoms and predicting the risk of potential preterm birth. These findings underscore the versatility and potential of wearable E-textile systems across a wide range of real-world applications, paving the way for professional sports tracking and personalized advancements in healthcare.
Electroencephalography (EEG) is a valuable tool for non-invasive monitoring of electrical activity from the scalp for clinical monitoring of neurological disorders. Clinical EEG typically involves gel-based electrodes, whose application is time-consuming and requires skin-irritating abrading and pastes. Recently, we have introduced dry EEG electrodes based on Ti$_3$C$_2$ MXene materials. These electrodes offer enhanced comfort and ease of use, requiring minimal skin preparation. Furthermore, they are conformable to the scalp, providing a comfortable fit for users. Here, we advance this technology towards research and clinical use by fabricating two different configurations of EEG headsets. The first configuration is a reduced-montage headband consisting of 8 channels placed at equal spacing on FP1, FP2, F7, F8, T3, T4, T5. The second configuration is a standard 10-20 montage with 21 recording sites at the canonical scalp locations. In both devices, the dry electrodes are fabricated from porous pillars infiltrated with Ti$_3$C$_2$ MXene (diameter: 8 mm, height: 6 mm), enabling access to the scalp through hair without the need for gel or pastes. The electrodes are connected to the recording amplifiers via snap connectors attached to snap leads. Owing to the high electrical conductivity ($155 \pm 4 \, \Omega$, n= 5 electrodes) and surface area, the average 10 Hz impedance of the scalp of these dry porous MXene-infused electrodes is $2.1 \pm 1.8 \, \Omega$ (n=5 subjects). To further validate the dry MXene EEG technology, we have benchmarked it against clinical gelled cup Natus electrodes. Briefly, we have recruited patients in the outpatient epilepsy clinic at the Hospital of the University of Pennsylvania. For each participant, we recorded EEG with the reduced-montage headset and MXene electrodes for 20 minutes prior to clinical EEG. We recorded EEG in the following conditions: resting state, eyes open/closed, and sleeping, which corresponded to the same tasks used during clinical EEG acquisition. A preliminary analysis of the recordings shows comparable quality of the EEG signals acquired with the dry MXene and clinical gelled electrodes, while the duration of the skin prep and electrode placement operation reduced by –2X. In conclusion, we have developed and validated a novel dry EEG technology that can improve user comfort, reduce electrode placement and skin preparation time, and reliably transmit signals of interest, providing a comfortable and efficient solution for EEG monitoring.

9:30 AM SB08.10.04
Detect The Undetectable in Wearables and Brain-Machine Interfaces: pM-Level Biomolecular Detection with Fast-Scanned Aptamer-OECT Xinyin Tian and Shiming Zhang; The University of Hong Kong, Hong Kong

Biomolecular detection is the next goal for wearable devices. The lower limit of detection (LoD) is a critical metric for wearable biosensors. In this study, we demonstrate that aptamer-based Organic Electrochemical Transistors (OECTs) can detect concentrations in the picomolar range ($155 \pm 4 \, \Omega$, n= 5 electrodes) and high frequency range where the leaking reaction resistance most vibrates with the binding of the molecules [2]. Thus, microscale OECTs are essential for achieving a higher cutoff frequency for rapid scanning purposes.

9:45 AM BREAK

SESSION SB08.11: Printed and Biocompatible Electronics
Session Chairs: Seongjun Park and Alina Rwei
Thursday Morning, April 25, 2024
Room 433, Level 4, Summit

10:15 AM *SB08.11.01
3D Printed Flexible and Stretchable Tissue-Like Electronic Devices for Neural Recording Tao Zhou; The Pennsylvania State University, United States

The utilization of neural recording technology has significantly transformed our comprehension of the brain, spinal cord, and other nervous systems. These technologies have provided essential insights into neural activity, hence facilitating the development of groundbreaking therapeutic approaches. Nevertheless, the development of neural recording devices that can match the properties of neural tissues remains a significant challenge. Furthermore, commonly used neural recording devices are usually time-consuming to fabricate and costly. This research presents a novel strategy to tackle the aforementioned obstacle, wherein we propose the utilization of 3D printa...
Although implantable neural electrode devices have been used in animals and human for neuroscience research and clinical applications, they face the challenge of signal degradation due to a myriad of reasons including implantation trauma, glial scarring, biofouling, and loss of signal-generating neurons. During implantation, the neural probe inflicts injury to the brain tissue by breaking blood vessels and inducing mechanical stress to the surrounding tissue. The implantation then triggers a cascade of immune response involving non-specific protein adsorption, inflammatory cell adhesion followed by the encapsulation of the probe by glial sheath. The disrupted blood flow may cause hypoxia, which along with the trauma and inflammation may compromise neuronal survival and function.

Here, we used chemically and biologically inert perfluorocarbon (PFC) as a multi-functional coating for implantable neural interfaces providing 1) lubrication during insertion to reduce insertion trauma, 2) anti-fouling surface, and 3) oxygen supply to the injury site. Preliminary data shows that the PFC coating can reduce peak insertion force of a single-shank silicon probe by at least 50%, translating to less acute trauma. The PFC coating also effectively decrease non-specific protein adsorption and inflammatory cell attachment. In addition, the same coating is capable of carrying oxygen and passively releasing it over at least six hours. We also studied the effect of the coating on the interfacial impedance of platinum electrodes and found no significant difference in impedance between the bare and PFC coated electrodes. Combined, these functionalities of the PFC coating showed great potential for reducing implantation trauma and improving neuronal survival near the neural electrode implants.

**SESSION SB08.12: Organic Materials**

**Thursday Afternoon, April 25, 2024**

**Room 433, Level 4, Summit**

**Development of Highly Biocompatible Ultra-Low Fouling Zwitterionic Materials, Coatings and Nanoparticles**

Shaovi Jiang; Cornell University, United States

An important challenge in many applications is the prevention of unwanted non-specific biomolecular and microorganism attachment on surfaces. We have shown that zwitterionic materials and surfaces are highly resistant to non-specific protein adsorption and microorganism attachment from complex media. Typical zwitterionic materials include poly(carboxybetaine), poly(sulfobetaine), poly(trimethylamine N-oxide), and glutamic acid (E) and lysine (K)-containing poly(peptides). Unlike poly(ethylene glycol) (PEG), there exist diversified zwitterionic molecular structures to accommodate various properties and applications. Furthermore, zwitterions are super-hydrophilic while their PEG counterparts are amphilic. In this talk, I will discuss the application of zwitterionic materials to implants, medical devices, stem cell cultures, and drug delivery carriers. With zwitterionic materials, coatings, hydrogels or nanoparticles, results show no capsule formation upon subcutaneous implantation in mice for one year, expansion of hematopoietic stem and progenitor cells (HSPCs) without differentiation, no anti-coaguants needed for artificial lungs in sheep, and no antibodies generated against zwitterionic polymers. I will also discuss a newly developed drug delivery system to delivery mRNAs or small molecules through the blood-brain barriers into the brain.

**Tailoring Thermogels: A Versatile Strategy for Functionalized Injectable Hydrogels and Controlled Drug Release**

Joey H. Wong1, Belyn Sim1,2, Jason Y. Lim1,3, Xin Jun Loh1,4,2 and Rubavan Goh1;1Institute of Materials Research and Engineering, Singapore; 2Nanyang Technological University, Singapore; 3National University of Sciences & Technology, Singapore; 4National University of Singapore, Singapore

Biocompatible injectable hydrogels provide a minimally invasive strategy for biofabrication. Depending on the encapsulated payload, these hydrogels can serve as a low-modulus interface for neural electrodes, provide localized and sustained delivery of drugs, or offer structural support to cells during proliferation and tissue regeneration. One strategy used to develop injectable hydrogels involves copolymerizing thermally-responsive blocks with a hydrophile polymer (e.g. pluronics). These thermally responsive injectable hydrogels, known as thermogels, undergo a sol-gel transition above a critical gelation temperature, such as when being warmed to 37°C. This is triggered by the formation of micellar crosslinks of the thermo-responsive domain.

In this study, we have developed a versatile synthetic strategy for creating a library of functionalized thermogels and have investigated the three-way interactions between functional groups, gel scaffolds, and encapsulated drugs. Our work will illustrate the impact of these functional groups on the sol-gel transition, the physical properties of these gels, and the sustained release of drug analogs. As a proof of concept, we were able to achieve sustained release of anionic orange II and cationic crystal violet of 5 to 6 months, with release profiles varying depending on the functionalized moieties.

**Advanced Microfabrication Strategies for Neuro-Inspired 3D Conductive Polymers**

Valeria Criscuolo1,2, Claudia Latte Bovio3, Kevin Lengefeld1,2 and Francesca Santoro1,2,3; 1RWTH Aachen University, Germany; 2Forschungszentrum Jülich GmbH, Germany; 3Istituto Italiano di Tecnologia, Italy

Neuroelectronic platforms aim at recapitulating neuronal communication and functions to monitor and eventually restore lost functionalities. Indeed, engineering neuroelectronic devices that can be smoothly interfaced with brain and neurons can provide a step forward in a better understanding of hampered electrical communication in e.g., neurodegenerative diseases. In this scenario, conductive polymers, such as PEDOT:PSS, have gained a prominent position in the realization of seamlessly integrated bioelectronic devices and soft flexible probes. However, existing polymer-based devices are not yet able to effectively mimic and reproduce the complex neuronal environment, being both non-conductive and bidimensional. Neurons indeed interact with and respond to a great variety of mechanical and topographical stimuli; thus it is imperative to take inspiration from the extremely complex architecture of the brain.

Moreover, the cell-device interface plays a crucial role for an effective electrical coupling between the cell and the device. Indeed, a cleft is typically formed between the cell and the electrode. For this reason, recent approaches demonstrated that non-planar substrates, featuring 3D and 2.5D structures, result in the reduction of the cleft and in an improvement of cell-device electrical coupling.

In the light of the above, here we introduce innovative microfabrication strategies for the realization of neuroelectronic platforms based on PEDOT that can recapitulate distinctive morphological neuronal features such as dendrites and dendritic spines. Dendrites were reproduced by the formation of PEDOT:PSS fibers by using AC electro polymerization on a multi electrode arrays (MEAs). By changing the parameters of the applied signal and the geometric relationship between the electrodes, the growth and morphology of the fibers was altered. Additionally, the fibers geometry and branching was tuned by changing the shape of the applied AC-signal and the manipulation of the electrical field. The so obtained dendrite-like fibers were morphologically characterized by means of scanning electron microscopy (SEM) and atomic force microscopy (AFM) and the neurite elongation and branching was compared to real neurons. Additionally, electrochemical properties as well as long term stability in aqueous media was investigated via electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV).

On the other hand, dendritic spines, biological structures essential in synaptic communication, were recreated by means of 2-photon polymerization (2PP) lithography, given its high resolution, versatility, and design freedom both achieving non-conductive and conductive material patterning via electropolymerization. The resulting 3D microstructures were characterized by SEM and electrochemical measurements (CV and EIS).

Finally, biocompatibility assays were carried out for both dendrite- and dendritic spines-like structures with neuronal cells, and the local adhesion processes to the 3D structures was characterized by means of optical and electron microscopy.

Overall, the proposed strategies allow for the fabrication of 3D/2.5D electrodes with different levels of complexity that can effectively mimic neuronal features and enhance the cell-chip interface. Such systems will open the way to the possibility of sensing and/or stimulating cells and tissues in a more realistic environment.

2. A. Mariano, et al., Nanotechnology, 2022, 33, 492501

**2:30 PM SB08.12.04**

**A Simple Animal Model to Discover Neuroactive Function of Semiconducting Oligomers**
Claudia Tortiglione¹, Giuseppina Tommasini¹, Mariarosaria De Simone¹, Silvia Santillo¹, Marika Iencharelli¹, Gwennâel R. Dufil², Daniele Mantine³, Eleni Stavrinidou² and Angela Tino¹; ¹Istituto di Scienze Applicate e Sistemi Intelligenti, Italy; ²Linköping University, Sweden; ³University of the Basque Country, Spain

Modulating neural activity with electrical or chemical stimulus can be used for fundamental and applied research. Beside intracellular and extracellular electrodes delivering brief electrical pulses for neural stimulation, wireless methodologies based on functional materials may represent superior alternatives to modulate neuronal function. Here we show that the organic semiconducting oligomer ETE-S induces precise behaviors in the freshwater polyp *Hydra*, a small invertebrate with a nerve net controlling a limited repertoire of behaviors. Through pharmacological and electrophysiological approaches we found that the ETE-S induced behavioral response relies on the presence of head neurons and calcium, and is prevented by drugs triggering ionotropic channels and muscle contraction [1]. Moreover, ETE-S affects *Hydra*’s electrical activity enhancing the contraction burst frequency. The unexpected neuromodulatory function played by this conjugated oligomer on a simple nerve net opens intriguing research possibilities on fundamental chemical and physical phenomena behind organic bioelectronic interfaces for neuromodulation, and on alternative methods that could catalyze a wide expansion of this rising technology for clinical applications.


**2:45 PM SB08.12.05**

**Polymer-Based Transparent Brains for 3D Evaluation of Brain Tumors without Tissue Sectioning**
Maryam Golshahi, Hamed Arami and Layla Khalifehzadeh; Arizona State University, United States

Conventional tissue sectioning, staining, and optical microscopy are used as standard clinical methods for diagnosis of the brain tumors (i.e., glioblastoma multiforme or GBM), studying their anatomical phenotypes and evaluating their response to therapies. Sectioning of the tissues is destructive and stained and analyzed tissues cannot be re-used for evaluation of additional biomarker. Also, histological microscopy data obtained from each tissue section are limited to that area of the tumor and are not ideal representatives of the whole tumor mass, especially for highly heterogeneous tumors such as GBM. Here, we will discuss a method for transforming the whole brain tumor tissues to optically transparent hydrogel masses without losing any anatomical, extracellular or sub-cellular features within the tissues. Different types of orthotopic brain tumors (e.g., human-derived U87 GBM with GFP signal) were generated in mouse brains (n=3-5) and analyzed using magnetic resonance and bioluminescent imaging (MRI and BLI). Brains were excised and immersed in an acrylamide monomer solution, followed by the polymerization of these monomer molecules within the entire brain tissue at 37°C. Brains were clarified by removing the lipid molecules from the tissue microenvironment. Transparent brains were analyzed using confocal and light-sheet microscopy techniques after being immersed in Focus Clear solution to adjust their refractive index for optimized microscopy. Three-dimensional macroscopic and microscopic maps were generated from the whole brains for analyses of the tumor growth pattern and their response to therapies, without losing the intactness of the proteins and tissue structure. Using various monomer derivatives enabled the tuning of the cross-linking rate and optical transparency of the hydrogels for improved analysis of heterogeneous tumor masses. This method enabled series of reversible staining de-staining, and re-staining of the tissues for clinical analysis of different brain tumors and a variety of neuropathological biomarkers.

**SYMPOSIUM SB09**

Bioelectricity and Recapitulation of 3D Environment in Microbial and Tissue Engineering
April 23 - April 23, 2024

Symposium Organizers
Sina Jamali, UNSW Sydney
Nathalia Peixoto, George Mason University
Frankie Rawson, University of Nottingham
Paulo Rocha, University of Coimbra

* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter
electrical stimulation of cells can elicit a variety of biological outcomes, e.g. the firing of action potentials in neurons, or the promotion of apoptosis in dividing cells. Clinical uses of electrical stimulation include the treatment of cardiac arrhythmia, profound deafness, movement disorders and different forms of cancer. Still, a unified description of the phenomena elicited by electrical stimulation does not exist and different communities focus on particular aspects within the general field (electrophysiology, tissue engineering, electroporation, tumour treating fields). I will discuss a generalised framework for discussing these phenomena, starting with experimental ways to avoid the production of chemical species at the electrodes, following with a review of the physical phenomena that take place upon electrical stimulation and ending with the elicited biological outcomes.

11:00 AM SB09.01.02
Investigating Electrical Stimulation to Mitigate The Foreign Body Response in Neural Implants Filip Wronowski and George G. Malliaras; University of Cambridge, United Kingdom

This research addresses a critical challenge in the field of neural interfaces: the foreign body response (FBR). Neural interfaces hold tremendous promise for treating neurological disorders and enhancing therapeutic outcomes, but the FBR often limits their long-term effectiveness.

The FBR is primarily driven by non-neuronal glial cells and results in chronic inflammation and fibrosis, ultimately compromising neural recording and stimulation capabilities. This study focuses on the potential of electrical stimulation to mitigate the FBR and enhance the performance and longevity of neural implants.

Preliminary findings indicate that electrical stimulation can influence astrocytes, fibroblasts, and other cell types involved in the FBR. The parameters of stimulation, including timing, intensity, and frequency are being investigated and can influence the glial response, ranging from driving cell alignment, affecting cell division and to exerting anti-inflammatory to pro-inflammatory effects.

To this end, we employ two novel in vitro platforms, followed by advanced microscopy techniques and cytokine assays. These insights will be further complemented by RNA sequencing. Our ultimate aim is to extend our findings to an in vivo context, enabling us to refine our understanding and improve strategies for addressing the foreign body response in neural implants. This research sheds light on these complex interactions, offering potential strategies to enhance the effectiveness of neural interfaces and reduce the impediments caused by the FBR.

11:15 AM SB09.01.03
Quantum Bioelectrochemistry for The Treatment of Hard-To-Treat Cancers Akhil Jain1,2, Jonathan Gosling1, Padma-Sheela Jayaraman1, Stuart Smith1, David Amabilino1, Mark Fromhold1, Yi-Tao Long3, Lluisa P. Garcia4, Lyudmila Turyanska1, Ruman Rahman1 and Frankie J. Rawson1; 1University of Nottingham, United Kingdom; 2State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, China; 3Institut de Ciencia de Materiales de Barcelona (ICMAB-CSIC), Spain; 4Departamento de Farmacología, Toxicología y Química Terapéutica, Facultat de Farmàcia i Ciències de l’Alimentació, Universitat de Barcelona, Spain

Quantum biological tunnelling for electron transfer (QBET) is involved in controlling essential functions for life such as cellular respiration and homoeostasis. Understanding and controlling the quantum effects in biology has the potential to modulate biological functions. Here we merge wireless nano-electrochemical tools with cancer cells for control over electron transfer to trigger cancer cell death. Gold bipolar nanoelectrodes functionalized with redox-active cytochrome c and a redox mediator zinc porphyrin were developed as electric-field-stimulating bio-actuators, termed bio-nanoantennae. We show that a remote electrical input of alternating current (A.C.) at high frequency (3MHz) and low voltages (0.65V/cm) regulates electron transport between these redox molecules, which results in quantum biological tunnelling for electron transfer to trigger apoptosis in cancer cells from various hard-to-treat tumors. Transcriptomics data show that the electric-field-induced bio-nanoantenna targets the cancer cells in a unique manner, representing electrically induced control of molecular signaling. Arthusien-kinetics confirmed the occurrence of moderate QBET in the system. In vivo studies in tumor bearing rats are underway to demonstrate first example of quantum medicine to treat cancers.

Nanoscale rheology: Dynamic Mechanical Analysis over a broad and continuous frequency range using Photothermal Actuation Atomic Force Microscopy, Piacenti AR, Adam C, …


References:

3:00 PM SB09.03.01

Mechano-Electrical Coupling in Neurons Sonia Contera; University of Oxford, United Kingdom

We have become used to studying the different aspects of biological function in isolation; biochemical, genetic, mechanical or electrical properties of biomolecules, cells and organisms are studied by different fields. Yet, it is precisely the coupling of the different aspects inside a "living shape" that underlies the functional diversity and the information processing capacity of living systems. By coupling their properties, biological systems can induce behaviours acting against the direction imposed by thermodynamic forces, which are characteristic of being alive. For example, a protein is able to work with great efficiency because it couples electrostatics, mechanics and chemistry; an embryo grows its shape by coupling mechanical, chemical, genetic and electrical oscillations.

In neurons, evidence gathered over half a century shows that local mechanical changes in the membrane propagate along with the action potential in neurons. These observations effectively point towards the hypothesis that the action potential is not merely an electrical pulse, but a complex multiscale electro-mechanical "multiphysics" process that affects and is affected by all components of the membrane [1]. Due in part to the emergence of experimental techniques such as atomic force microscopy (AFM) that allow to measure and alter the mechanical properties of membranes and living cells in physiological environments, research interest in the role of mechanics of the neuronal membrane has grown, essentially driven by its potential in medical applications, e.g. in ultrasound neuromodulation (expected to find applications in the treatment of epilepsy and chronic pain, to promote neuroplastic repair mechanisms for post-stroke recovery).

Using new techniques that allow us to apply mechanical signals to living neurons from the Hz to the 100s of KHz range and to quantify correctly viscoelastic properties from these measurements [2], and coupling them to electrophysiological and fluorescence measurements, our work shows that alterations of electrophysiological activity (e.g., with anaesthetics or electrical oscillations) correlate linearly with a change in viscoelastic properties such as the loss tangent, the ratio of mechanical energy stored and dissipated in the cell [3]. And the other way around, ultrasound stimulation alters neuronal firing. I will discuss these results in the context of building a "multiphysics" nonequilibrium framework to study neurons that allows us to create models to predict/interpret the oscillatory systemic behaviours of physical/chemical properties of neuronal networks [1].

References:


3:30 PM SB09.03.02

Bioactive Piezoelectric Nanofibers for Electromechanical Stimulation and Neuronal Regeneration Leyla Esfandiari1,2; 1University of Cincinnati, United States; 2Cincinnati Children Hospital, United States

One of the important signaling networks in embryonic development, regeneration, and homeostasis of tissue is the endogenous bioelectricity. It has been observed that electric fields can promote axonal regrowth in nerve injury and bioelectric stimuli can be crucial to induce regeneration in peripheral and central nervous systems. Severe peripheral nerve injuries disrupt nerve pathways, connections, and the extracellular matrix (ECM) surrounding the nerve, which affects distal innervation targets. If the injury gap is large enough, functional recovery is extremely limited and absolute clinical therapies don’t exist. A key reason for poor functional recovery is that neurons lack the proper guidance, alignment, and signaling from the damaged ECM to allow for targeted growth across injured tissue.

We have developed an ultrasound-mediated, bioactive scaffold that addresses these challenges by offering controllable electrical, physical, and chemical signaling capabilities. Piezoelectric poly(vinylidene fluoride-trifluoroethylene)(PVDF-TrFe) is integrated with decellularized ECM through electrospinning fabrication technique. The bioactive piezoelectric nanofibers are capable of producing controllable electrical stimulation in response to cellular mechanobiology and remote ultrasound activation without the need for electrodes due to its piezoelectric property. The tissue-specificity of the ECM combined with the piezoelectric scaffold improved the cell-biomaterial interactions and host immune response. Extensive characterization of material properties was conducted on resultant bioactive scaffolds. The bioactive scaffold's piezoelectric nature remained intact, and cell-matrix interactions showed enhanced cell viability, proliferation, and adhesion. This new and multi-parametric biomaterial is envisioned to be used as next-generation nerve guidance conduits (NGCs) and will be tested for its efficacy in the future.

4:00 PM SB09.03.03

Observation of Cell Behavior by Waveform Measurement using Lithium Niobate-Based Surface Acoustic Wave Device Shan Koda1, Takahiro Yamada2, Hiroaki Otoe3, James Friend2 and Yuta Kurashina1; 1Tokyo University of Agriculture and Technology, Japan; 2University of California, San Diego, United States; 3Keio University, Japan

Introduction: Highly matured cells and tissues are essential to improve the quality of regenerative medicine and drug discovery research. Fluorescence observation by immunostaining with
antibody labeling of maturation makers is one of the gold standards for evaluating such cells and tissues. To deliver antibodies to antigens in the cell membrane, fixation and permeabilization of cells are necessary for fluorescence observation. Recently, living cells can be observed by gene transfer (Kasahara et al., Sci. Adv., 2023), but with the risk of altering the cellular morphology. That is, observation of living cells is difficult without damaging cells.

Here, we propose a non-invasive evaluation method of cultured cells using surface acoustic waves (SAW) for sensing cell behavior without administering any invasive chemicals to the cells or altering their genetic traits. For cell behavior observation, a cell evaluation system with surface acoustic waves transmitted from a SAW device to the cells was fabricated. The SAW device consists of lithium niobate (LN) substrates having a high mechanical quality factor. Thus, LN is suitable for the material of the SAW device because of its low elastic loss and low attenuation of surface acoustic waves.

Materials and methods: The waveform of the transmitted and received waves was measured to observe cell behavior by this cell evaluation system. The cell evaluation system was composed of the SAW device and energizing probes. The SAW device was fabricated by a lift-off method using an LN substrate with chromium and aluminum deposited to form IDT fingers. To micropattern the cells to the measurement spot, the seeding area was limited by the dimethylpolysiloxane (DMS) chamber sandwiched between acrylic covers to adhere the chamber to the SAW device. The slit surface was then cleaned using peracetic acid and plasma. The cells were incubated for 6 hours after modifying fibronectin on the surface of the SAW device. After incubation, the acrylic cover and cell-seeding chamber were removed from the cell evaluation system. After seeding cells, an alternating current of around 40 MHz was applied to the IDT to measure the received wave with an oscilloscope.

Results and discussion: The resonance frequency of the SAW device on the transmitter side of the fabricated cell evaluation system was measured with an impedance analyzer at 37.8 MHz. The SAW devices freely control the frequency band of irradiating SAW by changing the design of the distance between the interdigital transducer (IDT) fingers. In this study, by setting the distance between the IDT fingers to 25 µm, the target resonance frequency of the SAW device was 40 MHz. From the measurement of the impedance analyzer, the SAW device with a resonance frequency close to the target resonance frequency was successfully fabricated. This reproduces a wavelength (≈100 µm) that provides sufficient resolution for observing cell behavior. The cell sensing area was 5 mm × 5 mm, which was considered to be the irradiation area with the SAW surface displacement at the LN-water interface is 1.24 mm. The SAW was irradiated by applying an alternating current at around 40 MHz band to the IDT fingers of the SAW device on the transmitting side. Waveforms were measured at two different cell counts. The ratio of the amplitude of the received wave to the amplitude of the transmitted wave was 0.88 when the cell density was 627 cells/mm², and 0.97 when the cell density was 83 cells/mm², respectively.

Comparing them, the surface acoustic waves were attenuated as the number of cells increased. These results suggest that this system is effective in measuring cell counts. Since ultrasound is capable of reaching deep into tissues, waveforms using this system could be applied to the development of more effective biomaterials including 3D cellular tissues.

Bioelectricity in Diatom Phaeodactylum Tricornutum

**5:00 PM SB09.04.01**

PEDOT-PSS Porous Electrodes for Probing Cohort Signaling in Escherichia Coli

**Session Chairs:** Frankie Rawson and Paulo Rocha

**University of Coimbra, Portugal; University of Bath, United Kingdom**

Bacteria are known to coordinate gene expression to control their phenotypic characteristics to the most favourable condition in harsh environments. This smart communication mechanism enables the bacteria to efficiently manage the behaviour of their surrounding community. One important mediator of communication processes in bacteria is the dynamics of their membrane potential, mainly studied through single-cell patch-clamp - which is difficult due to bacteria small size, and through the use of genetic modified bacteria that produce changes in fluorescence intensity as a function of membrane polarization. Despite being a direct response to the external electric stimuli and chemical agents (such as ion channel inhibitors, stimulants or antibiotics) these fluorescence methods usually require toxic fluorescent probes hindering stress-free long-term recordings and fail to probe important sub-thresholds regimes in the measuring cell or cellular cohort.

Non-invasively sensing the minuscule electric activity of bacterial populations is therefore a major challenge in bioelectronics and microbiology. To overcome this challenge, we have devised a highly sensitive transducer based on Au/Polyurethane(PU)/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) electrodes, to visualize the electrogenic activity of cohorts of bacteria without the need of genetic modification or the use of stimuli to address intercellular communication.

For the first time, the electric activity of large Escherichia coli populations is directly measurable. By submerging the recording electrodes into LB broth with the model bacteria E. coli MG1655, we were able to sense the bacterial electric behaviour without any physical disruption or interference into their physiology. E. coli demonstrated fluctuations of their basal voltage level, which is much higher in amplitude than the background acquisition noise of about 1 µV. The extracellular analysis reveals asynchronous and synchronous electrical spikes, with amplitudes ranging from 10 µV up to 100 µV, spike widths from 50 ms to 2 s and sporadic events of quasi-periodic bursts with interspike intervals mostly between 0.5 to 10 s, which can be attenuated by using a protonophore carbonyl cyanide m-chlorophenylhydrazine (CCCP).

The electric noise analysis combined with compound screening indicated that the E. coli likely communicate through a diffusion-limited paracrine signalling mechanism where the diffusion of H⁺ plays an important role. Our ultra-sensitive transducer is a unique screening tool to study the electrophysiological properties of large bacterial populations under different pharmacological compounds effects and metabolic states contributing to more effective drug developments.

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Bioelectricity in Diatom Phaeodactylum Tricornutum Cohorts

**Session Chairs:** Frankie Rawson and Paulo Rocha

**University of Coimbra, Portugal; University of Bath, United Kingdom**

Diatoms are a large and highly diverse group of photosynthetic microalgae, mostly oceanic, with a major environmental role on the planet due to a significative contribution to global fixation of carbon and to the biogeochemical cycling of silica. The peculiar evolutionary history of diatoms equipped them with a unique genetic and metabolic makeup which likely contribute to their ecological success in the contemporary oceans. The presence of intracellular signaling and intercellular communication mechanisms in diatoms upon stress plays a role in the acclimatory response to (a)biotic stressors. Diatoms thrive and may proliferate into pernicious harmful algal blooms through their resourceful communication mechanisms, not yet fully understood.

The setup was in a Faraday's cage connected to instrumentation tailored to record minute electric fluctuations stemming from extracellular signaling. The resonance frequency of the SAW device on the transmitter side of the fabricated cell evaluation system was measured with an impedance analyzer at 37.8 MHz. The SAW devices freely control the frequency band of irradiating SAW by changing the design of the distance between the interdigital transducer (IDT) fingers. In this study, by setting the distance between the IDT fingers to 25 µm, the target resonance frequency of the SAW device was 40 MHz. From the measurement of the impedance analyzer, the SAW device with a resonance frequency close to the target resonance frequency was successfully fabricated, which reproduces a wavelength (≈100 µm) that provides sufficient resolution for observing cell behavior. The cell sensing area was 5 mm × 5 mm, which was considered to be the irradiation area with the SAW surface displacement at the LN-water interface is 1.24 mm. The SAW was irradiated by applying an alternating current at around 40 MHz band to the IDT fingers of the SAW device on the transmitting side. Waveforms were measured at two different cell counts. The ratio of the amplitude of the received wave to the amplitude of the transmitted wave was 0.88 when the cell density was 627 cells/mm², and 0.97 when the cell density was 83 cells/mm², respectively.

Comparing them, the surface acoustic waves were attenuated as the number of cells increased. These results suggest that this system is effective in measuring cell counts. Since ultrasound is capable of reaching deep into tissues, waveforms using this system could be applied to the development of more effective biomaterials including 3D cellular tissues.
SYMPOTIUM SB10

Bioinspired Organic Materials and Devices for Sensing and Computing
April 23 - May 9, 2024

**Symposium Organizers**
Simone Fabiano, Linkoping University
Sahika Inal, King Abdullah University of Science and Technology
Naoji Matsuhisa, University of Tokyo
Sihong Wang, University of Chicago

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**SESSION SB10.01: Organic Electrochemical Transistors—Fundamentals and Materials I**
Session Chairs: Hans Kleemann and Sihong Wang
Tuesday Morning, April 23, 2024
Room 429, Level 4, Summit

**10:30 AM **SB10.01.01
**Novel Approaches for High-Performance Organic Transistors**
Lukas M. Bongartz, Matteo Cucchi, Anton Weissbach, Ali Solgi, Hans Kleemann and Karl Leo; IAPP, Germany

The first organic transistors reported were organic electrochemical transistors (OECT, 1984) historically before the organic field effect transistor (OFET, 1986), the organic inversion transistor (2011), and the organic bipolar transistor (2022). After a longer phase of limited interest, OECT have recently been investigated intensively since they offer switching and sensing functionality in an electrolytic environment compatible with biological systems. The mixed electron-ion transport of the devices has consequence for many parameters of the devices including dynamics and hysteresis. In this talk, our recent work on a better understanding of OECT operation is discussed. Recently, we have shown that the so far used electrostatic “FET-like” description of OECT is needs to be extended to a model including entropic and enthalpic terms. The model elegantly describes a multitude of effects, including bistability and a peculiar temperature behavior of subthreshold slopes. Besides offering new insight into the basic operation, it also allows novel device applications.

**11:00 AM **SB10.01.02
**Novel Material for n-Type Organic Electrochemical Transistors**
Thue-Quyen Neuvey; University of California, Santa Barbara, United States

Organic electrochemical transistors (OECTs) are attractive for applications in chemical and biological sensors, neuromorphic computing, and reconfigurable electronics. An OECT consists of three electrodes (source, drain, and gate), an organic mixed ionic-electronic conductor (OMIEC) channel connecting the source and the drain, and an electrolyte between the gate and the channel. The development of OECTs has been strongly linked to advances in OMIECs. The OECT active material needs to accommodate ion transport, electronic transport, ion-electronic coupling, and air stability. For these reasons, early development of OMIECs has focused mostly on p-type polymer materials because of their superior air-stability and processability. As for n-type OECT polymer active materials, the bottle-neck is usually air-stability because n-type polymers with lowest unoccupied orbital (LUMO) higher than -4.0 eV react with oxygen at ambient condition. In this work, we report an approach to make n-type OECTs from a solution-processable perylene diimide-based material. Our model material shows good n-type electronic transport, ionic transport, ion-electronic coupling, and air-stability. Via device engineering, we achieve n-type OECTs with high transconductance (49 mS) and good stability (stable after hundred-cycle weekly operation across five weeks stored in ambient air). We demonstrate the use of n-type perylene diimide-based OECTs in glucose sensors.

**11:30 AM **SB10.01.03
**Electric Field Contributions to Ion Motion in Organic Electrochemical Devices**
Loren G. Kanke; Simon Fraser University, Canada

Organic electrochemical devices include biosensors, transistors, electrophoretic displays, and light emitting electrochemical cells. One key step in device operation is the movement of ions within the electronically-conductive π-conjugated material. The mechanisms of ion motion and the structure-property relationships that govern those mechanisms continue to be a source of keen interest. One important vantage point to understanding this motion is through the fundamental equations of mass transport (the drift-diffusion equation). Because both electronic charge carriers and ions are in motion, the details of this coupling can, in principle, be quite complex. In order to develop a first-order model that encapsulates typical behavior in the most common systems, we performed spectrotellectrochemical measurements on thin films of PEDOT:PSS, a common mixed conducting material. Specifically, we examined what role, if any, applied electric fields have on the transport of ions in PEDOT:PSS. This was accomplished by comparing a device with potential applied at the electrolyte interface to a device where a potential is applied across the PEDOT:PSS thin film, in an attempt to use fields to draw the ions more rapidly through the bulk of the material. No discernable difference in the electrochemical charging dynamics was observed, demonstrating that macroscopic fields are not an important influence in ion motion. To better rationalize this result, finite element simulations were performed. These simulations highlight the importance of local fields as established by both the electronic charge carriers and the intermolecular forces between the ions and the polymeric medium in which it is embedded.

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SESSION SB10.02: Organic Electrochemical Transistors—Fundamentals and Materials II
Session Chairs: Sahika Inal and Sihong Wang
Tuesday Afternoon, April 23, 2024
Room 429, Level 4, Summit
1:30 PM *SB10.02.01
Electrochemical Transistors Monolithically Integrated for Sensing Arrays
Antonio Facchetti1,2, 1Georgia Institute of Technology, United States; 2Northwestern University/Flexterra Inc, United States

Organic electrochemical transistors (OECTs) have stimulated new research in biosensor, wearable/e-textile, and neuromorphic applications. However, limitations in micro/nanopatterning of organic semiconductors and topological irregularities often limit their implementation in monolithically integrated circuits as is common in silicon-based electronics. In this presentation we first report on a new vertical OECT architecture (vOECT) enabling excellent and balanced behavior. Next, we demonstrate the successful realization of high-density (up to ~7.2M OECT/cm²) and mechanically flexible vOECT arrays and circuits via facile and generalizable micropatterning of the semiconductor materials by electron-beam lithography. The resulting p- and n-type vOECT active-matrix arrays exhibit excellent electronic characteristics with transconductances of 0.08 – 1.7 S, fast transient times (<100 um) and ultra-stable switching properties (>100k cycles). Furthermore, we demonstrate vertically stacked complementary logic circuits, including NOT, NAND, and NOR gates, which are essential components for digital processing and logic operations.

2:00 PM *SB10.02.02
Organic Electrochemical Transistors Based on Polymer Blends
Shunsuke Yamamoto; Tohoku University, Japan

We examine the organic electrochemical transistors (OECTs) based on polymer blends of a mixed conductor (PEDOT:PSS) and an ion conductor (PSSNa) or other functional polymers, including thermoresponsive PNIPAM. The phase separation structures, especially surface segregation, were examined to discuss the distribution of PEDOT and other components in the channel layers. For example, we found that the blend films of PEDOT:PSS and PNIPAM have a surface skin layer of PNIPAM on top of the PEDOT layer. This talk will cover the tendency and driving force of the surface segregation phenomena in PEDOT:PSS-based blend films for a rational design of functional OECT devices.

2:30 PM BREAK

SESSION SB10.03: Neuroromorph Computing I
Session Chairs: Simone Fabiano and Wei Huang
Tuesday Afternoon, April 23, 2024
Room 429, Level 4, Summit

3:00 PM *SB10.03.01
Physical Reservoir Computing with Dendritic Polymer Structures – Understanding Internal Dynamics, Scale-up and Integration in All-Solid-Systems
Anton Weissbach, Peter Steiner, Lukas M. Bongartz, Richard Kantelberg, Peter Birkholz, Karl Leo and Hans Kleemann; Technische Universität Dresden iAPP, Germany

Physical Reservoir Computing is an emerging field of research as such recurrent neural networks offer power-efficient real-time classification on edge devices thereby utilizing the inherent temporal dynamics of the underlying physical, chemical or biological system. In particular, the use of organic mixed ionic-electronic conductors enables a close connection to biological systems due to the strong coupling between ionic and electronic conduction as well as the possibility to chemically modify the polymer to interact with bio-molecules. Previously, we have shown a first realization of a physical reservoir composed of polymer dendrites integrated onto a flexible substrate for on-chip heartbeat classification. However, the systems was limited due to an insufficient complexity and the use of an external delayed feedback line (single-node reservoir), requiring significant data pre-processing and increasing the power consumption. In this contribution I will discuss the internal dynamics of such dendritic reservoirs and how we tuned them by external parameters such as the ion conductivity or ion mobility. Furthermore, I will demonstrate the integration of such reservoirs into a solid-state electrolyte, which allows us to scale-up the network to a large number of nodes covering the bandwidth relevant for bio-signal processing. The scale-up results in an improvement of the classification accuracy up to 95% without any silicon-based component. Moreover, the scale-up study shows us that the classification accuracy and power consumption can be decoupled in sparse network configurations, enabling us to achieve such a high accuracy with a power consumption of only 100nW. This integration strategy of sparse networks into a solid-state electrolyte opens up new perspectives to further increase the efficiency of intelligent edge devices based on organic semiconductors.

3:30 PM *SB10.03.02
Coordination Compound Materials for Neuroromorph Computing and Brain-Computer Interfaces
Alec Talin; Sandia National Laboratories, United States

As we near the limits of conventional digital Si based transistor technology, neuromorphic computing using analog devices based on functional materials that emulate neuronal and synaptic characteristics has emerged as a powerful approach to realize the energy efficiency and dynamic adaptability of animal brains. While most efforts have focused on inorganic materials due to their compatibility with Si CMOS processing and scalability, a wide range of neuromorphic functionality has also been demonstrated in devices based on organic polymers, coordination polymers and molecular coordination complexes. In my presentation I will give a snapshot of how these different materials are being explored for analog neuromorph computing, and then focus on our recent work with the mixed valence coordination polymers like the Prussian blue analogues (PBAs), attractive because they have an open framework structure and ability to conduct both ionic and electronic charge. Using inkjet-printing, I will demonstrate flexible artificial synapses that reversibly switch electronic conductance by more than four orders of magnitude based on electrochemically tunable oxidation state. Retention of programmed states is improved by nearly two orders of magnitude compared to the extensively studied organic polymers, thus enabling in-memory compute and avoiding energy costly off-chip access during training. We demonstrate dopaminergic detection using PBAs synapses and biocompatibility with living neurons, evoking prospective application for brain-computer interfacing. By application of electron transfer theory to in-situ spectroscopic probing of intercalation charge transfer, we elucidate a switching mechanism whereby the degree of mixed valency between N-coordinated Ru sites controls the carrier concentration and mobility, as supported by DFT.

4:00 PM *SB10.03.03
Large-Scale Stretchable Neuromorphic Computing Circuits for Acute Disease Detection and Soft Robotics
Songsong Li1, Max Weires1, Zixuan Zhao1, Fangfang Xia2 and Sihong Wang1; 1The University of Chicago, United States; 2Argonne National Laboratory, United States

Developing wearable edge computing electronics with skin-like stretchability has a significant impact on precision medicine and soft robotics. To implement edge computing function, integrated neuromorphic systems with artificial synapses and neuron functionalities are necessary, which can emulate biological neural networks and enable the replication of complex cognitive abilities within an artificial system. Recent explorations have identified organic electrochemical transistors (OECTs) as a promising device platform for stretchable neuromorphic computing. However, challenges remain in the scalable fabrication of stretchable large-scale synaptic arrays and additional stretchable components, such as artificial neurons. In this work, we develop intrinsically stretchable integrated neuromorphic systems by stretching the network to stretchable 10 x 10 neuromorphic arrays via a standard cleanroom microfabrication process, subsequently constructing artificial neurons to realize neuromorphic activation functions. Various machine learning algorithms are deployed using our neuromorphic integrated system to detect acute disease and regulate the movement of soft robots. Overall, this work will shed light on the promising pathway toward realizing wearable on-body edge computing.

4:15 PM *SB10.03.04
Structural Plasticity with PEDOT-Based Dendritic Electropolymerization for Neuromorphic Engineering
Kamilia Janzakova1, Corentin Scholaert1, Ismael Balafrej2, Ankush Kumar1, Dominique Drouin1, Jean Roux2, Sébastien Peccqueur1, Yannick Coffinier1 and Fabien Albaret1,2; 1IMEN-CNRS, France; 2University of Sherbrooke, Canada

Neuromorphic computing and engineering is capitalizing heavily on the new physical properties offered by nantechologies to engineer biological processes. At the frontiers in between biomimetics and bio-inspiration, various solutions have been proposed for synaptic plasticity or neuronal features based on discrete memory elements, bistable switches or transistors circuits. One missing element that has been missing in the neuromorphic toolbox is the ability to reproduce the complex 3D interconnections observed in biological neural networks. Here, we propose to take advantage of bipolar electropolymerization of PEDOT dendritic fibers to reproduce the ability of neural networks to generate complex topologies. The electropolymerization mechanism is used to realize structural plasticity based on Hebbian-like plasticity rules. We explore how such bottom-up process can find optimal topologies for specific computing tasks. We demonstrate that such optimal topologies results in a drastic reduction of interconnects for classification and reconstruction tasks, thus offering an interesting option for neural network design.
As point-of-care testing (POCT) is becoming the new paradigm of medical diagnostics, there is a growing need to develop reliable POCT devices that can be conveniently operated in a minimally invasive manner. However, the clinical potential of POCT diagnostics is yet to be realized, mainly due to the limited and inconsistent amount of collected samples on these devices, undermining their accuracy. This study proposes a new biosensing platform modified with a functional polysuccinimide (PSI)-silica nanoparticle (SNP) composite system that can substantially increase the protein conjugation efficiency by modulating physicochemical interaction with proteins by several hundred percent from an unmodified device. The efficacy of this PSI-SNP system is further validated by applying it on the surface of a microneedle array (MN), which has emerged as a promising POCT device capable of accessing interstitial fluid through minimal penetration of the skin. This PSI-SNP MN is demonstrated to detect a wide array of proteins with high sensitivity on par with conventional whole serum analysis, validated by in vivo animal testing, effectively displaying broad applicability in biomedical engineering.
Stimulus-responsive, i.e. smart, hydrogels are polymers capable of exhibiting a reversible volume change in response to external physical and chemical influences, for example pH value, light, temperature or specific analyte molecules. This makes the material a very interesting candidate for novel sensing elements, especially since the properties can be tailored for specific applications from a wide variety of monomers and mixtures thereof, as well as additives [1,2].

The smart hydrogel’s volume change is usually mediated by the uptake and release of liquid and consequently, most applications are centered on liquid environments. However, the hydrogel’s capabilities for selective and sensitive analyte detection hold great potential beyond that and we have therefore started to explore how to harness the material’s properties for sensing in gaseous media. The specific target application of our research is volatile organic compound (VOC) detection in exhaled breath to enable monitoring of disease biomarkers such as acetone. For this purpose, synthetic acrylamide-based hydrogels were chosen as the model material. In a first step, different polymers comprising polyacrylic acid (PAA), polyacrylamide (PAM), poly(N-isopropylacrylamide) (PNiPAAm) and their co-polymer combinations were investigated with respect to their ability of maintaining a measurable volume change in air with relative humidity variation from 0% to 100%. These studies were performed without and with added acetone gas as test VOC (concentrations: 20 ppm - 100 ppm) and the hydrogel’s swelling response was characterized by gravimetry and piezoresistive pressure sensing. PNiPAAm showed the best responsiveness in terms of humidity range, dependence of swelling response on the target analyte concentration and potential for selectivity [3].

However, these studies also revealed a significant challenge for using hydrogels in a gaseous atmosphere: A large surface area is crucial for a strong and fast response in VOC detection, hence the hydrogel should ideally feature a very porous structure (surface and bulk). While the porosity can be adjusted by the use of pore-forming additives or by ice-templating during polymerization, the pores are likely to collapse after polymerization and subsequent drying in air.

To address this challenge, the second step of our research focused on the development of a procedure enabling the creation of defined porosity which is maintained under the conditions of a gas atmosphere with varying humidity conditions. We found that templating with PEG during polymerization, followed by freeze drying (either at -196°C or -20°C, depending on the desired pore size) and subsequent conditioning in high relative humidity (90% – 100%) is the key to achieve stable porosity. The material properties were characterized and compared in scanning electron microscopy and FT-IR analyses, and the volume change performance again evaluated by gravimetry and piezoresistive pressure sensing [4].

These investigations have been conducted for PNiPAAm which was identified as the most promising material candidate for our target application. However, the developed process for tailoring and stabilizing a porous polymer structure in gaseous environments is of general nature and can easily be applied to other types of hydrogel since there are no components or steps specific for PNiPAAm.

To enhance the responsiveness (i.e. swelling strength, time constants, reversibility) of the smart hydrogel even further, the focus of our future work is on the integration of additives such as graphene- and MXene-based materials.

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Controlling The Optical Properties of Near-Infrared Nanotube Sensors through Bioengineering

SB10.05.06

10:30 AM

and generate biomarker specific signal. We observe an increased conductivity by tuning the bias from 600 to -800 mV indicating an increase of the injected charge. More in detail, we report a positive real accompanied by a negative imaginary part of the conductivity, as already shown in the literature. This behavior is well described by the Drude-Smith model that considers charge localization effects due to the finite polymer chain size and the energetic disorder. From the fit, we extract the charge density injected in the OMIEC as a function of the applied voltage bias and its carrier mobility.

To demonstrate the effectiveness of the charge carrier screening effects in p(2G-TT) at THz frequencies, we investigate the amplitude modulation performances of a THz metadevice based on this OMIEC. The prototypical device is based on metallic Split Ring Resonators with a resonance at 0.7 THz, which are electrostatically tuned with the p(2G-TT). We show that despite the relatively low mobilities of the charge carriers, their large density modulation leads to excellent modulation depth – exceeding 60% - with polarization voltages below 1 V.

Our results highlight the potential of organic THz devices based on OMIECs, for instance as optical modulators for telecom applications. Further research efforts in this direction could lead to a new generation of reconfigurable photonic technologies that take benefit of the many desirable properties of organic semiconductors, such as the ease of processability on large-area flexible substrates.

References:

8:30 AM

Translational Neuroelectronics Dion Khodapour; Columbia University, United States

Our understanding of the brain’s pathophysiology relies on discoveries in neuroscience and neurology fueled by sophisticated bioelectronics enabling visualization and manipulation of neural circuits at multiple spatial and temporal resolutions. In parallel, to facilitate clinical translation of advanced materials, devices, and technologies, all components of bioelectronic devices have to be considered. Organic electronics offer a unique opportunity for device design, due to their mixed ionic/electronic conduction, mechanical flexibility, enhanced biocompatibility, and capability for drug delivery. We design, develop, and characterize conformable, stretchable organic electronic devices based on conducting polymer-based electrodes, particulate electronic composites, high-performance transistors, conformable integrated circuits, and ion-based data communication. These devices established new experimental paradigms that allowed monitoring of the emergence of neural circuits during development in rodents and elucidated patterns of neural network maturation in the developing brain. Furthermore, the biocompatibility of the devices also allowed intra-operative recording from patients undergoing epilepsy and deep brain stimulation surgeries, highlighting the translational capacity of this class of neural interface devices.

In parallel, we are developing the fully-implantable, conformable implantable integrated circuits based on high-speed internal ionic gated organic electrochemical transistors that can perform the entire chain of signal acquisition, processing, and transmission without the need of hard Si-based devices. This multidisciplinary approach will enable the development of new devices based on organic electronics, with broad applicability to the understanding of physiologic and pathologic neural network activity, control of brain-machine interfaces, and therapeutic closed-loop devices.

9:00 AM

SB10.05.03

Organic Neuromorphic Electronics for Sensory Coding and Biohybrid Systems Yoeri van de Burgt; Eindhoven University of Technology, Netherlands

Neuromorphic engineering takes inspiration from the efficiency of the brain and focuses on how to utilise its functionality in hardware. Organic electronic materials have shown promising solutions for the manipulation and the processing of biological signals, with applications ranging from bioinformatics to brain-computer-interfaces and smart robotics.

This talk describes state-of-the-art organic neuromorphic devices and provides an overview of the current challenges in the field and attempts to address them. I demonstrate two device concepts based on novel organic mixed-ionic electronic materials and show how we can use these devices smart robotics and at the interface with biology. This can pave the way for novel architectures with bio-inspired features, offering promising solutions for the manipulation and the processing of biological signals and potential applications ranging from brain-computer-interfaces to bioinformatics and neuromediator-mediated adaptive sensing. I will highlight our recent efforts for such hybrid biological memory devicesand artificial neurons.

9:30 AM

SB10.05.04

Zwitterionic Hydrogel Design of PEDOT:PSS Suppresses the Faraday Body Response against Organic Electrochemical Conductors Shinyu Wai; Nan Li, Seounghan Kang, Yahoi Dai, Lavoie Tera, Wei Liu, Matthew V. Tirrell and Shihong Wang; The University of Chicago, United States

Implantable medical devices (IMDs) are playing an increasingly important role due to an aging population and the associated increasing prevalence of chronic diseases. However, the foreign body response (FBR) has limited IMDs from realizing their full potential. The FBR is characterized by inflammatory and fibrotic processes that surround the implanted material. Degradative chemicals and enzymes produced in the process can damage the implant. Fibrotic encapsulation is particularly detrimental for biosensors and electrophysiological devices because it would impede the diffusion of analytes and ions. A class of materials with promising FBR suppressing properties are zwitterionic polymers which have been shown to nearly eliminate the FBR for at least a year in mice. As electronic materials for IMDS, poly(3,4-ethylendioxystyrene:poly(styrene sulfonate) (PEDOT:PSS) is of interest because it is chemically stable, highly processable non-cytotoxic, and has good mixed ion-electron conducting properties. Nonetheless, previous work addressing the FBR against PEDOT:PSS did not place their focus on long-term solutions or did not carry out FBR-specific characterization methods. We hypothesize that by combining PEDOT:PSS and a zwitterionic polymer into a double-network hydrogel and carefully tuning its phase separation morphology, the conductivity can be increased and the FBR can be suppressed indefinitely. In this work, we demonstrate a process for inducing PEDOT:PSS network formation in situ in a zwitterionic hydrogel matrix, which significantly improves its conductivity and reduces FBR-associated fibrosis. Our work demonstrates that controlling the phase separation morphology of composite materials can be an effective strategy for suppressing the FBR.

9:45 AM

SB10.05.05

Potentiometric Wearable Sensors with a Laser Engraved Graphene Layer as Transducer Farbod Amirghasemi, Abdulrahman Al-Shami, Victor Ong and Maral Mousavi; University of Southern California, United States

Laser-induced graphene has gained great attention recently for sensing devices. LIGs are generated through the process of irradiating carbon-rich polymers, primarily polyimide, using a laser beam. This procedure induces localized photothermal reactions, resulting in the conversion of SP3 carbon atom hybridization into a threedimensional graphic-like structure. This maskless, scalable, simple, reproducible, cost-effective, and fast technique produces high-quality graphene layers with outstanding flexibility, electrical conductivity, and electrocatalytic properties instead of using the conventional time-consuming, expensive, and complicated methods such as wet chemistry, inkjet printing, and chemical vapor deposition (CVD). In this work, we discuss surface modification and properties of graphene for achieving a stable interfacial potential in contact with a lipophilic sensing membrane, in a potentiometric readout mode. Specifically, surface topography and hydrophilicity of the material impacts the long-term and short-term properties of the wearable sensors. We will show how the engineering conditions impact water layer formation and drift of sensors, and how a highly stable readout can be achieved through surface modification. We use bio-inspired organic receptors to achieve ion specific binding at the electrode surface and generate biomarker specific signal.

10:00 AM BREAK

10:30 AM

SB10.05.06

Controlling The Optical Properties of Near-Infrared Nanotube Sensors through Bioengineering Ardenis A. Boghosian; Ecole Polytechnique Federale de Lausanne (EPFL), Switzerland

Single-walled carbon nanotubes (SWCNTs) emit fluorescence that is ideal for a breadth of optical sensing applications. The near-infrared emissions are minimally absorbed by biological tissue, biofluids, and other visibly opaque materials. This property motivates their use for packaging and deep-tissue applications. The indefinite photostabilities and optical sensitivity to changes in healthcare. Organic mixed ionic-electronic conductors (OMIECs) are organic materials that can transport both ionic and electronic charge. The large variety of organic molecules that can be synthesized and the number of ways in which they can be arranged provide a great number of degrees of freedom that influence the OMIECs’ properties and device functionalities. Recent progress in the design and synthesis of organic mixed ion-electron conductors is actively contributing to developing exciting new technologies based on organic electrochemical transistors (OECTs). Among recent applications, OECT-based resonant devices have been proposed in the microwave spectral region showing excellent amplitude and frequency tuning performances in the sub-5GHz range. In these devices, the 3-dimensional charge modulation capabilities of OMIECs are key in achieving excellent tunability of both individual and arrays of microwave resonators, hence leading to a novel class of microwave photonic devices based on organic materials. The next step is to explore the applicability of this approach toward the THz frequencies, as well as the investigation of the OMIEC charge transport properties in this spectral range. In this work, we study the far-infrared conductivity of a state-of-the-art OMIEC, namely p(2G-TT), with field-assisted THz Time Domain Spectroscopy (THz-TDS). Through this technique, we non-destructively investigate the dielectric and electronic properties of the OMIEC during operation, thus gaining crucial insights for the physical modeling of charge transport at high frequencies. By varying the applied voltage bias from -800 to 600 mV, we modulate the dielectric response of the polymer and obtain information about the charge injection and its effect on the polymer conductivity. We observe an increased conductivity by tuning the bias from 600 to -800 mV indicating an increase of the injected charge. More in detail, we report a positive real accompanied by a negative imaginary part of the conductivity, as already shown in the literature. This behavior is well described by the Drude-Smith model that considers charge localization effects due to the finite polymer chain size and the energetic disorder. From the fit, we extract the charge density injected in the OMIEC as a function of the applied voltage bias and its carrier mobility.
Ions are ubiquitous biological and physiological regulators, while abnormal ion concentrations in human body fluids are often fingerprints of ongoing pathological states, diseases, and even organ malfunctions (such as heart or kidney failure, and dehydration). Therefore, accurate and timely detection/monitoring of various vital ion concentrations in body fluids is highly desired. Here, we demonstrate ultra-sensitive and selective ionic sensors based on vertical organic electrochemical transistors (vOECTs). By combining the advantage of high transconductance ($g_{m} > 0.2$ S) and small footprint ($< 30 \times 30$ µm) of the vOECTs with specific ionic selective membranes, ultra-high sensitivities up to 13.9 mA/dec (for Na$^+$), 2.2 mA/dec (for K$^+$), and 187 mA/dec (for Ca$^{2+}$) are achieved, along with decent selectivity, stability, and reproducibility. Such sensitivities are the highest values among reported ion-sensitive transistors (including ISFETs, ECOFETs, and OECTs). By integrating different vOECT-based ionic sensors in an array, in-situ monitoring of the ionic level in the externally circulated bold fluid or the dialysate during an active continuous renal replacement therapy (CRRT) is demonstrated with high accuracy and reversibility. This work demonstrates the great potential of OECT-based sensors for complex sensing scenarios.

**References**

2. Hashima Parveen Anwar Ali, Zichen Zhao, Yu Jun Tan, Wei Yao, Quanxiao Li, and Benjamin C. K. Tee, *ACS Applied Materials & Interfaces* 2022, 14(46), 52486-52498, DOI: 10.1021/acsami.2c06453
Electronic/photon devices that are conformable to biological organs basically need to have extremely soft materials. Such devices usually have a multi-stack structure consisting of several functional layers, and can usually be realized using thin film devices. It is possible to reduce flexural rigidity and buckling load by simply reducing the film thickness of the device as well as reducing Young’s modulus of each layer. This approach creates a system that does not inhibit the movement of organs, becomes possible.

One example of our recent achievements is the establishment of a method for mounting ultrathin-film organic solar cell films on insect abdomens [1]. The abdominal segments consist of multiple segments, and the deformation is achieved through the overlap of the segments. To not inhibit the movement of the abdomen, we developed an adhesive method in which part of the films have adhered to abdominal surfaces, and the unbounded area secures the room for deformation during the bent of the abdomen. In the case of polymer films with Young’s modulus on the order of GPa, there is a tolerance threshold of around 5-10 μm in thickness to secure the basic motion ability of a specific insect, which was quantitatively clarified from the correlation with the bending load. Through such evaluations, we created a system of cyborg insects that can be recharged with ultra-thin organic solar cells adhered to abdominal surfaces. Another example is the construction of stretchable electrode systems for stimulation and sensing on PDMS [2]. The use of extremely thin PDMS (approx. 1 μm) improves its adhesion to living organisms. We developed a stretchable conductor using micro-crack structured gold onto such thin PDMS films, which contributes to nerve stimulation with lower power than thicker film-based electrodes. In addition, by combining it with conductive polymers, stable adhesion on the skin is achieved, making it possible to construct systems that enable daily activities such as hand washing and swimming.

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**References**


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**4:45 PM SB10.06.06**

**Chemical and Biosensing Using Enzyme Inspired Electropolymerized MIPS and Devices**

*Rigoberto C. Advincula*; The University of Tennessee/Oak Ridge National Laboratory, United States.

Bioinspired macromolecules can be prepared by co-polymerization or de novo biopolymer substitutes. The lock-and-key templating process can mimic molecular complexes inspired by biological enzyme-substrate interactions. Using functional monomers that can be electrochemically polymerized enables the formation of cross-linked polymer films with cavities that can enable high-binding assays of chemical and biological analytes. This talk will show the effective and bio-inspired artificial enzymes for detecting chemical and biological analytes. We will focus on demonstrating electropolymerized molecularly imprinted polymer (E-MIP) sensor elements and their ability to utilize transduction methods such as surface plasmon resonance (SPR) spectroscopy to enable high sensitivity and selectivity. The monomer and molecular design for optimized analyte interaction enables effective templating protocols in an electrically conducting polymer matrix with tunable redox states to enable a high volume of analyte-cavity sites. Optimized electropolymerization methods are important for film deposition and surface characterization based on SPR, XPS, and other microscopic and spectroscopic methods to confirm surface specificity. Several analytes, including drugs, organic pollutants, nerve agents, and epitopes of larger proteins. This was recently demonstrated in the detection of dengue-expressed proteins for disease diagnostics.

**Acknowledgments**

The current peak variations showed high linearity, with a linear regression coefficient \( R^2 = 0.9841 \), corresponding to the levels of ApoE4. Further studies will involve validation and interference tests, including the detection of other Alzheimer's disease (AD) biomarkers, such as Amyloid-\( \beta \) 42.
Ultrathin, Self-Adhesive, Sweat-Absorbing Janus Membrane Epidermal pH Sensor

possibility of simplifying the actual fabrication process by eliminating color filters in the sensor. Moreover, it implies the potential for various applications, such as light-controlled logic.

In conclusion, the IGZO phototransistor utilizing chlorophyll as an absorption layer has demonstrated the potential to differentiate between red, green, and blue light. This suggests the
respectively.

Wearable biomedical sensors have enabled non-invasive and continuous physiological monitoring for daily health management and early detection of chronic diseases [1,2]. Among the
biomedical sensors, wearable pH sensors attracted significant interest as pH influences most biological reactions [34]. However, the conformable pH sensor which can be self-adhesive to human skin, has sweat-wicking ability and gas permeability remains largely unexplored. Here, we present a novel approach to this problem through the development of a Janus membrane-based pH sensor with self-adhesive on the skin. The sensor consists of a hydrophobic polyeurethane-polydimethylsiloxane (PU-PDMS) porous nanomter-thick film and a hydrophilic polyvinyl alcohol-polyacrylic acid (PVA-PAAc) nanofiber film. This Janus membrane exhibits a thickness of a few micrometers, providing a firm and comfortable adhesion to the skin. The sensor demonstrates fast-responsive, accurate, and long-term pH measurements, enabling reliable wearable applications. The simultaneous realization of solution absorption, gas-permeability, and self-adhesiveness, make it suitable for long-term, continuous monitoring without compromising wearer comfort. The pH sensor has been tested successfully for continuous monitoring over an hour, demonstrating its potential for stable analysis of skin health conditions. This innovative Janus membrane-based pH sensor holds significant promise for comprehensive skin health monitoring and wearable biomedical applications.

Reference

SB10.07.06
Breathable, Structure-Gradient Pressure Sensing Textile for Rehabilitation Assistance Jinxing Jiang and Qiyaoting Huang; The Hong Kong Polytechnic University, Hong Kong

Triboelectric pressure sensing textile shows great potential in various wearable applications such as healthcare monitoring system due to their light weight, high permeability and flexibility. However, it’s difficult to achieve high sensitivity and large pressure sensing range simultaneously. Here, we innovatively crafted a skin-inspired fiber mat (SIFM) with a gradient structure using a template-assisted layer-by-layer electrospinning technique. Drawing inspiration from the human skin, our SIFM mimics its natural micro-bump texture, gradually transitioning from soft to rigid as one moves from its outermost surface towards its core. The distinct structural design of SIFM has led to the development of a breathable, structure-gradient pressure sensing textile (PSPST) with simultaneous high sensitivity, wide detection range and high breathability. In comparison to conventional pressure sensing textiles constructed from homogenous fiber mats, our PSPST exhibits a substantial enhancement in pressure sensing performance. Finally, We demonstrate its ability for rehabilitation assistance, including monitoring the quadripod, pulse and plantar pressure simultaneously.

SB10.07.07
Tissue-Like Skin-Device Interface for Wearable Bioelectronics by Using Ultrasoft, Mass-Permeable and Low-Impedance Hydrogels Yoonsoo Shin and Dae-Hyeong Kim; Seoul National University, Korea (the Republic of)

Hydrogels are composed of a cross-linked porous polymer structure with water molecules distributed within the gaps of the polymer chains. This unique composition renders hydrogels soft and hydrated, sharing mechanical and physical characteristics akin to human tissues. Consequently, hydrogels have the potential to emulate a tissue-like environment within the minuscule spaces between wearable devices and the human skin. In this study, we introduce strategies at both material and device levels to establish a quasi-solid, tissue-mimicking interface between wearable bioelectronics and human skin. A crucial element of this approach involves the ultra-thin functionalized hydrogel exhibiting exceptional properties like high mass-permeability and low impedance. This specialized hydrogel acts as a liquid electrolyte on the skin, creating a highly conformal and low-impedance interface suitable for wearable electrochemical biosensors and electrical stimulators. Moreover, its porous structure and ultra-thin profile enable efficient transport of target molecules across the interface, thereby maximizing the performance of diverse wearable bioelectronics.

SB10.07.08
Highly Elastic and Ultrathin Nanomembrane Using Kinked Ag Nanowires for Epidermal Electrode Minseong Kim1,2 and Dae-Hyeong Kim1,2; 1Seoul National University, Korea (the Republic of); 2Institute for Basic Science, Korea (the Republic of)

Skin electronic devices require a flexible conductor with properties such as metal-like conductivity, high flexibility, extremely thin thickness, and the ability to create simple patterns. Achieving these characteristics simultaneously has proven to be quite challenging. Previous research introduced a nano-membrane fabrication method using a flow assemble technique to successfully
address a significant portion of these challenges in creating electrodes for skin electronic devices. However, conventional nano-membranes often struggle to precisely control conductivity and flexibility due to the dense packing nature of nanowires. In this study, an innovative approach is presented to create highly flexible nano-membranes using twisted nanowires. Incorporating twisted nanowires in the nanomembrane fabrication process facilitates the formation of percolation networks at low concentrations. Furthermore, the use of twisted nanowires not only enhances flexibility but also reduces the likelihood of nanowire breakage during vertical deformation. This innovation advances the development of skin electronic devices and holds significant potential for improved flexibility, conductivity, and durability in various applications.

5:00 PM SB10.07.09

**Recognition of Peptide Sensory Systems Inspired by Human Skin Mechanoreceptors**

Eunpyung Yoon, Chun Seung-hwan, and Chang-soo Han; Korea University, Korea (the Republic of)

The human skin is an astonishing sensory organ that provides extensive information about our surrounding environment. It can detect various stimuli such as pressure, vibration, texture, temperature, and even chemical substances. Taking inspiration from ion channels and receptors, which are key components of cutaneous sensory organs from a biological perspective, a new approach is being pursued to address the limitations of conventional touch sensors and enable machines to interact with the world in a more human-like manner. Specifically, skin sensory organs perceive tactile sensations through the simultaneous and complex reactions of diverse and abundant receptors. Each receptor possesses a unique working mechanism that selectively responds to specific stimuli. Unfortunately, prior research has only hinted at the significance of this aspect and instead focused on independent studies or functions of individual receptors, neglecting to mimic the complex interactions that occur in the skin or incorporate them adequately.

The skin encompasses numerous transduction networks that detect stimuli and relay information to the brain. These networks consist of receptors that detect stimuli, ion channels that generate action potentials, and nerves that transport the electrical signals to the brain. Specifically, in the context of sensing physical stimuli, mechanoreceptors are generally classified into four types: Merkel discs (MD), Meissner corpuscles (MC), Ruffini endings (RE), and Pacinian corpuscles (PC). These mechanoreceptors play a crucial role in collecting information about the physical properties of objects we encounter in the environment, enabling us to perceive their shape, weight, texture, etc.

To truly mimic human skin functionality, it is essential to design and manufacture a diverse array of sensors capable of obtaining various information such as pressure, shear force, and tension from a limited size. This will allow for more accurate and diverse collection of mechanical stimuli from the surrounding environment. For instance, in our case, to emulate the vibrational touch sensor function observed in dermal papillae where MC is located, a bump-like structure and piezoelectric characteristics can be utilized for implementation. Additionally, to mimic the positional and functional features of PC, the finding in the MD, a cone-shaped ion gel and pico gel can be employed. As for RE, which has a dendritic branch form within the capsule and participates in stretch detection, this can be emulated using carbon nanotubes (CNTs) sheet with properties of tensile resistance within viscoelastic materials. Simulating the functions and features based on these receptor structures represents a future challenge that artificial skin should strive towards.

This study aims to develop a tactile sensor system that recognizes objects by mimicking the mechanoreceptors present in human skin. The sensor system is designed by emulating the unique structures and functionalities of three types of receptors (MD, ME, RE) crucial for object recognition. These sensors are embedded with a similar elasticity to human skin. The integrated sensors are arranged in a way that separates receptors (stimulus detectors) and ion channels (signal generators), enhancing selectivity to specific stimuli. The manufactured sensors exhibit stretchability similar to human tactile organs and demonstrate trends comparable to biological touch experiments. Furthermore, to achieve effective object recognition, an AI-based signal processing algorithm is employed to analyze and learn from the data generated by the sensors. The material design for the object recognition sensor incorporates materials such as piezogels and non-hydrogel ion gels, as well as substances like carbon nanotubes to control mechanical and electrical properties. The integrated sensor system successfully recognizes surface textures and various objects that are difficult to analyze using only one or two types of sensors.

5:00 PM SB10.07.12

**Conductive Carbon Fiber-Hydrogel Composites for Functional Tissue Engineering**

Sebastian Bibler and Julia Koerner; Leibniz University Hannover, Germany

Materials for tissue engineering rely on the mimicry of extracellular matrix environments, easily achievable biocompatibility and favorable mechanical properties. Hydrogels are a type of polymer that incorporate these properties and are widely used as tissue scaffolds [1]. In general, hydrogels are non-conductive material and therefore tailoring their electrical properties to enhance conductivity opens the possibility of extending their applications to include sensing and actuation.

One technique to tailor and modify the conductivity and mechanical properties of hydrogels is to embed carbon fibers in the polymer matrix. To date, carbon fiber-hydrogel-composites (CHC) with random fiber distribution within the hydrogel have been used as flexible and biocompatible sensors [2]. In addition, composites of epoxy-based polymers and unidirectional fiber bundles have been investigated for their properties under high strain and have shown piezoresistive behavior [3,4].

Our work targets the application of unidirectional carbon fiber as a novel approach for tailoring the hydrogel's electrical conductivity. The aim of this research is to study the capabilities of CHCs for directed electric signal transmission along the fibers which could be a first step towards applications as bioelectrical elements, e.g. in nerve grafts. In this regard, two forms of current flow inside the CHC need to be considered: electron- and ion-based. In the former, the carbon fibers and hydrogel matrix are exposed to an electric field and carry electric current. In the latter, the CHC is completely hydrated and the flow is ion-based. The ion flow is determined by an applied electric field and the concentration gradient of ions inside the CHC. These experimental results were accompanied by the electrical properties of the CHCs being modeled in a circuit model in order to gain insight into the causes of the differences observed in the transmission properties of the CHCs.

To truly mimic human skin functionality, it is essential to design and manufacture a diverse array of sensors capable of obtaining various information such as pressure, shear force, and tension from a limited size. This will allow for more accurate and diverse collection of mechanical stimuli from the surrounding environment. For instance, in our case, to emulate the vibrational touch sensor function observed in dermal papillae where MC is located, a bump-like structure and piezoelectric characteristics can be utilized for implementation. Additionally, to mimic the positional and functional features of PC, the finding in the MD, a cone-shaped ion gel and pico gel can be employed. As for RE, which has a dendritic branch form within the capsule and participates in stretch detection, this can be emulated using carbon nanotubes (CNTs) sheet with properties of tensile resistance within viscoelastic materials. Simulating the functions and features based on these receptor structures represents a future challenge that artificial skin should strive towards.

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5:00 PM SB10.07.13

**Fluorescence Imaging of Self-Assembled Peptides on h-BN Using Thioflavin-T**

Hiroki Maeda and Yuhei Hayamizu; Tokyo Institute of Technology, Japan

Peptides possess the capability to self-assemble into well-ordered structures on two-dimensional (2D) materials, such as graphene, rendering them promising candidates for biosensor applications owing to their design flexibility and biocompatibility [1]. Recent research has highlighted the potential of graphene biosensors functionalized with peptides, emulating ophthalmic receptors for applications in odor sensing [2].

Twist the surface structures of self-assembled peptides on 2D material-based biosensors is crucial for comprehending their performance. Atomic force microscopy (AFM) with high spatial resolution has conventionally been employed for the precise observation of these peptide structures [4]. However, due to its limited field of view, AFM is unsuitable for the in-situ observation of macroscopic structures of self-assembled peptides with sizes ranging in the hundreds of micrometers. This study focuses on the in-situ observation of macroscopic structures of self-assembled peptides on hexagonal boron nitride (h-BN) surfaces using fluorescence imaging with Thioflavin-T (T) as a fluorescent marker. h-BN, transparent in the visible region, is well-suited for fluorescent microscopy as a transparent substrate. T is known to exhibit strong fluorescence when attached to β-sheet structures, commonly found in amyloid fibers associated with diseases like Alzheimer's. Given that the peptides in this study are expected to form β-sheet structures, we assessed the feasibility of using ThT for real-time observation of the macroscopic surface self-assembly process [5].

AFM measurements revealed that peptides formed long-ordered structures on h-BN. Subsequently, under fluorescent microscopy, we observed strong fluorescence in regions where the order parameter values were high. The size of the ordered region containing peptide on the surface spanned over a few micrometers in length. This size exceeds the field of view of AFM measurements, and the fluorescent measurement with ThT molecules enables us to visualize the macroscopic self-assembly of peptide layers. Furthermore, weak fluorescence was also detected on partial surfaces of h-BN containing amorphous peptides. These findings underscore the potential of ThT as a tool for assessing the macroscopic self-assembly of peptides over a wide area. The ability to monitor these processes in real-time under liquid conditions using fluorescence microscopy provides insights into the spatial uniformity of molecular thin films, a critical aspect for enhancing the activity of peptide-based biosensors on graphene biosurfaces. This methodology opens avenues for the development of improved peptide biosensors with enhanced functionality and performance.


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Materials that have the ability to manipulate shapes in response to stimuli such as heat, light, humidity and magnetism offer a means for versatile, sophisticated functions in soft robotics or biomedical implants, while such a reactive transformation has certain drawbacks including high operating temperatures, inherent rigidity and biological hazard. Herein, we introduce biodegradable, self-adhesive, shape-transformable poly(l-lactide-co-e-caprolactone) (BSS-PLCL) can be triggered via thermal simulation near physiological temperature (~38 °C). Chemical inspections confirm the fundamental properties of the synthetic materials in diverse aspects, and study on mechanical and biochemical characteristics validates exceptional stretchability up to 800% and tuneable dissolution behaviors under biological conditions. The integration of the functional polymer with a biodegradable electronic system highlights potential for a wide range of biomedical applications.

Keywords: biodegradable polymers; shape-transformable elastomers; shape memory; self-adhesion; nerve stimulators

NIH Brain Behavior Quantification and Synchronization Program: Next Generation Sensor Technology and Related Materials Science Development

This session will highlight several Notice of Funding Opportunities (NOFOs) from the National Institutes of Health (NIH) Brain Research through Advancing Innovative Neurotechnologies® (BRAIN) Initiative that are intended to support the development of next generation sensor technologies and bioelectronic devices to further the goals of the Brain Behavior Quantification and Synchronization (BBQS) program. The BBQS funding opportunities broadly support 1) development of tools for simultaneous, multimodal measurement of behavior and synchronization of these data with simultaneously-recorded neural activity; and 2) development of novel conceptual and computational models that capture dynamic behavior-environment relationships. More information about the BRAIN Initiative including existing Notices of Funding Opportunities for the BBQS program can be found at www.braininitiative.nih.gov (search "BBQS") and there is a BBQS Sensors Request for Information at NOT-MH-24-125. The BBQS Program invites researchers in materials science to contribute to upcoming projects (large and small scale, and future sensor hubs) to develop next generation sensor technologies at the micro and nano scale, which must feature wireless, lightweight, compact designs with energy harvesting capabilities. Sensors must be noninvasive or minimally invasive in design. Sensor developer teams in a future Consortium will promote rigorous technology design, fabrication, testing, validation, and dissemination of information regarding sensors and bioelectronics toward improving our understanding of human and organismal behavior.

SESSION SB10.08: Flexible and Stretchable Electronics
Session Chairs: Shinya Wai and Cunjiang Yu
Thursday Morning, April 25, 2024
Room 429, Level 4, Summit

8:15 AM SB10.08.01
Wearable On-Skin Chemosensors
Le Yang1,2; 1Institute of Materials Research and Engineering *STAR, Singapore; 2National University of Singapore, Singapore

In an increasingly health-aware population and a move towards remote diagnostics, remote healthcare monitoring and cloud-based med-tech, we tap on the ubiquitous and unlimited reservoir of on-skin biomarkers, including sweat metabolites, in developing a wearable, non-invasive, continuous and real-time sensor – a printed, multiplexed biosensor. Such a device can be colorimetric or electrochemical in its sensing mechanism. Our integrated devices are designed and developed with scalability and translation in mind – ensuring printability (for scalable manufacturing), ease of fabrication routes, and solid-state and miniaturised prototype.[1-8]

In particular, firstly, we introduce a newly-published fully-printed paper-based patch, printed from our development of a ceramic-based ink along with nanoparticle-functionalisation, for multi-metabolite and sweat rate monitoring.[1]

Next, we highlight the importance of enzymes in such enzymes-based biosensors (enzymatic reactions to detect target analytes), where their intrinsic instability poses a bottleneck in practical long-term use. Previous methods at enhancing enzyme stability had always been met with a trade-off in selectivity, sensitivity or performance/efficacy. Herein, we showcase a novel material-based approach, a one-pot synthesis of co-encapsulating enzymes and carbon-dots in a metal-organic framework, overcoming the aforementioned compromise. We achieve an electrochemical highly-stable and highly-sensitive device, and demonstrate it as a touch-based sweat sensor.[2]

Lastly, we briefly highlight an even more holistic approach in developing a printable, non-invasive, real-time and continuous electrochemical sensor for sweat-based and ‘dry-skin’ based on-skin chemosensing.[3-7]
rest (dry skin) and after doing a physical exercise (sweaty skin) to evaluate the biosignal acquisition stability against sweat. Exhibiting a sweat pulling property, the electrode was able to maintain a high signal-to-noise ratio (SNR) of 30 dB on the sweaty skin. This result could potentially provide more insight for the medical doctors, especially when evaluating cardiovascular health of a subject that may require the subject to do physical exercise or under a dynamic ambient (temperature/humidity) conditions.

8:45 AM *SB10.08.03 Intrinsically Stretchable Subthreshold Polymer Transistors for Highly Sensitive Low Power Skin Like Temperature Sensors Jim Young Oh, MinWoo Jeong, Phuong N. Vo and Kyu Ho Jung; Kyung Hee University, Korea (the Republic of)

Stretachable wearable sensors ultimately require low power consumption and high response to physiological signals with skin conformability. However, power response tradeoff and strain dependent sensing instability remain key challenges for electronic skin (e skin) sensors. In this talk, I will address an intrinsically stretchable organic subthreshold transistor operating at low voltage (~1 V) is presented, leading to ultralow power consumption (~1 nW) for highly sensitive skin like temperature sensory devices. The highly temperature dependent hopping transport of the fully stretchable subthreshold transistor exhibits high temperature sensitivity (9.4 °C⁻¹) and excellent sensing stability up to 100% strain. A skin like subthreshold organic transistor active matrix array is successfully fabricated that sensed the surface temperature distribution under a 3D deformation.

9:00 AM *SB10.08.04 Biomimetic Rubbery Synaptic Electronics and Integrated Systems Cunjiang Yu; The Pennsylvania State University, United States

Synapses are unique and critical biological structures that allow for the transmission of electrical or chemical signals thus to enable neurons to communicate with each other. Embodied within human or animals, the synapse is usually soft and able to accommodate various forms of mechanical deformations. Artificial synapse electronics that can be stretched similar to those appearing in human or animals could be seamlessly integrated other soft functional systems towards enabled neurological functions. This presentation will show our recent efforts on developing stretchable synaptic electronics fully made out of rubbery electronic materials. Rubbery synaptic devices are enablers for various soft systems with implemented neurologic functions. Examples including soft neurorobots, cognitive smart skins, neuromorphic imaging devices will be introduced.

9:30 AM DISCUSSION TIME

10:00 AM BREAK

10:30 AM *SB10.08.06 Self-Healing, Stretchable and Recyclable Electronics Fabio Cicoira; Polytechnique Montréal, Canada

Materials able to regenerate after damage have attracted a great deal of attention since the ancient times. For instance, self-healing concretes, able to resist earthquakes, aging, weather, and seawater are known since the times of ancient Rome and are still the object of research. While several mechanically healable materials have been reported, self-healing conductors are still relatively rare, and are attracting enormous interest for applications in electronic skin, wearable and stretchable sensors, actuators, transistors, energy harvesting, and storage devices, such as batteries and supercapacitors. Self-healable and recyclable conducting materials have the potential to reduce electronic waste by enabling the repair and reuse of electronic components, which can extend the lifespan of electronic devices. Furthermore, they can be used for wearable electronic and biomedicinal devices, which are often subject to mechanical stress causing damage to their components. Conducting polymers exhibit attractive properties that makes them ideal materials for bioelectronics and stretchable electronics, such as mixed ionic-electronic conductivity, leading to low interfacial impedance, tunability by chemical synthesis, ease of process via solution process and printing, and biomechanical compatibility with living tissues. However, they show typically poor mechanical properties and are therefore not suitable as self-healing materials.

In our group, we produced several self-healing and stretchable conductors by mixing aqueous suspensions of the conducting polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) with other materials providing the mechanical characteristics leading to self-healing, like for instance polyvinyl alcohol (PVA), polyethylene glycol, polyurethanes and tannic acid. In this talk, various types of self-healing will be presented and correlated with the electrical and mechanical properties of the materials. The use of the self-healing gels and films as epidermal electrodes and other devices will be also discussed.

REFERENCES

X. Zhou et al., Advanced Sensor Research, in press, 2023
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11:00 AM *SB10.08.07 Integrated Biodevices for Smart Contact Lenses Takeso Miyake; Waseda University, Japan

Smart contact lenses—contact lenses with built-in electronics—are a next-generation wearable product with capabilities beyond simple vision correction. Since the electrical lenses are in continuous contact with the eyeball surface, they have three main applications: (i) biomedical sensing of tears and intraocular pressure to monitor health conditions, (ii) wearable displays for augmented reality (AR), and (iii) actively regulating eye accommodation to ensure perfect vision. Thus, a smart contact lens has substantially greater functionality than an electrical eyeglass. We have developed several prototypes of an ultrasensitive diagnostic smart contact lens [1-5] with high sensitive biosensors and high efficient parity-time (PT) symmetric wireless transfer systems, a wireless electrochromic lens using conductive polymer-based film, and multi-electrode electroretinogram (ERG) lens system. I will present a detail in my invited talk.

REFERENCES


11:30 AM *SB10.08.08 Tissue-Interfaced Electronics for Directing Biological Functions Toshinori Fujii; Tokyo Institute of Technology, Japan

Integration of flexible electronics into the living body is expected for advancing medical diagnostics and therapeutics. Such devices should be seamlessly conformal to the physical and mechanical environment of living body, in which acquired biosignals are expected to be transmitted wirelessly to external device. In this regard, we envisage the development of tissue-interfaced electronics for wearable and implantable applications based on polymer nanosheet technology. The polymer nanosheet shows tens- to hundreds-of-nanometer thickness close to the scale of biomembranes, in which various types of polymers (e.g., biodegradable polymers, conductive polymers, and elastomers) are formed into the ultra-thin structure. Free-standing polymer nanosheets showed flexible and adhesive properties derived from their ultra-small flexural rigidity (< 10⁻² nN m). In this talk, polymer nanosheet (or thin film)-based devices are introduced by combining polymer nanosheet and printing technologies with variety of unique inks. A microgravure coater was employed for the preparation of flexible substrates or electrodes, an inkjet printer allowed for the tailor-made design of multielectrode array, and a laser processing machine was used for making the microchannels for insulating the circuit. The ultra-conformable structure has been utilized as tissue-interfaced electronics to direct biological functions in the applications of healthcare and medicine, represented by the wirelessly-powered light emitting device for photodynamic cancer therapy, and the flexible, thin-film neural electrode for diagnosis and treatment of epileptic seizure.

SESSION SB10.09: Neuromorphic Computing II
Session Chairs: Simone Fabiano and Songsong Li
Organic Neuromorphic Electronics for Emulating and Interfacing Biological Systems

Paschalis Gkoupidenis; Max Planck Institute for Polymer Research, Germany

Neurons are the fundamental elements of the nervous system, coping with a great diversity of electrobiochemical signals. Neuronal function is an archetype for biomimicry with neuromorphic electronics. However, artificial neurons based on electronics are insufficiently capable of operating in situ in biological environments, thus hampering the seamless sensing and biointerfacing as well as the biocompatible neuronal emulation. A few examples of soft-matter artificial neurons are based on conventional circuit oscillators and therefore require many elements for their implementation. An organic artificial neuron consisting of a compact non-linear electrochemical element will be presented. The artificial neuron displays in situ operation in biologically relevant environments that displays spiking dynamics sensitive to common ions of the biological aqueous milieu, within physiopathological concentration ranges (~5–150mM), and with ion specificity. Small-amplitude (~1–150 mV) electrochemical oscillations and noise in the electrolyte medium shape the neuronal dynamics, while changes of ionic (≥ 2% over physiological baseline) and biomolecular concentrations (≥ 0.1 mM dopamine) modulate the neuronal excitability. The artificial neuron operates synergistically with bio-membranes, forming real-time biophysiological interfaces. This electrochemical artificial neuron opens new possibilities for the seamless communication and the realistic emulation of biology with electronics.

References


3:45 PM SB10.09.04
Face-On Orientation Matches Vertical Organic Electrochemical Transistors for High Transconductance and Superior Non-Volatility

Moon Jong Han1 and Vladimir V. Tsukruk2; 1Gachon University, Korea (the Republic of); 2Georgia Institute of Technology, United States

The transmission of signals in the nervous system is controlled by neurotransmitters. Neurons can be either stimulated or suppressed depending on the specific neurotransmitter released by the sending neurons. It is crucial for the nervous system to maintain a balance between these excitatory and inhibitory responses in order to be versatile, flexible, and capable of parallel processing.
Neuromorphic Organic Devices as Building Blocks for Neuroelectronics

Michele Di Lauro; Italian Institute of Technology, Italy

Organic electronic neuromorphic components and devices operated in electrolyte are being investigated as powerful tools for bio-sensing, since their response is quantitatively determined by the composition of operational electrolyte, or as signal processing units, thanks to their selective response to frequency which enables low-power computation at the hardware level. Given the inherent match between the timescales, the chemical identity of the charge carriers and the signal processing logic paradigms in the brain and in organic neuromorphic devices, the latter are - ideally - the natural choice when tackling the convoluted task of efficiently interfacing neural tissue, establishing bidirectional exchange of information. Nonetheless, the implementation of neuromorphic devices and concepts in neuroelectronic interfaces designed specifically for clinical applications comes with a number of practical and conceptual hurdles which should be addressed, from both sides of the biotic/abiotic interface.

Scope of this presentation is to discuss some of these critical issues, which have so far impaired translation of neuromorphification in clinical scenarios, and to present strategies for overcoming them, with a focus on connection schemes and characterization strategies as well as on device geometry and material processing, hoping to trace a useful vademecum for Organic Neuromorphic Neuroelectronics development.

References

8:30 AM *SB10.01.10
Colloidal Electronic Tongue Jihepeng Sun and Albert T. Liu; University of Michigan–Ann Arbor, United States

Arming nanoelectronics with mobility extends artificial systems into traditionally inaccessible environments. Carbon nanotubes (1D), graphene (2D) and other low-dimensional materials with well-defined lattice structures can be incorporated into microelectrochemical systems, granting them unique electronic functions. The resulting colloidal electronic 'tongue', comprised of microscopic circuits connecting artificial organs (e.g., generators, sensors, logic gates, etc.), combine the modularity of modern electronics with the characteristic mobility found in dispersive colloidal systems. In this talk, I will discuss our efforts to fabricate colloidal electronic systems that perform autonomous functions integrating energy harvesting, chemical detection and digital memory recording - all within a form-factor no larger than biological cells.

8:45 AM *SB10.01.03
Paper-Based Electronic Tongue for Rapid and Reusable Quantitative Sensing of Water in Organic Solvents Using Principal Component Analysis Gregory Moore and Anthony Dichiara; University of Washington, United States

Rapid and quantitative recognition of trace amounts of water in organic solvents is of great importance in industrial operations. Currently the standard methods of determining water content in such cases include the Karl Fischer (KF) titration and fluorescence colorimetry, which are expensive, time-consuming, and require skilled operators to perform. Electronic tongues are sensor systems with the ability to analyze and classify complex samples by their chemical composition [1]. Principal Component Analysis (PCA) is a multivariate statistical technique used to reduce the dimensionality of data while retaining as much of the initial variation as possible and is commonly used in electronic tongue applications [1], [2]. In this work, a multifunctional liquid sensing and classification system was developed based on paper comprising pulp fibers adsorbed with multi-walled carbon nanotubes. Paper electronics is a field of increasing interest due to the biodegradable nature, flexibility, and light weight of lignocellulosic paper and its ability to be produced at large scale using well-established and cost-effective manufacturing processes [3]. The

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hygroscopic nature of cellulose fibers causes them to swell radially in response to water molecules, which alters the conductive pathway within the percolated carbon nanotube network present on their surface, leading to a significant change in the paper resistance when wet. Importantly, the swelling behavior strongly depends on the nature of the solvent, which makes it an exceptional material for liquid sensing applications [4]. The electrical response of the sensor was tested and replicated for several liquid solutions of different solvents, concentrations of water in solvents, and ionic strengths of water. Specific features were identified from the response profiles, generating over 800 data points which were implemented in the PCA and used to differentiate between the liquids. The sensing platform can quantify the amount of water in the organic solvent with a sensitivity below 100 ppm and high resolution which makes it competitive with the KF titration. The proposed paper-based electronic tongue demonstrates the ability to rapidly differentiate low concentrations of water in organic solvents, providing economic alternative to current methods, and enables future discoveries in biosensing and bioelectronics.


9:00 AM SB10.10.05 Flow-Cell Sensor for Bacteria Detection Using Gate-Modified Organic Electrochemical Transistor Jinchu Huang, Daewoo Han and Andrew J. Steckl; University of Cincinnati, United States

Organoelectronic transistors (OECTs) have been previously demonstrated in the sensing of cells and metabolic products. In this study, we report a novel approach on the universal detection of bacterial contamination in liquid-based materials through the utilization of a microfluidic flow-cell that has been integrated with OECT technology. The flow-cell device has been developed for the purpose of detecting minimal concentration (~10^9 CFU/ml) of several bacterium types (Escherichia coli, Pseudomonas fluorescens and Staphylococcus aureus) in various commercial household liquid product blends (cf. Air Freshener, Tide, Old Spice bodywash). This process can be completed in a testing period of one hour or less and does not require amplification or a designated binding agent. The flow-cell configuration uses a microporous filter membrane (Au coated PETE, 0.2 µm pore diameter) designed to concentrate the bacteria within the chamber. The membrane also functions as a gate electrode for the operation of OECT. The presence of bacteria on the gate filter membrane leads to an increase in the total effective gate voltage (V_G), which in turn causes a decrease in the OECT source-drain channel current (I_DS). Based on the shift of I_DS the OECT provides good discrimination between bacteria and sterile solutions (0.4 mA difference). The OECT transconductance (g_m) exhibits a maximum value at different levels of V_G for sterile and bacteria solutions. g_m shifts to positive value at lower gate operating voltage due to bacteria attachment on Au gate. The flow-cell filtration and OECT gate sensing approach has the capability to identify a diverse range of bacteria, encompassing both gram-positive and gram-negative strains, across multiple testing media. This approach exhibits potential for biosensing systems that will enable real-time monitoring at the production line.

9:15 AM SB10.10.06 3D-Printed Epidermal Microfluidic Systems: Opportunities to Expand Access to Personalized Health Monitoring Tyler Ray, University of Hawaii, United States

Persistent disparities exist in access to state-of-the-art healthcare and disproportionately affect underserved and vulnerable populations. Advances in wearable sensors enabled by additive manufacturing (AM) offer new opportunities to address such disparities and enhance equitable access to advanced diagnostic technologies. Additive manufacturing processes, particularly stereolithography (SLA)-based printing, offer powerful pathways for circumventing existing barriers to innovation for resource-limited settings by providing significant reductions in prototype development cost and cycle time while substantially expanding device capabilities with fully 3D device designs. Here, we present a simplified 3D-printing prototyping process to fabricate flexible, stretchable, epidermal microfluidic devices (3D-epifluidics) suitable for direct on-body interfacing. These wearable sensors integrate microfluidic channel networks with biochemical sensors and flexible electronics to enable the noninvasive, real-time monitoring of sweat-based biochemical signals with health and wellness. By reducing fabrication time to [0]min, this approach enables the integration of spatially-engineered features including 3D-structured passive capillary valves, monolithic channels, and reservoirs with spatially-graded geometries. With geometric features comparable to established epifluidic devices (channels >50 µm), benchtop and on-body testing validate the performance of 3D-epifluideic devices. We utilize these platforms to showcase how these devices hold the potential for addressing some of the formidable obstacles to delivering comprehensive medical care in under-resourced settings, especially in remote or geographically isolated areas.

9:30 AM SB10.10.07 Transfer-Printed PEDOT on Stretchability-Enhancing, Biodegradable PVA Substrates Towards Stretchable OECTs Carla Volker1, Renan Colucci1, Mateusz Brzezinski1, Pablo Gomez Argudo1, Jasper Michels1, Pol Besenius2, Paul W. Blom1 and Ulrike Kraft1; 1Max Planck Institute for Polymer Research, Germany; 2Johannes Gutenberg University, Germany

Extensive efforts have been invested in advancing flexible devices1, including biosensors, optoelectronic devices, organic field effect transistors (OFETs), light emitting diodes (LEDs) and organic electrochemical transistors (OECTs)2. Building on these achievements, stretchable electronic devices have evolved within the last decade3,4. To further advance and fully exploit the next generation of stretchable electronic devices, the innovation of novel device fabrication processes and materials is needed. Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS)2. Building on these achievements, stretchable electronic devices have evolved within the last decade3,4. To further advance and fully exploit the next generation of stretchable electronic devices, the innovation of novel device fabrication processes and materials is needed. Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) stands out as a popular material in electronic applications due to its high conductivity, optical transparency, mechanical resilience, commercial availability and biocompatibility. Consequently, significant efforts have been undertaken to transform PEDOT:PSS from a brittle into a flexible and stretchable material. Conventional approaches involve the addition of chemicals such as ionic liquids3, surfactants, plasticizers and other organic additives4. Here, we propose an alternative approach towards stretchable electronics: rather than inducing stretchability through such additives, we demonstrate that the mechanical properties of PEDOT:PSS can be adjusted by utilizing diffusion-active substrates. The substrates are infused with a plasticizer that diffuses into the PEDOT:PSS, modifies its glass transition temperature and consequently leads to an enhanced stretchability and an increased conductivity. Chain-alignment and -mobility during elongation are evidenced by a higher crack-on-set-strain (>150%) and an increased conductivity upon strain. A comprehensive (concentration-dependent) analysis, including electrical measurements, atomic force microscopy, and Raman spectroscopy, was undertaken to study the substrate- and PEDOT:PSS chain-alignment upon strain and was correlated with the concentration-dependent diffusion of the plasticizer. This novel approach towards stretchable electronics is furthermore compatible with our recently developed transfer-printing method for (plasma-patterned) electronic devices and finally led to the successful fabrication of intrinsically stretchable organic electrochemical transistors on biodegradable substrates.


10:15 AM SB10.10.08 Edible Logic Circuits Giulia Coce1,2, Valerio F Annese2, Valerio Galli1,2 and Mario Cairoli1; Politecnico di Milano, Italy; 1Istituto Italiano di Tecnologia, Italy

As single-use and disposable electronic devices are becoming widespread for food and gastrointestinal tract monitoring, safe and sustainable materials development is emerging as a fundamental objective for technological innovation. The EU-funded ROBOFOD project explores food-derived materials - an unprecedented and unconventional approach – to fabricate robots that could be metabolized (or degraded) in the body (or environment) after performing their function. In this perspective, the challenge consists of realizing stable edible electronic circuits that can provide synchronization, perform simple computation, and serve as memory, starting from notoriously unstable materials. Here we present the fabrication and characterization of edible logic circuits. For this aim, a printed edible electrolyte-gated transistor with a lateral gate configuration was fabricated using food-based inks. A comprehensive characterization was carried out revealing performance comparable with state of the art. Hence, edible logic gates operating at low voltage (<1 V) were demonstrated, integrating the transistor in unipolar configurations. Different edible materials and fabrication techniques compatible with the proposed transistor were also explored for implementing the required resistive load. Edible NOT and NAND gates were successfully fabricated and characterized using well-established metrics. More complex circuits, such as an edible ring oscillator working at a frequency around 1 Hz and a set/reset latch, were demonstrated. We believe that this work leads the way to edible logic circuits performing complex functions and to their integration into devices that can interact safely with humans and animals.

10:00 AM BREAK

10:30 AM SB10.10.09 A Fingertip Force Microscope (FFM) for Micro-Scale Morphology Characterization Jiaju Tu and Xiaodong Chen; Nanyang Technological University, MSEE, Singapore

Texture sensing is an essential part of tactile sensing, which extracts morphology, roughness, and hardness information during object manipulation. However, biological texture sensing is only
Elastic Metal Microtube for Flexible Ultralow-Hysteresis Tactile Sensor

11:15 AM

SB10.10

QuantumDock: An Automated Computational Framework for Wearable Sensor Design

Daniel Makasa, Minqiang Wang, Jihong Min, Yiran Yang, Samuel A. Solomon, Hong Han, Cui Ye and Wei Gao; California Institute of Technology, United States

Wearable soft sensors have the potential to revolutionize precision medicine as they can non-invasively collect molecular information closely associated with an individual's health status. However, the majority of clinically relevant biomarkers cannot be continuously detected in situ using existing wearable approaches. Molecularly imprinted polymers (MIPs) are a promising candidate to address this challenge but haven't yet gained widespread use due to their complex design and optimization process yielding variable selectivity. Here, QuantumDock is introduced, an automated computational framework for universal MIP development toward wearable applications. QuantumDock utilizes density functional theory to probe molecular interactions between monomers and the target/interfering molecules to optimize selectivity, a fundamentally limiting factor for MIP development toward wearable sensing. A molecular docking approach is employed to explore a wide range of monomers, and to identify the optimal monomer/cross-linker choice for subsequent MIP fabrication. We further employ a molecular generation scheme that allows us to generate molecules with much higher sensitivities and selectivities than traditionally used monomers. Using an essential amino acid phenylalanine as the exemplar, experimental validation of QuantumDock is performed successfully using solution-synthesized MIP nanoparticles coupled with ultraviolet–visible spectroscopy. Moreover, a QuantumDock-optimized graphene-based wearable device is designed that can perform autonomous sweat induction, sampling, and sensing. For the first time, wearable non-invasive phenylalanine monitoring is demonstrated in human subjects toward personalized healthcare applications.

11:00 AM

SB10.11

Development of Water-Resistant Au-PVA/WBPU Nanomesh Electrodes for Stable Monitoring of Skin Impedance

Maho Mimura, Sunghoon Lee, Tomoyuki Yokota and Takao Someya; The University of Tokyo, Japan

Electrodermal activity, which is known to vary due to factors such as psychological states like stress level [1], and environmental factors like temperature [2] and humidity [3] is one of the important biological signals for early detection of disease and preventive healthcare. Previously, ultrathin and lightweight Au-PVA nanomesh electrode which does not cause discomfort when they were attached on skin has been developed [4] and continuous measurement of skin resistance and skin impedance were achieved by using the nanomesh electrodes [5, 6]. However, these electrodes were vulnerable to water and prone to damage, requiring careful handling during attaching to the skin and being susceptible to breakage with slight movements or sweat. To address this issue, we developed nanomesh electrodes with excellent water resistance and stable measurement capabilities by mixing hydrophobic WBPU (waterborne polyurethane) with the conventional material PVA (polyvinyl alcohol). The Au-PVA/WBPU nanomesh electrodes were fabricated by following method. First, a mixture of a 15 wt% PVA aqueous solution and a 30 wt% WBPU solution in 2:1 ratio was made into a nanofiber sheet by electrospinning method. And then, a heat-press treatment was applied to the nanofiber sheet to improve the inner connection between fibers. After a heat-press treatment at 150°C for 1 minute, a 100 nm thick layer of gold was deposited by vacuum evaporation method. To check the water resistivity of the nanomesh electrode, we conducted a water immersing test. After a 1-minute stirring test in the pure water, the conventional Au-PVA nanomesh electrodes completely disappeared from the artificial skin, whereas Au-PVA/WBPU nanomesh electrodes remained more than 95% area on the artificial skin. In addition, we checked the stability of the nanomesh electrodes on the skin. After attaching the electrodes on the skin for 2 hours, the resistance of the Au-PVA/WBPU nanomesh electrodes were almost constant while that of conventional nanomesh electrodes showed a deterioration, increasing by 3 to 4 times.

REFERENCES


11:15 AM

SB10.12

Elastic Metal Microtube for Flexible Ultralow-Hysteresis Tactile Sensor

Yanzen Li and Xiaodong Chen; Nanyang Technological University, Singapore

Low-hysteresis and fast-response tactile sensors that mimic the human sense of touch can empower robotic systems to manipulate diverse objects rapidly and accurately. However, current tactile sensors, which mostly rely on viscoelastic polymers as functional materials, suffer from high hysteresis and slow response time, limiting their applicability in intelligent robotics. Here, we introduce an elastic metal microtube enhanced (EMME) tactile sensor with ultralow hysteresis and fast response. The microtube structure is achieved by utilizing the inner stress of thermally evaporated metal films after dissolving a sacrificial layer. The superior elasticity of the metal microtubes minimizes energy dissipation during deformation under external mechanical stimuli, contributing to ultralow hysteresis and fast response of EMME tactile sensor. Furthermore, the positive correlation between hysteresis and energy dissipation is theoretically and experimentally established in capacitive tactile sensors based on parallel plate structure. Our flexible EMME tactile sensor possesses ultralow hysteresis (~0.8%), fast response time (~1 ms), high endurance (10000 cycles), and the ability to keep up with high-frequency vibration. Upon integration with the robotic hand, accurate and autonomous manipulation of shape-changing objects with a feedback loop is achieved, mimicking air pressure monitoring via balloon volume change in chemical experiments, exhibiting its potential in future intelligent and autonomous laboratory robotic systems.

SESSION SB10.11: On-Demand Presentation
Thursday Morning, May 9, 2024
SB10-virtual

10:30 AM

SB10.05.08

Shape-Actuated Bioelectronics

Christopher M. Proctor; University of Oxford, United Kingdom

Significant advances have been made in the last two decades in interfacing electronic devices with the nervous system. To that end, research efforts are being pursued to develop minimally invasive, implantable bioelectronic devices integrating sensing, stimulating, and dynamic control of geometry. Here we report recent developments towards such multimodal devices for neural interfacing that take full advantage of the favorable properties offered by flexible electronics, conducting polymers and polymer substrates. It is shown that thin, flexible devices can incorporate microfluidic channels to enable new sensing and therapeutic functionalities. One such technology leverages the mixed conducting properties of conducting polymers and molecularly imprinted polymers for real time sensing of cortisol. Furthermore, we show fluidic components can open the door to novel implantation strategies that can reduce the surgical footprint required for implantation of widely used bioelectronic devices. We anticipate this work will accelerate the development of a new generation of bioelectronic devices for diagnostics and therapy.

SYMPOSIUM SB11
Bio-based and Biomimetic Polymers in Soft Robotics
April 23 - May 8, 2024

Session Chairs: Michael Dickey and Danielle Mai
Tuesday, April 23, 2024
Room 430, Level 4, Summit

10:30 AM *SB11.01.01
Leveraging Biological Motor Control for Soft Robotics Ritu Raman; Massachusetts Institute of Technology, United States

Human beings and other biological creatures navigate unpredictable and dynamic environments by combining compliant mechanical actuators (skeletal muscle) with neural control and sensory feedback. Abiotic actuators, by contrast, have yet to match their biological counterparts in their ability to autonomously sense and adapt their form and function to changing environments. We have shown that engineered skeletal muscle actuators, controlled by neuronal networks, can generate force and power functional behaviors such as walking and pumping in a range of untethered robots. These muscle-powered robots are dynamically responsive to mechanical stimuli and are capable of complex functional behaviors like exercise-mediated strengthening and healing in response to damage. Our lab uses engineered bioactuators as a platform to understand neuromuscular architecture and function in physiological and pathological states, restore mobility after disease and damage, and power soft robots. This talk will cover the advantages, challenges, and future directions of understanding and manipulating the mechanics of biological motor control.

11:00 AM *SB11.01.02
Vapor-Deposited Polymeric Biointerface to Direct Living Behavior Rong Yang; Cornell University, United States

Polymer is often considered one of the most prevalent materials in the modern age. The interactions between polymers and a highly ubiquitous living system – bacteria – are of great interest in applications ranging from fouling control to living materials, but details of those interactions are poorly understood. The sub-micron size of most bacteria, whose sensory apparatus often operates on the nanoscale, requires precise placement of chemical functionalities and nanostructures at the synthetic-living interface. The need for nanoscale resolution challenges most traditional synthesis and processing approaches, which have been predominantly performed in solution. Recent advances in vacuum-based synthesis technologies, such as the initiated Chemical Vapor Deposition (iCVD), have enabled a new mode of control over polymeric material properties during polymerization. Distinct from prior research that has placed strong emphasis on the design of monomer molecular structure and controlled polymerization, the all-dry synthesis enables manipulation of the physical phenomena, such as nanoscale dewetting, Knudsen diffusion, and molecular complexing, to achieve programmable material properties. In this talk, we will discuss several strategies to achieve the nanoscale control over the vapor-deposited polymeric biointerface. Such control in turn led to improved understanding and manipulation of bacteria-material interactions, such as suppression of virulence. Taken together, the synthetic advances are poised to open up a new dimension in the design of polymeric materials for the programmable material-bacteria interactions, which extend beyond “kill or repel” towards signaling and control.

11:15 AM SB11.01.03
Programmable Tissue Folding in Magneto-Active Structured Hydrogels Zenghao Zhang, Avinava Roy, Claudia Loebel and Abdon Pena-Francesch; University of Michigan–Ann Arbor, United States

Biological tissues are structurally complex and heterogeneous, making the in vitro recapitulation challenging if using a traditional flat cell-culture substrate. Although recent development in engineering tissue patterns has been achieved through top-down approaches including micro-molding and 3D bioprinting, reversible and on-demand dynamic patterning is still underdeveloped. Among soft actuation systems, magnetic actuation shows little toxicity to cells, and can penetrate tissue and media to generate pulling forces and torques remotely, enabling fast and reverse untethered actuation. In this study, we developed hydrogel cell-culture systems based on bilayer folding hydrogels composed of a rigid hyaluronic acid (HA) hydrogel and a stretchable double-network (DN) with ferromagnetic particle dopants. Building upon recent advances in the design of magnetoactive soft materials, our approach further uses magnetoactive hydrogels to provide dynamic patterning upon applying magnetic fields. Using this method, we generated cell-laden hydrogel substrates that display on-demand folding/unfolding reversible shape transformations, providing a culture system for mimicking dynamic tissue folding in vitro and recapitulating 3D complex structures to probe cellular mechanisms.

1:45 PM *SB11.02.01
The Synergy of Electronic Polymers and Self-Driving Laboratories for Innovations in Soft Robots Jie Xu; Argonne National Laboratory, United States

In the realm of soft robotics, electronic polymers have emerged as important materials owing to their unique combination of mechanical viscoelasticity and electronic properties. These materials, including conductive and semiconductive polymers, are instrumental in crafting flexible coverings that empower soft robots to sense intricate environments and relay information to human counterparts. However, the quest to identify electronic polymers capable of realizing desired functionalities remains a formidable challenge. Traditional, manual methods, relying solely on human expertise, could entail decades of arduous research and development. In this context, self-driving laboratories, leveraging robotic automation and artificial intelligence, are revolutionizing the exploration and development of electronic polymers and soft devices tailored for soft robotics. In this presentation, I will begin by introducing our autonomous laboratory, aptly named ‘Polybot.’ Subsequently, I will delve into recent research, exemplifying autonomous electrochromic polymer discovery for applications in optical communication and autonomous polymer electrochemical sensor discovery, with the potential to serve as bio-sensing platforms within soft robotic systems.

2:15 PM SB11.02.03
Liquid-Metal-Based All-Soft Pressure Sensor and Machine Learning Application for Multidirectional Detection Osman Gul1,2, Jeongnam Kim2,3, Yulim Min2,3, Hye Jin Kim2,3 and Inkyu Park1; 1Korea Advanced Institute of Science and Technology, Korea (the Republic of); 2Electronics and Telecommunications Research Institute, Korea (the Republic of); 3University of
Electronic skin needs to be able to sense different types of pressures, such as radial pressures, which require the development of a soft multidirectional pressure sensor. Although previous studies have developed multidirectional pressure sensors, the investigation into discerning the direction and magnitude of applied pressure remains an unexplored domain in multidirectional pressure sensor research. Multidirectional pressure sensors have been extensively developed for their extensive application opportunities. Recently, the trend has shifted towards developing soft sensors with a focus on the design of the structure and sensing materials. The four-element sensing structure is the most commonly used structure for multidirectional sensors. In the case of the four-element sensing structure, the four sensing element is positioned at 90-degree intervals from one other, forming a cube-like structure. The four-element sensing structure facilitates the measurement of multidirectional forces. Wide-ranging 3D bump structures are used at the top of the four-element sensing materials to identify the applied multidirectional forces effectively. Lee et al. demonstrated trapezoid structure and CNT array as the sensing material. Jung et al. proposed a multidirectional force sensor with the sensing materials placed on the sidewalls of the 3D bump structure. Vogt et al. and Kim et al. presented liquid-metal-based multidirectional sensors with rigid pressure transducer structures on the top of the liquid metal channels. In these sensors, the multidirectional force is generated by applying shear pressure to the four-sensing structure of the sensor. Nevertheless, extracting directional information from a four-sensing element-based sensors’ setup when exposed to applied radial pressure remains a formidable challenge, because the four-sensing element method is primarily designed for shear force-based applications.

In the present study, we present a new solution to address the limitations of existing multidirectional sensors. Our approach involves the development of a soft sensor using liquid metal with a dome-shaped design that enables discrimination of directional pressures. Additionally, we leverage machine learning algorithms to identify the direction and magnitude of applied pressure. The microchannels of the soft pressure sensor were created using fused deposition modeling (FDM). A 3D printed mold made of poly(vinyl alcohol) (PVA) was embedded into the elastomer and dissolved with water to create the microchannels. The empty microchannels were filled with liquid metal, and a vacuum process was applied to create the dome structure for multidirectional pressure sensing. The microchannels within the liquid-metal-based sensor form a single covalent network with controllable polymer- and solvent-rich phases that form in situ due to the phase behavior of the polymer in liquid metal. The polymer-rich phase forms hydrogen bonds that dissipate energy and thereby toughen the ionogel during extension, while the solvent-rich phase remains elastic to enable large strain. The copolymer ionogels composed of acrylamide and acrylic acid exhibit extraordinary mechanical properties, including fracture strength (12.6 MPa), fracture energy (~24 kJ m−2), and Young’s modulus (46.5 MPa), setting new records among reported ionogels. The tough ionogels are highly stretchable (~600% strain) and possess good self-recoverability, as well as excellent self-healing and shape-memory properties. This concept extends to other monomers and ionic liquids, which offers a promising and general way to tune microstructure in situ during one-step polymerization that solves the longstanding mechanical challenges in ionogels.

### SESSION SB11.03: Stimuli-Responsive Soft Robots

#### Tuesday Afternoon, April 23, 2024

#### Room 430, Level 4, Summit

**SESSION SB11.03: Stimuli-Responsive Soft Robots**

**Session Chairs:** Daniela Mai and Abdón Pena-Francesch

**SB11.02.04**

_Ultra-Tough Ionogels for Stretchable Ionic Devices_  
_Michael Dickey and Meixiang Wang; North Carolina State University, United States_

**SB11.03.01**

_The Design, Fabrication and Structural Modeling of Biomimetic Soft Materials for Robotic Applications_  
_Oing Chen; EMPA, Switzerland_

**SB11.03.02**

_Soft Sensory Robots based on Stimuli-Responsive Hydrogels for Electronic Implants_  
_Wubin Bai; University of North Carolina, Chapel Hill, United States_

Ionogels are compelling materials for energy storage devices, ionotronics, and actuators due to their excellent ionic conductivity, thermal and electrochemical stability and nonvolatility. However, most existing ionogels suffer from low strength and toughness. Here, we report a simple one-step method to achieve ultra-tough and stretchable ionogels by randomly copolymerizing two common monomers in ionic liquid. Copolymerization leads to a single covalent network with controllable polymer- and solvent-rich phases that form in situ due to the phase behavior of the polymer in liquid metal. The polymer-rich phase forms hydrogen bonds that dissipate energy and thereby toughen the ionogel during extension, while the solvent-rich phase remains elastic to enable large strain. The copolymer ionogels composed of acrylamide and acrylic acid exhibit extraordinary mechanical properties, including fracture strength (12.6 MPa), fracture energy (~24 kJ m−2), and Young’s modulus (46.5 MPa), setting new records among reported ionogels. The tough ionogels are highly stretchable (~600% strain) and possess good self-recoverability, as well as excellent self-healing and shape-memory properties. This concept extends to other monomers and ionic liquids, which offers a promising and general way to tune microstructure in situ during one-step polymerization that solves the longstanding mechanical challenges in ionogels.

**References**


**Soft Sensory Robots based on Stimuli-Responsive Hydrogels for Electronic Implants**  
_Wubin Bai; University of North Carolina, Chapel Hill, United States_

Living organisms with motor and sensor units integrated seamlessly for exhibit effective adaptation to dynamically changing environments. Taking inspiration from coherent integration between skeletal muscles and sensory skins in humans, we present a design strategy for soft robots, primarily consisting of an electronic skin (e-skin) and an artificial muscle, that naturally couples multifunctional sensory and on-demand actuation in a soft, biocompatible platform. Here, we will describe an in situ solution-based method to create the e-skin layer with a series of sensing materials (e.g., silver nanowires, reduced graphene oxide, and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) incorporated within a polymer matrix (e.g., polyimide and polydimethylsiloxane), imitating human skin with complex receptors to perceive various stimuli. Biomimicry designs (e.g., starfish and chiral seedpods) of the soft robots enable various active motions (e.g., bending, expanding, and twisting) on demand and realize good fixation and stress-free contact with tissues. Furthermore, integration of a battery-free wireless module into these soft robots enables robotic operation and communication without tethering, thus enhancing safety and biocompatibility of the soft robots as minimally invasive implants. Demonstrated examples range from a robotic cuff enclosing around a blood vessel for precise detection of blood pressure, a robotic gripper holding onto a bladder for accurately tracking bladder volume, an ingestible robot residing inside stomach for pH sensing and on-site drug delivery, to a robotic patch wrapping onto a beating heart for quantifying cardiac contractility, temperature and applying cardiopacing, highlighting the application versatility and potentials of the bioinspired soft robots. Our designs of soft robots could establish a promising strategy to integrate a broad range of sensing and responsive materials, for forming highly integrated systems for medical technology and beyond.
Printable Liquid Metal Foams that Grow when Watered Febby Krisnadi1, Seoseon Kim2, Sook Im1, Dennis Chacko1, Man Hou Vong1, Konrad Rykaczewski3, Sungjiune Park2 and Michael Dickey1,2, North Carolina State University, United States; Jeonbuk National University, Korea (the Republic of); Arizona State University, United States

Pastes and “foams” containing liquid metal as the continuous phase (LMFs) exhibit metallic properties while displaying paste or putty-like rheological behavior. These properties enable LMFs to be patterned into soft and stretchable electrical and thermal conductors through processes conducted at room temperature, such as printing. The simplest LMFs, featured in this work, are made by stirring liquid metal in air, thereby entraining oxide-lined air “pockets” into the liquid metal. Here, we report that mixing small amounts of water (as low as 1wt%) into such LMFs gives rise to significant foaming by harnessing known reactions that evolve hydrogen and produce oxides. The resulting structures can be 4–5x their original volume and possess a fascinating combination of attributes: porosity, electrical conductivity, and responsiveness to environmental conditions. This expansion can be utilized for a type of 4D printing in which patterned conductors “grow”, fill cavities, and change shape and density with respect to time. Excessive exposure to water in the long term ultimately consumes the metal in the LMF. However, when exposure to water is controlled, the metallic properties of porous LMFs can be preserved. We characterize the physical changes of water-containing LMFs and explore prospective applications including a “growing” conductor that fills a gap in a circuit and an unattended pressure-driven actuator. We also demonstrate the printability of LMFs and present a printed pattern that changes shape over time.

**4:30 PM • SB11.03.04 Fast and Autonomous Soft Robots enabled by Snap-Through Instabilities Shu Yang; University of Pennsylvania, United States**

Soft robots offer a myriad of potentials due to their intrinsic compliance and adaptivity to unpredictable environments. However, most of them have limited actuation speeds and require complex control systems to maneuver various tasks. Inspired by the snap-through instabilities utilized by Venus flytrap to catch prey, the hummingbird’s beak to catch insects, and corkscrew-like stalk of Erodium seed, we combine materials intrinsic anisotropy and mechanical metastructures to program the snapping behaviors, enabling several autonomous and unprecedented soft robotic functionalities. Specifically, I will discuss the design and performance of several examples of soft robots, including a centimeter-sized, sensor-less metacarpal gripper that can grasp objects in 3.75 ms upon physical contact or pneumatic actuation, lobed loops made from liquid crystal elastomer fibers capable of gait-like synchronization and directed locomotion, and laminated wood enabled seed carrier with helical tails capable of soil drilling with high success rate upon exposure to water.

**SESSION SB11.04: Self-Healing Soft Robots**

**Session Chairs: Minkyu Kim and Daniella Mai**

**Wednesday morning, April 24, 2024**

**Room 430, Level 4, Summit**

**8:30 AM SB11.04.01 Self-Healing Semiconducting Polymers for Use in Soft Robotics via Coordination Chemistry Yun Liu and Bob C. Schroeder; University College London, United Kingdom**

Robots are increasingly assisting humans in performing various tasks. The requirement for safe physical human-robot interactions has led to the emergence of the field of soft robotics. Typically, soft robots consist of flexible and deformable materials such as elastomeric polymers, which have an inherent compliance comparable to biological tissues (10^5 to 10^9 Pa), greatly enhancing human interaction safety.1,2 Their intrinsic softness and compliance further endow them with features such as resilience to impacts and collisions due to shock absorbance, making soft robots an ideal candidate for handling delicate tasks in uncertain and unstructured environments.3 Despite the many advantages of soft materials, their usage in robotics does present challenges in terms of damage resistance. Synthetic soft polymers are highly susceptible to fatigue, overload and cuts, and tear or perforation by sharp objects arising from uncontrolled working environments, which would induce irreversible damage to the material, massively reducing the functional performance of robots.4 Inspired by a powerful feature of living organisms, an economic and ecological solution to this vulnerability is to construct future soft robotic systems out of self-healing semiconducting polymers, permitting the healing of microscopic and macroscopic damages as well as recovering material functionalities. Various strategies have been applied to synthesise self-healable semiconducting polymers via non-covalent interactions such as hydrogen bonding, π-π stacking, host-guest interactions and ionic interactions.5,6 Multiple advantageous features are associated with metal-ligand complexes, in general, most coordination complexes can chelate spontaneously, resulting in easily processable materials.7 However, achieving high mechanical strength within self-healing semiconducting polymers remains a crucial challenge. Due to the broad variety of possible metal and ligand combinations, the coordination bonds are highly tuneable, with accessible bond energies ranging from strong covalent to weak supramolecular forces such as van der Waals.8 By tuning the coordination bond strengths, the presence of metal-ligand complexes in the polymer matrix could result in a synergistic effect on mechanical toughness and self-healing efficiency, offering new insights into the design of self-healing soft robotics.

Herein, we describe a new self-healing semiconducting polymer system based on metal-ligand coordination between transition metal ions (Cu(ii), Zn(ii)) and bipyridine moieties incorporated in a cyclopentadithiophene-derived (CPDT) conjugated polymer backbone. Drastic changes to the polymer structure have been observed through spectroscopic measurements with varying ratios of metal complexes.7,8 C. H. Li and J. L. Zuo, Adv. Funct. Mater. 2016, 28, 10024-10032. Despite the many advantages of soft materials, their usage in robotics does present challenges in terms of damage resistance. Synthetic soft polymers are highly susceptible to fatigue, overload and cuts, and tear or perforation by sharp objects arising from uncontrolled working environments, which would induce irreversible damage to the material, massively reducing the functional performance of robots.4 Inspired by a powerful feature of living organisms, an economic and ecological solution to this vulnerability is to construct future soft robotic systems out of self-healing semiconducting polymers, permitting the healing of microscopic and macroscopic damages as well as recovering material functionalities. Various strategies have been applied to synthesise self-healable semiconducting polymers via non-covalent interactions such as hydrogen bonding, π-π stacking, host-guest interactions and ionic interactions.5,6 Multiple advantageous features are associated with metal-ligand complexes, in general, most coordination complexes can chelate spontaneously, resulting in easily processable materials.7 However, achieving high mechanical strength within self-healing semiconducting polymers remains a crucial challenge. Due to the broad variety of possible metal and ligand combinations, the coordination bonds are highly tuneable, with accessible bond energies ranging from strong covalent to weak supramolecular forces such as van der Waals.8 By tuning the coordination bond strengths, the presence of metal-ligand complexes in the polymer matrix could result in a synergistic effect on mechanical toughness and self-healing efficiency, offering new insights into the design of self-healing soft robotics.

Reference:

**8:45 AM SB11.04.02 Unithered, Autonomous Self-Healable, and Self-Powered Actively-Perceiving and Energy-Harvesting Triboelectric Skins and Their Applications in Soft Robotics Ying-Chih Lai; National Chung Hsing University, Taiwan**

Soft robots with organism-like adaptive bodies have shown great potential in vast robot-human and robot-environment applications. Developing skin-like sensory devices (that are e-skins) enables them to naturally sense and interact with environment. It would be better if the capabilities to feel can be active like real skin. However, conventional e-skins are developed using passive sensing technologies, including resistive, capacitive, and optical types. Such passive sensors suffer from limited materials, poor scalability, complicated architectures, scant stretchability, large driving-voltage, and huge power dissipation in large-area uses. Those drawbacks greatly hinder the development of unithered and deformable robotic skins.

In this talk, we will present diversified cutting-edge self-powered triboelectric skins (tribo-skins) [1-6] with various fascinating attributes, including autonomous ability of self-healing (30 min, 100% efficiency at 900% strain) [3], omnidirectional stretchability (>900%) [1-4, 6], transparency (98.6%) [3], environmental-inert (-30 °C - 60 °C) [4, 6], and electromagneto-bioenergetic capability [5]. The tribo-skins can actively sense proximity, contact, and pressure to external stimuli via self-generating electricity. The driving-energy comes from natural triboelectric effect involving a cooperation of contact electrification and electrostatic induction. We will demonstrate the first actively perceivable and responsive soft robots using the unithered and ultra-stretchable tribo-skins [1,2]. The perfect integration of the tribo-skins and soft actuators enables soft robots to perform various actively sensing and interactive tasks including actively perceiving their muscle motions, working states, textile’s dampness, and even subtle human physiological signals. The diversified self-powered tribo-skins with various desired attributes will be introduced. Last, we will demonstrate a transparent, self-healing, and self-powered perceiving soft robotic hand. These works will inspire lots of great ideas and show tremendous potentials of wearable/stretchable/deformable electronics, artificial e-skins, smart interfaces, and soft robots.

[2] Ying-Chih Lai, et al, Advanced Materials, 2018, 30, 1801114-180111-6. This work is highlighted in Nature Perspective "The rise of intelligent matter", Nature, 2021, 594, 345. [Ref 47], presenting the first soft robots driven by self-generated electricity via the triboelectric effect, which can sense and embrace close objects. [This work is also highlighted in MIT Review Tech. ]
Autonomous Self-Aligned Multilayer Self-Healing Polymers and High Energy Density Artificial Muscle based on Periodic Non-Covalent Dynamic Polymer Networks

Zhenan Bao,
Stanford University, United States

Polymer networks formed through dynamic noncovalent or covalent bonds exhibit a range of interesting and tunable mechanical properties (e.g., tough, elastic, self-healable, stimuli-responsive, and reconfigurable). In nature, hierarchically ordered structures are formed through weak but cooperative interactions to perform precise functions. Learning from nature, we designed and investigated flexible polymer chains linked with periodically placed and directional dynamic bonds. Through understanding the structure property relationships, we discovered unique applications of designing such polymers for self-healing electronic materials, “morphing” electronics, artificial muscle and reconfigurable soft robots.

Biomimetic Nanostructures Incorporated with Synthetic Melanin for Advanced Soft Robot Materials

Marina P. Chang, Alana P. Gudinas, Kenny M. Hernandez and Danielle J. Mai; Stanford University, United States

The miniaturization of untethered robots poses new challenges in powering, actuation, and control since traditional electro-mechanical mechanisms are not applicable due to their inherent size and weight limitations. While different strategies based on different stimuli have been developed, there is a rising need for new biocompatible methodologies to power and control small-scale robots. Inspired by the surface locomotion of aquatic insects, we propose the use of structural proteins as a porous matrix for the development of surface tension-propelled micromotors. These protein motors can change their nanostructure and nano-porosity to regulate the diffusion of chemical fuel and thus regulate the propulsion. We integrated these protein motors into photomechanical liquid crystal networks to provide steering control via bending and surface deformation, mimicking the posture change of swimming insects. We demonstrated diverse locomotion control and active direction transition in milli swimmers across length scales. This new strategy offers orthogonal power and control solutions for autonomous swimming soft robots.

Harnessing Protein-Based Motors and Liquid Crystal Networks for Bioinspired Locomotion Control of Small-Scale Soft Robots

Chung Huan1, Natalie Pinchin2, Chia-Heng Lin1, Hamed Shahsavanan and Abdon Pena-Francesch1,1,1; 1University of Michigan–Ann Arbor, United States; 2University of Waterloo, Canada

The diversity of naturally occurring proteins offers bioinspiration to develop engineered proteins that respond to specific stimuli. Calcium responsiveness emerges in a class of “Repeats-in-Toxin” (RTX) protein domains that undergo reversible conformation changes from random coils to β-sheet structures in the presence and absence of calcium using small angle x-ray scattering (SAXS). The addition of calcium results in a 70% decrease in overall size and tertiary structure of RTX domains in the presence and absence of calcium using small angle x-ray scattering (SAXS). The addition of calcium results in a 70% decrease in volume of an RTX domain, representing a large contractile range. To harness this mechanical response, we genetically fused RTX domains between hydrogel-forming associative domains. The mechanical properties of the resulting hydrogels were characterized using shear rheology, which revealed calcium-dependent increases in hydrogel stiffness. By incorporating RTX domains in hydrogel systems, we demonstrate a tunable platform for calcium-responsive biomolecular actuators. RTX-based biomolecular actuators are poised to enable the development and manufacture of artificial muscles to aid in the repair or replacement of injured muscle.

Engineering Biomolecular Actuators from Calcium-Responsive Repeat Proteins

Martina P. Chang, Alana P. Gudinas, Kenny M. Hernandez and Danielle J. Mai; Stanford University, United States

Protein-based hydrogels provide a platform for functional, biocompatible materials in soft robotics. Stimuli-responsive protein hydrogels can function as soft actuators by transforming environmental signals into mechanical motions without the need for an external power source. For soft robotics systems to interface or integrate with biological systems, they must respond to physiological stimuli. Calcium ions act as critical signaling molecules for a wide variety of biological functions, including muscle cell contraction, cell replication, and neurotransmitter release. Calcium-responsive actuators would enable broad biomedical applications, such as artificial muscles and implantable, responsive materials.

The diverse functionality of naturally occurring proteins offers bioinspiration to develop engineered proteins that respond to specific stimuli. Calcium responsiveness emerges in a class of “Repeats-in-Toxin” (RTX) protein domains that undergo reversible conformation changes from random coils to β-sheet structures upon binding to calcium. We characterize the changes in the overall size and tertiary structure of RTX domains in the presence and absence of calcium using small angle x-ray scattering (SAXS). The addition of calcium results in a 70% decrease in volume of an RTX domain, representing a large contractile range. To harness this mechanical response, we genetically fused RTX domains between hydrogel-forming associative domains. The mechanical properties of the resulting hydrogels were characterized using shear rheology, which revealed calcium-dependent increases in hydrogel stiffness. By incorporating RTX domains in hydrogel systems, we demonstrate a tunable platform for calcium-responsive biomolecular actuators. RTX-based biomolecular actuators are poised to enable the development and manufacture of artificial muscles to aid in the repair or replacement of injured muscle.

Overcoming Challenges in Processing Biobased Materials for Soft Robotics

Blair K. Brettmann; Georgia Institute of Technology, United States

Electronic materials and robotic devices are pervasive throughout modern society and with increasing demand comes a growing interest in improving the sustainability of these products. One of the most promising methods to improve sustainability is to replace key components with biobased materials, which are derived from renewable biomass sources. However, these materials are often very challenging to process due to a large degree of heterogeneity, impurities from the feedstock, batch-to-batch variation, and abundance of functional groups with strong molecular interactions. This becomes even more important for applications such as soft robotics where small changes in microstructure can lead to large changes in performance. Applying systematic study of the formulation and the processing conditions in tandem, we can provide insights into how to overcome these unique challenges in biobased materials, working with materials from cellulose nanocrystals to sodium alginate to silk fibrin. Strong hydrogen bonding and the presence of charged functional groups leads to changes in rheology that require adjustments in processing parameters, while impurities from the biomass source lead to inconsistency in the materials and development of additional purification schemes to reduce variability in the output product and improve quality. Underlying the design of these soft materials from biobased sources is a strong link between the formulation and the process and only with this vision towards manufacturability can we realistically improve the sustainability of these complex products.

Biomimetic Nanostructures Incorporated with Synthetic Melanin for Advanced Soft Robot Materials

Suyoung Lee, Damask Grinnell, Mark Van Dyke, Roberto Guzman and Minkyu Kim; The University of Arizona, United States

Soft robotics opens up new opportunities in a variety of fields, including biotechnology, agriculture, manufacturing, and defense, by replacing traditional rigid robots in complex scenarios. Soft robots are designed to imitate the flexibility and adaptability found in natural systems. Moreover, the materials employed in soft robotics typically require durability, with the necessity of biocompatibility, contingent upon the desired performance. Keratin, a fibrous protein comprising a major biomaterial in hair, skin, nails, wool, and feathers, can be an ideal candidate for soft robotics. The natural keratin-based materials offer biocompatibility and attractive mechanical properties, such as high tensile strength, hardness, toughness, and flexibility. However, materials developed from extracted keratin from natural sources often exhibit inferior mechanical properties compared to their natural counterparts, limiting their application in soft robotics.
In natural keratin-based biomaterial, melanin is commonly observed, and its catechol groups are known for their contributions to self-healing, enhanced mechanical properties, and chemical stability, in addition to their primary role as pigments. Polydopamine (PDA) has garnered attention as an artificial melanin due to its similar chemical structure and properties to its natural counterpart. The customizable design parameters of melanin-like PDA particles (MLPPs) make them even more intriguing than natural melanin. In this study, we introduced MLPPs into the keratin biomatrix to investigate the relationship between MLPP design parameters and the mechanical properties of the biomatrix. Specifically, we synthesized MLPPs using PDA alone or by coating PDA onto various particles and then incorporated these MLPPs into the keratin matrix. We correlated the mechanical properties of the biomatrix with PDA coating thickness, particle sizes, and concentrations of embedded MLPPs. We anticipate that the improved mechanical properties of keratin-based materials achieved through the integration of MLPPs, along with the multifunctional capabilities offered by diverse MLPPs, will not only render them suitable for soft robotics but also broaden their potential applications, including light harvesting, 4D printing, color-switching, and metal scavenging.

11:45 AM SB11.05.06
Phase Transition in Polymeric Systems for Biomimetic Materials Working with Water Kosuke Okeyoshi, Taisuke Hatta, Yuto Watanabe, Reina Hagiwara, Thi Kim Loc Nguyen and Leiji Wu; Japan Advanced Institute of Science and Technology, Japan

Inspired by history of natural environment and biomaterials, we are designing and fabricating functional soft materials through organizing polymeric materials [1-3]. To propose advanced energy converting systems, materials living with water are the target. From a viewpoint of biomimetics, the air-water interface is expected to play an important role in establishing a universal model of dissipative structures. Viscous fingering, as an example of nonlinear fluid flow, is an unstable situation that is widely known as tears of wine. This has been explained through the Marangoni effect, coffee ring effect, Saffman-Taylor instability, etc. However, due to the transitional nature of these phenomena, there are few strategies for immobilizing such fluidically regulated interfaces. Recently, such phenomena have been applied successfully to an immobilized structure by controlling the evaporation of a mixture of biopolymer and water. In this study, we present a brief discussion of nonequilibrium phenomenon, “meniscus splitting”. More precisely, an air-liquid interface is divided into multiple interfaces to partition a space. By using a mixture of polysaccharides and water, a macroscopic pattern following a specific rule could be confirmed. When the mixture is dried from a top open cell, the polymer forms deposits at specific positions to split the meniscus by bridging a millimeter-scale gap. Because water irreversibly evaporates from the liquid phase to the air phase through a gap, the air-liquid interface is in a nonequilibrium state between polymer deposition and water evaporation. The interfacial instability is comparable to the mechanical instability of gels at the phase transition or to the skin layer of gel surfaces during shrinking. Furthermore, by controlling the deposition, the polymeric self-assembly could act as vapor-sensitive materials or super moisturizing materials [1-2]. Here, the phenomenon and the material’s behaviour would be discussed from a physicochemical viewpoint.


SESSION SB11.06: Animate Matter in Soft Robots II
Session Chairs: Qing Chen and Minkyu Kim
Wednesday Afternoon, April 24, 2024
Room 430, Level 4, Summit

3:30 PM SB11.06.02
Charge and Energy Transfer Dynamics in Organic Solar Cells Using Extracts of Algae Mmantsae M. Diale; University of Pretoria, South Africa

The relationship between photosynthesis and photovoltaics is often viewed from different perspectives by researchers, whilst in fact, these two are related. Photovoltaics is a direct copy of photosynthesis, where the green leaf is the oldest solar cell with almost 100% photo conversion efficiency. The mechanism of solar energy conversion in photosynthesis is sustainable and environmentally safe, has a great potential as an example of renewable energy device. The efforts to collect all photons in the visible light has been unsuccessful due to bandgap limitations of inorganic materials. Recent advances in the design of optimal organic solar cells include the creation of converters in which thylakoid membranes, photosystems and cyanobacteria immobilized on nanostructured electrodes are used. Application of carotenoids and thylakoids pigments has extended light absorption from ultraviolet to infra-red photons, an effort to improve solar cell performance and photo conversion efficiency. This presentation aims review charge and energy transfer dynamics in organic solar cells to produce maximum efficiency using algae-related matter.

4:00 PM SB11.06.03
Microstructures of Anisotropic pH-Responsive Chitosan Hydrogels prepared by Meniscus Splitting Method Thi Kim Loc Nguyen and Kosuke Okeyoshi; School of Materials Science, Japan Advanced Institute of Science and Technology, Japan

Polymeric microstructures have been expected to be a useful material in wide fields of food packaging, drug delivery, cosmetics, etc., toward a sustainable society. In addition, numerous natural polymers, like chitosan and cellulose, have also demonstrated pH-responsive swelling behavior. However, the hierarchical structures have not been used for materials under physiological conditions. In this study, to reorganize the polymeric systems, aqueous mixtures of chitosan as viscous fluid are used through the meniscus splitting method, for preparation of a chitosan membrane. To understand the factors on the specific deposition in the meniscus splitting, the nucleus position is analyzed thoroughly verifying the effect of the cell width. Furthermore, the dried chitosan membrane shows anisotropic pH-responses as a hydrogel because of the oriented structures in submicron scale. To clarify the characteristic anisotropy in ion- or pH-sensitive hydrogels, the pH-dependence of three-dimensional swelling ratios and the cyclic pH-changes were validated. Especially, the dried membrane was directly immersed into each buffered solution in a wide range of pH (pH2.2–pH8.0). Under the acidic conditions, the protonation allowed the water molecules to penetrate the interspace not only among the fibers but also among the chains in fibers. As a result, some of the crosslinking points by the hydrogen bond should be dissolved. Besides, toward the use of the membrane in the physiological pH condition, like pH7.4, the repeatability of swelling/deswelling as the hydrogel was validated. In the pH cyclic changes between pH8.0 and pH2.2, the gels showed no reversibility. Through a repeat test of stepwise pH-changes between pH8.0 and pH2.2, it was clarified that the sample continued swelling and redissolved into the aqueous solution, suggesting that the chitosan gel had irreversibly dissolved crosslinking points between pH8.0 and pH2.2. In the pH2.2, the protonation of the chitosan chain would induce the dissolution of the hydrogen bonds between the hydrosol groups and exchange of the citric acid. Interestingly, in the cyclic pH changes between pH8.0 and pH5.0, the chitosan gels had reversibility both in the Y- and the Z-directions. This result suggests that the water molecules can go in and out of the interval of the oriented structure without dissolution of the crosslinking points. The membrane would have a hierarchical architecture: nanofiber as a molecular bundle, and microfibers as a nanofiber bundle. In the presentation, to clarify the nano- and micro-anisotropic structure in DRY/WET states, the surface and cross-section positions of the chitosan membrane will be discussed.

4:15 PM SB11.06.03
Soft Robots Meet Bioelectronic Interfaces: A Promising Use-Case of Bio-Based and Biomimetic Polymers for Minimally Invasive Implantable Devices Sukho Song1,2; Florian Fallegger1, Alix Trouillet1, Kyungjin Kim1,3 and Stephanie P. Lacour1; 1École Polytechnique Fédérale de Lausanne, Switzerland; 2Empa Swiss Federal Laboratories for Materials Science and Technology, Switzerland; 3University of Connecticut, United States

This presentation shares an emerging research field of minimally invasive implantable devices that utilize soft robotics, which offers promising applications for bio-based and biomimetic polymers. The talk first highlights a recent work published in Science Robotics (1) concerning the development of deployable electrocorticography (ECOG) electrode arrays enabled by soft robotic sensing and actuation. ECOG is a minimally invasive method commonly used to map epileptogenic regions of the brain. It aids in leston resection surgery and is increasingly explored in brain-machine interface applications. However, current devices present limitations, leading to trade-offs in cortical surface coverage, spatial electrode resolution, aesthetics, and risk factors. These limitations often restrict the use of the mapping technology to the operating room.

The presented work introduces a scalable technique for fabricating large-area soft robotic electrode arrays. These arrays can be deployed on the cortex through a square-centimeter craniotomy coating PDA onto various particles and then incorporated these MLPPs into the keratin matrix. We correlated the mechanical properties of the biomatrix with PDA coating thickness, particle sizes, and concentrations of embedded MLPPs. We anticipate that the improved mechanical properties of keratin-based materials achieved through the integration of MLPPs, along with the multifunctional capabilities offered by diverse MLPPs, will not only render them suitable for soft robotics but also broaden their potential applications, including light harvesting, 4D printing, color-switching, and metal scavenging.

This talk will also discuss insights into the future prospects of soft robotic implant technologies, which hold potential for multifunctional chronic health monitoring and treatment. Beyond the existing research field, there are opportunities to explore various soft robotic actuation to adapt to the geometries and movements of specific target organs, such as bending, unfurling, coning, and unfolding. Additionally, there are promising applications for these robotic implants to deploy a diverse range of sensing or stimulating components. Examples include strain sensors for cardiac activity monitoring, microfluidic systems for drug delivery, and optical elements for optogenetic stimulation. Bio-based and tissue-mimetic soft polymers are especially...
Biomimetic Phenolic Hydrogels

5:00 PM

Xueju (Sophie) Wang

SB11.07.05

concentration relative to the PEG chains. Likewise, various findings have suggested that incorporating nanocomposite clay into the network can enhance the gel’s cohesive strength. Suitable for use as a surgical adhesive. The hydrogel network consists of 4-arm PEG chains grafted with either catechol or gallol units, crosslinked using Ferric ions or sodium periodate as adhesion and with customizable properties (for example, modulus, degradation and swelling rate). Our two-part device simplifies on-site preparation prior to administration, making it also extensive on-site preparation and special storage conditions prior to use. The adhesion is often inadequate, and swelling rate cannot be controlled.

PEG (polyethylene glycol)- based hydrogels stand out as promising candidates for these applications. Nevertheless, many commercially available PEG-based adhesives or gels demand extensive on-site preparation and special storage conditions prior to use. The adhesion is often inadequate, and swelling rate cannot be controlled.

To that effect, here we report a non-toxic biomimetic hydrogel based on PEG polymer chains functionalized with phenolic functional groups (Gallol and Catechol) developed for robust adhesion and with customizable properties (for example, modulus, degradation and swelling rate). Our two-part device simplifies on-site preparation prior to administration, making it also suitable for use as a surgical adhesive. The hydrogel network consists of 4-arm PEG chains grafted with either catechol or gallol units, crosslinked using Ferric ions or sodium periodate as agents. Other polymer backbones like Polyethyleneimine (PEI) have also been investigated. The concentration of crosslinking agents with respect to that of phenolic groups dictate the dominant mode of interaction, either coordination or covalent crosslinking. Furthermore, the overall self-healing ability, adhesive strength, and cohesive strength are tunable by the crosslinker’s concentration relative to the PEG chains. Likewise, various findings have suggested that incorporating nanocomposite clay into the network can enhance the gel’s cohesive strength.

In a comparative adhesion study, our optimal formulations, when tested alongside commercial PEG based adhesives on leather, exhibited shear strength of up to 253kPa, which was almost 12 times higher than Coseal™’s shear strength of 22kPa after two hours of application. No delamination from the substrates (e.g., pig skin, leather, or collagen) was observed.

5:00 PM SB11.07.07

Stimuli-Responsive, Morphing Liquid Crystal Elastomer Structures for Intelligent Systems

Xueju (Sophie) Wang

University of Connecticut, United States

Intelligent systems with capabilities of sensing, actuation, and closed-loop control are promising for many applications such as augmented reality, rehabilitation, and soft robotics. In this talk, I will present our work on stimuli-responsive materials, structures, and electronics toward this effort. I will start with our study on liquid crystal elastomers (LCEs), a type of smart material that has capabilities of soft elasticity and large, reversible shape-changing behaviors due to liquid crystal-polymer network couplings. Through introducing a versatile mechanical programming technique, previously inaccessible reconfigurable three-dimensional structures made of LCEs and their magnetic composites are created and their potential applications in soft robotics are demonstrated. I will present further our facile strategy to locally tailor the stiffness and the morphing behavior of these reconfigurable LCE structures by harnessing molecular-material-structure interactions, i.e., locally controlled mesogen alignment and crosslinking densities. Selective photopolymerization of spatially aligned LCE structures yields well-controlled tightly and highly crosslinked domains of distinct stiffness and selective permanent mesogen programming, which enables various previously inaccessible stiffness-heterogeneous geometries, as demonstrated in diverse morphing LCE structures via integrated experimental and finite element analysis. Furthermore, programming of the non-photopolymerized regions allows for reshaping, as shown in a sequentially shape morphing LCE rod and “face”. The heterogeneous morphing LCE structures have the potential for many applications including in artificial muscles, soft robotics, and many others. In addition, a simple strategy for creating 3D thermochromic LCE structures with synchronous shape-morphing and color-changing capabilities for biomimetic robotics will also be introduced. I will conclude my talk with soft sensing devices for in situ pressure measurements, beyond the actuation capabilities enabled by LCEs. The introduced actuation and sensing strategies and concepts are promising for many intelligent platforms.

5:00 PM SB11.07.06

Design Optimization of The Directly 3D-Printed Jamming Structure Using Machine Learning Models

Yuna Yoo, Zeqing Jin and Grace Gu; University of California, Berkeley, United States

Modifying the stiffness of soft robots presents a significant challenge, with the goal of enabling free deformations at low stiffness, while increasing the robustness of grasping at high stiffness values. Among the promising approaches, the utilization of jamming structure stands out for its ability to achieve high stiffness modification with minimal volume variation. However, most of the jamming structures require a complicated fabrication process, which limits the prototyping speed, repeatability, and reliability. To address this issue, attempts have been made to directly 3D-print jamming structures; however, these attempts were limited to 3D-printing the standardized jamming structures and the optimized designs relied on heuristic searches based on trial-and-error experiments. In this study, we introduce a directly 3D-printed jamming structure with optimized design through machine learning. The stiffness of the generated jamming structure design is estimated by finite-element-based simulations and the design is optimized using machine learning models. To validate the optimization results, benchmark designs and the optimized design are fabricated and the stiffness of the designs are compared. Finally, the feasibility of the optimized 3D-printed jamming structure is verified by grasping demonstrations, including its implementation into a pneumatically actuated soft gripper.

5:00 PM SB11.07.07

A Self-Healing Electrically Conductive Organogel Composite

Yongyi Zhao1,2 and Carmel Majidi1; 1Carnegie Mellon University, United States; 2Massachusetts Institute of Technology, United States

Self-healing hydrogels use spontaneous intermolecular forces to recover from physical damage caused by extreme strain, pressure or tearing. Such materials are of potential use in soft robotics and tissue engineering, but they have relatively low electrical conductivity, which limits their application in stretchable and mechanically robust circuits. Here we report an organogel composite that is based on poly(vinyl alcohol)–sodium borate and has high electrical conductivity ($\sim 10^3 \text{ S m}^{-1}$), low stiffness (Young’s modulus of ~20 kPa), high stretchability (strain limit of ~400%) and spontaneous mechanical and electrical self-healing. The organogel matrix is embedded with silver microflakes and gallium-based liquid metal microdroplets, which form a percolating network. The material’s self-healing properties are systematically determined compatible materials systems for the creation of fully biodegradable, high-performance electrohydraulic soft actuators. These embodiments reliably operate up to high electric fields, show performance comparable to non-biodegradable counterparts, and survive over 100,000 actuation cycles. We elucidate their fundamental operating principles and provide materials combinations that enable power-efficient electrohydrodynamic actuators void of detrimental interfacial charging. Finally, concepts for energy-autonomous soft aquatic robots and aerial drones are introduced.
network, leading to high electrical conductivity in the material. We also overcome the rapid drying problem of the hydrogel material system by replacing water with an organic solvent (ethylene glycol), which avoids dehydration and property changes for over 24 h in an ambient environment. We illustrate the capabilities of the self-healing organogel composite by using it in a soft robot, a soft circuit and a reconfigurable bioelectrode.

5:00 PM SB11.07.08
Fabrication of Reentrant Micromesh Suspended by Shape Memory Polymer for Liquid-Repellency

Ga-in Lee, Moon Kyu Kwak, Minsu Kim, Han Jun Park and Dokyung Kyeong; Kyungpook National University, Korea (the Republic of)

Onnephobic surfaces, which are referred as having both hydrophobic and oleophobic behaviors under environments involving interaction with liquids, have been vigorously studied due to its robust liquid-repellency. By its non-wetting properties, the liquid-repellent surfaces have potential to be utilized in various applications such as self-cleaning, oil/water separation, droplet manipulation, and antifoiling. Accordingly, scientists are developing the liquid-repellent surface by forming microscale structures with a specific functional morphology. Among the representations of the morphology, reentrant topography inspired by springtail in nature have enormous influences on microstructure engineering fields for its exceptional wetting resistance even under liquids with low surface tension than water. Reentrant structures show an overhanging profile, by which a surface can uphold liquids so as to have liquid-repellency. Surface engineers have been consistently trying to imitate the reentrant topography by 3D printing, capillary interaction, self-assembly, photolithography, and imprint lithography ever since the studies of onnephobic surfaces have manifested. Among the aforementioned methods, imprint lithography by the UV light is one of the most commonly employed techniques due to its ability to achieve macro/nanoscale resolution affordably and rapidly. However, imprinting has limited feasibility in complex topography due to the difficulties in demolding process, for which 3-D structures with a semi-freestanding feature that below the surface is excavated and penetrated can be hard to be achieved. This shortcoming limits the practical realization of functional structures present in nature such as springtails, gecko, and so forth. Shape memory polymer (SMP) is a switchable material that has double states which are defined as a permanent shape and a temporary shape. Through manipulation of the shape under external stimuli such as heat or light, the temporary shape can be newly formed and fixed. Then SMP switches back to the permanent shape if triggered again by a stimulus. Recently, we have been utilizing SMP’s unique property in developing functional surfaces including wetting controllable structures, diffractive optical elements, and dry adhesive surfaces. Herein, we fabricated suspended micromesh structures along with three different periods of the meshes. The meshes were imprinted on temporary-shaped flattened SMP and recovered to its permanent pillar shape when heat was applied above the glass transition temperature. Accordingly, the meshes were suspended as SMP recovered to its initial pillar shape and reentrant topography was formed consequently. In comparison with simple meshes, suspended micromeshes can realize the Cassie-Baxter state even with a liquid that has the intrinsic contact angle under 90 degrees by the geometry of the reentrant structure. Also, the apparent contact angle of suspended micromeshes increased compared to the simple meshes because of the created air surface of the meshes. Considering the reentrant geometry, we calculated the breakthrough pressure of suspended micromeshes based on the Laplace pressure and compared its value to the measured breakthrough pressure. In addition, drag reducing effect of suspended micromeshes were also evaluated to prove its robustness in liquid-repellency. In this work, we proposed a new method to fabricate the reentrant topography with the meshes by a combination of imprint lithography and SMP’s own property. Wettability and hydrostatical robustness of fabricated suspended micromeshes were investigated via measurements of the contact angle, and breakthrough pressure, by which it is demonstrated that the reentrant topography was successfully established based on the calculated values and the measured values. In addition, slip lengths were measured to further present the liquid-repellency of the structures owing to its created air layers.

5:00 PM SB11.07.09
Multifunctional Droplet Manipulation of Heterogeneous Structures using Magnetic Responsive Shape Memory Ridge Arrays and Superhydrophobic Silicon Thin Film

Sanjeong Kim, Sanyeep Lee, Junhyung Kim, Uyeon Kim and Seok Kim; Pohang University of Science and Technology, Korea (the Republic of)

The manipulation of droplets finds applications across diverse fields such as materials synthesis, healthcare, and chemistry. Traditional methods for droplet manipulation involve techniques such as electrowetting and fluidic-based platforms. In this study, we propose a novel approach to induce multifunctional droplet manipulation by utilizing nanostructured superhydrophobic silicon thin films integrated on magnetic-particle-embedded SMP (Shape Memory Polymer) ridge arrays. Our approach capitalizes on the inherent Laplace pressure gradient resulting from the interaction between a created heterogeneous structure's ratchet surface and the droplet, overcoming challenges like biofouling associated with externally applied forces. The incorporation of SMP introduces elastic properties, while the silicon thin film contributes superhydrophobicity, optimizing both mechanical characteristics and hydrophobicity of overall platform.

Our choice of SMP is deliberate, as it allows for diverse functionalities through controlled magnetic torque. Unlike traditional magnetic responsive polymers, we employ SMP to perform various functions with partial heating and cooling of the platform. The heterogeneous structure comprising SMP exhibits shape fixing without the need for continuous external stimuli, enhancing energy efficiency.

We believe that this heterogeneous structure, exploiting Laplace pressure gradient, holds promise for applications beyond our study, extending to fields such as digital microfluidics, potentially impacting technologies like lab-on-a-chip devices. The unique combination of SMP and superhydrophobic silicon thin film offers a versatile and energy-efficient platform for advanced droplet manipulation.

5:00 PM SB11.07.10
Universal Manipulation of Macro-To-Microobjects by Controlling Adhesion of Nanotip Shape Memory Polymer Surface

Junhyung Kim, Sanyeep Lee, Seunghoem Kim, Uyeon Kim and Seok Kim; Pohang University of Science and Technology, Korea (the Republic of)

Shape memory polymer (SMP) possesses the capability to undergo dynamic variations in stiffness when subjected to external stimuli such as heat or light. It exhibits the unique ability to be shape-fixed into desired shapes and can revert to its original form from through the shape memory effect. Exploiting these attributes, SMP serves as smart adhesives in applications like soft grippers and transfer printing, providing a solution to challenges posed by the adhesion paradox, a feature distinct from traditional elastomer adhesives.

Here, we report a nanotip SMP surface with extreme reversible adhesion, demonstrating its adeptness in manipulating objects across a spectrum ranging from macro-scale (≥10cm) to micro-scale (≤5μm). This innovative approach leverages the distinctive features of SMP to effectively resolve challenges related to the adhesion paradox, while also capitalizing on the adhesion paradox through a return to the original rough surface, thereby achieving excellent reversible adhesion. The nanotip SMP surface, characterized by an RMS roughness (R,) exceeding 100nm, mitigates surface adhesion to zero through its created air layers. In its rubbery state, the nanotip SMP surface exhibits liquid-repellency. In this work, we proposed a new method to fabricate the nanotip shape and reentrant topography was formed consequently. In comparison with simple meshes, suspended micromeshes can realize the Cassie-Baxter state even with a liquid that has the intrinsic contact angle under 90 degrees by the geometry of the reentrant structure. Also, the apparent contact angle of suspended micromeshes increased compared to the simple meshes because of the created air fraction of the surfaces. Considering the reentrant geometry, we calculated the breakthrough pressure of suspended micromeshes based on the Laplace pressure gradient resulting from the interaction between a created heterogeneous structure's ratchet surface and the droplet, overcoming challenges like biofouling associated with externally applied forces. The incorporation of SMP introduces elastic properties, while the silicon thin film contributes superhydrophobicity, optimizing both mechanical characteristics and hydrophobicity of overall platform.

8:45 AM SB11.08.01
The Hole Dynamic in PEDOT:PSS/Bacterial Cellulose Actuators
Sukesh Kumar1,2, Aimin Yu1 and Madrika Khandelwal1; 1Indian Institute of Technology Hyderabad, India; 2Swinburne University of Technology, Australia

Actuators are one among numerous applications that have emerged from the utilization of conducting polymers. This class of material has attracted wide interest in the field of electronics, because they conduct both electronic and ionic charges through the bulk of their volume. This makes possible the application of electronic devices as electrochemical devices, which are termed as organic electrochemical transistors (OECT) despite the extensive use as OECTs, there are still numerous discrepancies in the descriptions of the fundamental physics underlying the performance of these devices. Therefore, there is a growing emphasis on modeling the ion-electron interaction within conducting polymers. Recent publications have contributed fresh insights into the conduction mechanisms. However, the actuator community has yet to fully integrate these newfound understandings into their efforts to comprehend and model the mechanical response of conducting polymer actuators. Existing models for these actuators have primarily focused on ionic diffusion, which fails short of explaining all the existing experimental observations.

This study draws from three distinct bodies of literature, comprising the most pertinent existing model for conducting polymer actuators, advancements in the comprehension of ionic-electronic
conduction in conducting polymers, and empirical observations that defy current models for conducting polymer actuators. Also, Electrochemical Impedance Spectroscopy (EIS) is used extensively to understand the actuation mechanism under dynamic conditions, considering the progress made in comprehending the physics of conducting polymers as previously mentioned.

The conducting polymer actuator is prepared using PEDOT:PSS and bacterial cellulose (BC) (as a substrate), which is operated in both depletion mode and enhancement mode, for different time scales. The doping (compensation) and dedoping (displacing) in PEDOT:PSS/BC bi-layer. Notably, the actuator displacement is found to be asymmetric, contingent on the polarity, magnitude, and frequency/time period of the applied potential. The observed asymmetry in displacement as a function of these parameters remains unaccounted for by existing models for conducting polymer actuators.

**Experimental Process**

Electrochemical Impedance Spectroscopy (EIS) is performed on a PEDOT:PSS/Bacterial cellulose bi-layer actuator, while the actuator is subjected to various electrostatic potential. The displacements of the actuator under these potentials are also recorded for different time periods. The EIS data is used to model electrical circuit for actuators under given potentials. Mott-Schottky analysis is performed to understand the energy band structure of the actuator-electrolyte system. Density Functional Theory simulations are performed to aid the conclusions derived from experimental data.

**Significance**

The results and discussion which follows in this paper is significant in deriving an updated model for conducting polymer actuators, delving into quantum capacitance effects given the low charge density in conducting polymer, which is essential for reliable device performance and in defining the operating ranges for such actuators. This study becomes significantly important in the background of the development happening in the field of OECT, as it brings in the mechanical deformation corresponding to those findings.

**Fabrication of Responsive 4D Micro-Structures for Dynamic Structural Color and Optical Sensing**

**Teodora Farnaone**1, Jing Qian2, Louise Bradley2, Larisa Florea1,3 and Colm B. Delaney1,3, 1Trinity College Dublin, Ireland; 2Trinity College Dublin, The University of Dublin, Ireland; 3Centre for Advanced Materials and BioEngineering Research, Ireland

Self-assembly of colloidal particles into crystalline colloidal arrays have attracted great interest from chemists, physicists and materials scientists alike due to their broad applications in the fields of optics and photonics. In particular, application of colloidal crystal arrays offers a means for controlling and manipulating light flows, and gives rise to some of the most brilliant structural colors. This phenomenon is also present in nature, where many species of birds, insects, butterflies, fish and even flowers, owe their vivid color to hierarchical assemblies of photonic structures.

Changing the structural color of photonic crystalline structures typically requires the synthesis of different size particles, in order to modulate inter-particle distance. This can add different degrees of difficulty as precise control of particle size and inter-particle distance in the self-assembly process can be time-consuming. In this work, we prove how using just one size polymer particle spheres, a wide gamut of reflected colours can be obtained in a range of different polymer matrices.

Using direct laser writing (DLW) in nanocomposite photoresists (at particle concentrations conducive to self-assembly), we can fabricate complex 3D microstructures with sub-micron feature sizes. Furthermore the DLW fabrication technique allows for fine control over a series of fabrication parameters, such as laser power, structure slicing and harnessing, thereby providing minute control over the inter-particle distance in all 3 dimensions, to obtain hierarchically ordered nanocomposite microstructures showing a wide gamut of color.

We present the expansion of this work to encompass soft, stimuli-responsive polymers in which an external stimulus can be further used to vary periodicity of the ordered nanocomposite, thereby further changing the reflected colour in and out of the visible spectrum. We will show routes of exploitation for this approach which span sensing and encryption.

In conclusion, the strategy presented herein offers a novel and efficient route for creating responsive photonic microstructures that can be used qualitatively (for analyte determination) or quantitatively (for go/no go interventions).

**Functional Hybrid Materials on Bio-Basis for Sensors and Actuators**

**Stephan V. Roth**1,2, 1KTH Royal Institute of Technology, Sweden; 2Deutsches Elektronen-Synchrotron DESY, Germany

Cellulose nanofibrils (CNFs) are an abundant, bio-based, and renewable material with excellent mechanical properties. They show highest strength and allow for light-weight applications. In this talk I will present the fundamental aspects of using CNF and characterizing its response to water and humidity. The nanoporous structure of CNF thin films is the key-point for their applications in fibers and textiles. Chemistry Methods, e20220081.

**Acknowledgment**

The authors are grateful for the financial support from the Swedish Research Council (VR) and the Swedish Energy Agency (Energimyndigheten). We also acknowledge partial support from the Royal Society, the Swiss National Science Foundation, and the China Scholarship Council.

**9:00 AM SB11.08.02**

**9:15 AM SB11.08.04**

**9:45 AM BREAK**

**10:15 AM SB11.08.05**

**Artificial Sharkskin: Fabrication of Staggered Overlapped Microdenticles**

**Jeong Jae Won**1,2, 1Hanyang University, Korea (the Republic of); 2State University of New York College of Environmental Science and Forestry, United States

In liquid crystalline elastomers, anisotropy in molecular alignment governs direction of mechanical actuation upon exposure to external stimuli. Similarly, the arrangement direction of magnetic particles determines magnetomechanical actuation of polymer composites. In micropillar arrays, chain-like arrangement of magnetic particles can induce bending or twisting actuation of micropillars under linear external magnetic field. When magnetic particles are arranged along the principal axis of the micropillar, the perpendicular external magnetic field produces bending actuation. In the same magnetic field condition, twisting actuation is induced with magnetic particles arranged along the short-axis of micropillars. The strain responsivity of magnetic actuation can be enhanced by employing anisotropic micropillar geometry for anisotropic stress distribution. Based on the magnetic bending actuation of anisotropic microdenticles, staggered-overlapped three-dimensional microarchitectures are constructed to mimic artificial sharkskin, a feat difficult to achieve by conventional microfabrication techniques. In this presentation, various anisotropic functionalities of this artificial sharkskin will be discussed.

**Acknowledgment**

The authors are grateful for financial support from the Korea Research Institute of Chemical Technology (KRICT) and the Korea Ministry of Trade, Industry and Energy (MOTIE).
These types of micro-robots open new opportunities for minimally invasive surgeries, sensing and photonics. We can incorporate multiple functionalities into a single microdevice by showcasing the effect of structure design, hydrogel composition and writing parameters on the performance of microgrippers. The characterization of such microstructures was complemented by optical microscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM). We responsive material.

In this work, we present functional microgrippers fabricated by direct laser writing via two-photon polymerization (2PP). This technique allows the creation of complex 3D structures on a macroscale by scanning a polymer hydrogel with the femtosecond laser, building the structure layer by layer. By tuning the fabrication parameters such as slicing and hatching as well as laser power and scanning speed it is possible to adjust the mechanical and chemical properties for the desired application.

The actuation of the microgripper is controlled by pH-responsive polymer materials which react to the pH changes of the environment. Their shape-morphing feature is inspired by the artificial muscles which can contract and expand in response to pH changes. The microgripper is powered by this type of responsive polymers that can move its arms reversibly close and open. The actuation takes a few seconds due to the miniature scale of these devices. By mimicking the blood vessels, we can implement such microgrippers as valves and use them in the pH sensitive microsystem. The characterization of such microstructures was complemented by optical microscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM). We showcased the effect of structure design, hydrogel composition and writing parameters on the performance of microgrippers.

These types of micro-robots open new opportunities for minimally invasive surgeries, sensing and photonics. We can incorporate multiple functionalities into a single microdevice by adapting the design and adjusting fabrication parameters. It offers a high degree of flexibility and presents a wide range of potential applications for 2PP-fabricated micro-robots.

References:

10:45 AM SB11.08.06
Micro-Robots with Fast and Reversible Actuation via Two-Photon Polymerization
Yekaterina Tske1, Srikanth Kolagatla1, Alex J. Thompson2,2, Colm B. Delaney1 and Larisa Florea1;
1Trinity College Dublin, Ireland; 2Imperial College London, United Kingdom

The additive manufacturing and its application in micro-robotics have demonstrated the high potential for the fabrication of tiny smart devices. These microscale tools can be used in surgeries to manipulate objects with precision and control while reducing damage and making patient recovery faster. The key element for the movements and actuation of such microsystems is stimuli-responsive material.

In this work, we present functional microgrippers fabricated by direct laser writing via two-photon polymerization (2PP). This technique allows the creation of complex 3D structures on a macroscale by scanning a polymer hydrogel with the femtosecond laser, building the structure layer by layer. By tuning the fabrication parameters such as slicing and hatching as well as laser power and scanning speed it is possible to adjust the mechanical and chemical properties for the desired application.

The actuation of the microgripper is controlled by pH-responsive polymer materials which react to the pH changes of the environment. Their shape-morphing feature is inspired by the artificial muscles which can contract and expand in response to pH changes. The microgripper is powered by this type of responsive polymers that can move its arms reversibly close and open. The actuation takes a few seconds due to the miniature scale of these devices. By mimicking the blood vessels, we can implement such microgrippers as valves and use them in the pH sensitive microsystem. The characterization of such microstructures was complemented by optical microscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM). We showcased the effect of structure design, hydrogel composition and writing parameters on the performance of microgrippers.

These types of micro-robots open new opportunities for minimally invasive surgeries, sensing and photonics. We can incorporate multiple functionalities into a single microdevice by adapting the design and adjusting fabrication parameters. It offers a high degree of flexibility and presents a wide range of potential applications for 2PP-fabricated micro-robots.

References:

11:00 AM *SB11.08.07
Flexible Electronic Skins for Sensing and Haptic Actuation
John A. Rogers; Northwestern University, United States

Mechanoreceptors in the skin present compelling targets for selective and noninvasive neural interfaces. This presentation summarizes our recent work in systems for independently rendering sensations in these different channels using miniatured mechanical actuators configured in programmable, dense arrays as untethered, wearable devices. The actuators combine with the skin as an elastic, energy storing module to support bistable, self-sensing modes for inducing controlled deformations at the surface of the skin. The result renders both dynamic and static stimuli, sensations in these afferent channels using miniaturized mechanical actuators configured in programmable, dense arrays as untethered, wearable devices. The actuators combine with the skin as an elastic, energy storing module to support bistable, self-sensing modes for inducing controlled deformations at the surface of the skin. The result renders both dynamic and static stimuli, through either normal or shear forces. Studies in the context of rehabilitation with human subjects demonstrate this wireless, skin-conformable haptic array as an interface to a physical environment, reconstructed and tracked from an advanced suite of smartphone-based sensors. The diversity in modes of engagement, the density of power delivery, and the efficiency in operation of these small-scale mechanical transducers represent key, enabling advances over alternatives based on electrostatic, pneumatic, and electromagnetic approaches.

SESSION SB11.09: Virtual Session
Session Chairs: Artur Braun and Minkyu Kim
Wednesday Morning, May 8, 2024
SB11-virtual

10:30 AM *SB11.09.01
Bioinspiration from Photosynthetic Light-Harvesting Protein Complexes
Tijsart Krüger; University of Pretoria, South Africa

Proteins execute their programmed functions in a finely regulated way with extraordinary efficiency, despite ample environmental disorder and densely crowded, heterogeneous environments. These capabilities serve as a useful source of inspiration for polymer design. The way in which photosynthetic light-harvesting proteins establish robustness to conformational disorder is particularly meaningful for conjugated polymers where such disorder gives rise to spatial localization of excitons and the formation of electronic traps, whereby exciton lifetimes and charge diffusion lengths are significantly reduced. In photosynthetic light-harvesting proteins, these limitations are largely overcome by the binding of chromophores in dense arrangements, allowing the formation of molecular excitons that are coherently shared across a number of neighboring chromophores. Having a significantly reduced susceptibility to structural disorder, these spatially delocalized excitations offer various functional benefits such as faster energy transport and less trapping and ensuing loss of excitation energy. These functions are often enhanced by mixing of the excitons with charge-transfer states. In the first part of the presentation, I will discuss molecular design strategies of conjugated polymers with enhanced robustness to static disorder. I will also show how subunit aggregation types can be quantified, using as an example the application of three computational methods to the experimental absorption and photoluminescence spectra of a benzodithiophene-isodindigo copolymer. In the second part of the presentation, I will discuss how the photosystem organization of cyanobacteria serves as inspiration for the design of conjugated terpolymers whereby the use of one donor and two acceptor units mimics the design of one main type of light-harvesting complex channeling excitation energy to two different types of photosystems.

11:00 AM *SB11.09.02
Shape Change Mechanisms in Biological Materials
Peter Fratzl; Max Planck Institute, Germany

The shape change of plant and animal tissues fulfills a variety of functions from organ growth to locomotion or seed dissemination. Various physical mechanisms, from fiber contraction to osmotic pressure and atmospheric dehydration, are at the origin of such shape changes. Fiber orientation distributions control the geometry of shape change and constitute, therefore, the alphabet for such programmed transformations. The talk reviews recent work on seed locomotion and capsule opening, on collagen fiber contraction as well as fiber tension-controlled tissue growth.

11:30 AM *SB11.09.03
Micro and nanopatterning of rigid materials such as semiconductors, metals, and dielectrics has revolutionized human life by enabling integrated circuits, microsensors, and smart phones. Imagine applying the same micro/nano patterning principles and multi-scale integration to hydrogels and living materials. We could then create adaptable implants, living robots, microphysiological systems, and homeostatic materials.

This talk will describe our efforts to apply micro and nanoscale patterning and heterogeneous integration to hydrogels and living cells/organoids. I will describe the first demonstration of the patterning of live cells with nanolithographic arrays of gold dots and wires using a biocompatible biotransfer process. Integrating lithographic patterns on live cells offers the potential to create living material interfaces and incorporate electronic/optical tattoos. I will also describe shape-changing temperature responsive and DNA polymerization gels that display diverse functions such as gripping, locomotion, and complex programmable shape change. I will give examples where such hydrogel transformers can be applied widely, including for adaptive implants, soft-robots, digitally programmable materials, and automata. These studies indicate the potential for the design of a range of intelligent materials, robots, and integrated devices that have the touch and feel of biological matter.

12:00 PM SB11.09.04
Ultra-Thin Graphene Oxide Composite DNA Polymerization Gels Ruohong Shi, Qi Huang, Rebecca Schulman and David H. Gracias, Johns Hopkins University, United States

DNA polymerization gels exhibit high swelling, as high as a 100-fold volumetric increase, based on the sequential insertion of DNA hairpins. They offer programmability based on DNA hybridization with high specificity and the potential for the integration of biomolecular circuits, which is of broad relevance to tissue engineering and soft robotics. Here, we incorporated graphene oxide (GO) nanosheets into the polymerization gels to enhance functionality. The composites are stiffer and enable the gels to be structured in significantly thinner films, as thin as 8 µm. We observe that the GO-DNA polymerization gel composites retain their sensitivity to DNA-induced shape transformation, such as swelling and shrinking, akin to controls without GO, but with accelerated shrinking rates. We anticipate that the combination of thinner gels with more rapid shrinking, combined with the functionality of GO (such as optical absorbance), enhances their potential for use in flexible devices, soft robotics, and drug delivery. The study also highlights the potential to incorporate other nanoparticles (e.g., noble metal, semiconducting, ferromagnetic) into DNA polymerization gels to enhance optical, electronic, and magnetic functionality.

12:05 PM SB11.09.05
Harnessing Gradients for Self-Assembly of Peptide-Based Nanocapsules Xuliang Qian, Haopeng Li, Harini Mohanram, Xia Han, Huitang Qi, Guijin Zou, Fenghui Yuan, Ali Miserez, Qing Yang, Tian Liu, Huajian Gao and Jing Yu; 1Nanyang Technological University, Singapore; 2Dalian University of Technology, China; 3A*STAR, Singapore; 4Chinese Academy of Agricultural Sciences, China

Biological systems ingeniously craft materials with complex structures for specialized functions, a feat often challenging to replicate in man-made materials. We report a serendipitous discovery where insect cuticle peptides (ICPs) spontaneously form nanocapsules through a single-step solvent exchange process. This phenomenon occurs as a concentration gradient, arising from the mixing of water and acetone, drives the localization and self-assembly of the peptides into hollow nanosized capsules. The intrinsic affinity of these peptides for specific solvent concentrations, coupled with the diffusion-driven gradient interface, triggers their localization and self-assembly. This gradient-mediated self-assembly process not only mimics biological systems in its simplicity and efficiency but also paves the way for next-generation drug delivery systems using ICP nanocapsules. Furthermore, it showcases the potential of protein/peptide-based materials in self-healable robotic skin, and stimuli-responsive sensors and detectors.

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**SYMPOSIUM SF01**

High Entropy Oxides and Related Materials
April 23 - May 7, 2024

Symposium Organizers
Ben Breitung, Karlsruhe Institute of Technology
Alannah Hallas, The University of British Columbia
Scott McCormack, University of California, Davis
T. Zac Ward, Oak Ridge National Laboratory

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* Invited Paper
+ JMR Distinguished Invited Speaker
** Keynote Speaker
^ MRS Communications Early Career Distinguished Presenter

SESSION SF01.01: Local Characterization of High Entropy Materials
Session Chairs: Christina Rost and T. Zac Ward
Tuesday Morning, April 23, 2024
Terrace Suite 1, Level 4, Summit

10:30 AM *SF01.01.01
Investigations of Local Structure in High Entropy Oxides Christina Rost; Virginia Tech, United States

Many properties we observe in materials are a direct consequence of their composition and local structure. High entropy oxides are a unique class of systems that do not have a primary composition; rather they contain a near-equimolar distribution of several elements—where no single element serves as host. Such compositional disorder is accompanied by a unique distribution of localized structural distortions which may affect properties such as thermal conductivity, magnetic interaction, diffusion, and more. A key point of interest in these high entropy systems is the implied breadth of property tunability, which ranges in compositionally dependent functionalities from amorphous-like thermal conductivities to exotic magnetic states. In this talk, we review the beginnings of high entropy oxides then present ongoing work on the local characterization of several high entropy compositions exhibiting numerous crystal structures. X-ray absorption fine structure (XAFS), both near-edge and extended, is demonstrated to aid in understanding such chemical and structural disorder. The strengths and challenges of such characterization are discussed.

11:00 AM *SF01.01.02

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High entropy oxides (HEOs) exhibit unconventional properties, which have attracted intensive interest for a wide variety of applications such as electrochemical energy storage [1,2] and (electro) catalysis [3] as well as in fundamental studies on strongly correlated materials with competing magneto-electric phases [4] giving rise to interesting properties such as colossal magnetoresistance (CMR) and metal-insulator transitions (MIT). The recent advances in (scanning) transmission electron microscopy (S)TEM techniques have enabled a detailed structural analysis of HEOs providing atomic level chemical and oxidation state information together with local structural distortion and strain analysis providing a fundamental understanding of structure property correlations allowing to disentangle the complex high entropy and ‘cocktail’ effects. In this presentation, I will illustrate some of these advanced TEM capabilities for a detailed analysis of HEOs. I will discuss how this information enabled deciphering the synergistic effects of the cations in a Mg$_2$O$_{1.5}$N$_{1.5}$Cu$_{0.5}$O$_{2}$ structure in lithium ion batteries [2] as well as the correlation between composition, oxidation state, structural distortions and magneto-electric properties in strongly correlated high entropy manganeseates [4].

The TEM investigation of a Mg$_2$O$_{1.5}$N$_{1.5}$Cu$_{0.5}$O$_{2}$ electrode during various charging stages [3] revealed a nanoscale phase segregation during the initial discharging of the homogeneous HEO into a metallic CoNiCu alloy phase, a Zn(II) and a Mg oxide phase, which forms a highly defective, semi-coherent fcc composite structure. Although the material appears X-ray amorphous, 4D-STEM crystal orientation analysis shows that the composite structure extends throughout the originally single crystalline zone. Segregation of the metallic alloy at the grain boundaries gives rise to an interconnected conductive network throughout the composite particle. During recharging, Zn and partially Cu are reoxidized (electrochemically active elements) forming a mixed fcc oxide with Mg (providing the structural stability) while the metallic NiCu(II) phase (providing electrical conductivity) is maintained. This self-assembled nanostucture enables stable micronsized particles and bypasses the need for nanoscale pre-modification required for conventional metal oxides. It demonstrates that the elemental diversity with a defined role of each element is key for optimizing these multi-electrode composite materials.

In a series of single-phase orthorhombic (Gd$_{x}La_{0.5}$Nd$_{0.5}$Sr$_{x}$MnO$_{3}$, x=0-0.5) HE-manganese, which combines the high entropy (HE) concept with property control by Sr$^{2+}$ (hole) doping, we extend the HE approach to design strongly-correlated systems. [4] Using atomic resolution STEM imaging, an orthorhombic distortion has been identified for x=0, which is reduced with increasing Sr concentration to pseudo-cubic for x=0.5. Atomically resolved elemental maps reveal a homogeneous distribution of the rare-earths cations and Sr on the A-site and Mn on the B-site sub-lattice. The oxidation state change of Mn has been evaluated by EELS using the O K and Mn L-edge features, unambiguously confirming that Sr$^{2+}$ doping results in increased Mn$^{4+}$.

These electronic and structural changes correlate with a transition of the magneto-electric properties from an insulating antiferromagnetic to a metallic ferromagnetic phase with good CMR values. This initial study signals the excellent potential to achieve complex magneto-electric phase diagrams with unique temperature dependencies that stem from competing magneto-electro-interactions, which can be tuned by merging high entropy design with strongly correlated electron systems.

References

SESSION SF01.02: Functional Properties of High Entropy Materials I—Batteries
Session Chairs: Ben Breitung and Torsten Brezesinski
Tuesday Afternoon, April 23, 2024
Terrace Suite 1, Level 4, Summit

1:30 PM *SF01.02.01
From High-Entropy Solid Electrolytes to Batteries Torsten Brezesinski: Karlsruhe Institute of Technology, Germany

Solid-state batteries represent a promising next-generation energy storage technology, with the prospect of delivering higher energy densities and exhibiting better safety characteristics than conventional liquid-electrolyte-based batteries, but are currently limited by short cycle life, among others because of electro-chemo-mechanical degradation. Especially superionic lithium phosphates solid electrolytes are being considered for use in bulk-type solid-state batteries. Nonetheless, many of the solid electrolytes reported in the literature tend to lack in room-temperature ionic conductivity and stability; thus, the continuous search for materials with improved properties. High-entropy conductors may offer a potential solution by enabling tailorable properties through compositional design. However, the correlation between configurational entropy and ion mobility is largely unexplored.

In this presentation, I will show recent findings on the effect that configurational entropy has on charge transport in chemically complex lithium phosphates for solid-state battery applications. In addition, I will demonstrate that performance improvements of high-entropy hexacyanoferrate cathodes are mainly due to suppression of phase transitions and gas evolution during cycling.

2:00 PM SF01.02.02
Entropy-Mediated Stable Structural Evolution of Prussian White Cathodes for Long-Life Na-Ion Batteries Yuehua He1, Sören L. Dreyer1, Yin-Ying Ting2, Yang Hu3, Thomas Diemant4, Maximilian Fichtner5, Horst W. Hahn1, Jasmin Aghassi-Hagmann1, Torsten Brezesinski1, Yanjiao Ma6 and Ben Breitung1; 1Karlsruhe Institute of Technology, Germany; 28THW Aachen University, Germany; 3Helmholtz Institute Ulm (HIU) for Electrochemical Energy Storage, Germany; 4Western University, Canada; 5University of California, Santa Barbara, United States

The high-entropy approach is applied to monophasic Prussian White (PW) cathode materials for sodium-ion batteries to address the issue of unfavorable multilevel phase transitions, leading to structural degradation and poor cycling stability. A series of Mn-based PWs was prepared, composed of up to six metal atoms sharing the N-coordinated positions (with Mn predominating), enabling the materials with unique structural properties. The high-entropy PW material of composition Na$_{1.65}$Mn$_{0.74}$Fe$_{0.11}$Ni$_{0.11}$Cu$_{0.12}$Co$_{0.12}$Cd$_{0.12}$Fe(CN)$_{6}$$_{0.92}$ was found to exhibit...
superior cyclability over medium-entropy, low-entropy and conventional single-metal PWs. In addition to the promising electrochemical performance, we report, to our knowledge for the first time, that the high-symmetry crystal structure (cubic form in this study) is favorable for high-entropy PWs during battery operation. Computational comparisons of the formation enthalpy of high-, medium- and low-entropy materials show that the compositionally less complex systems are prone to phase transitions that negatively affect the cyclability, especially in the deep de-/sodiated state. Based on data from complementary operando and ex-situ characterization techniques, an intrinsic mechanism for the stability improvement of the disordered PW structure during Na− insertion/extraction is proposed, namely the dual effect of suppression of phase transitions and gas evolution.

2:15 PM *SF01.02.03
High-Entropy Disordered Rock-Salt Cathodes for Lithium-Ion Batteries
Beil Zhou1, Elmar Kataev2, Görtz Schuck2, Matteo Bianchini1,3 and Olimpino Wann1,3; 1Bavarian Center for Battery Technology, Germany; 2Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany; 3University of Bayreuth, Germany

Traditional layered oxides consist of well-ordered alternating Li and transition metal (TM) with Li transport in two-dimensional (2D). In the disordered rock-salt (DRX) structure, Li and TM cations are randomly distributed at the 4a sites in the cationic sublattice. The three-dimensional (3D) DRX cathodes are considerably more stable than the conventional layered oxides which often suffer from collapse of the interlayer spacing upon Li extraction at high voltages. The disordered arrangement of Li and TM opens the possibility of using a variety of TMs. The high-entropy DRX oxyfluorides, firstly reported by our group, of which the underlying reaction mechanism has been intensively investigated recently especially by synchrotron-based techniques, operating hard/X-ray absorption spectroscopy (XAS) and ex situ resonant inelastic x-ray scattering (RIXS).

References:

2:45 PM SF01.02.04
Segregation Phenomena in Rock-Salt High-Entropy Oxides for Lithium Battery Applications Studied by In Situ Annealing in a Scanning Transmission Electron Microscope
Albina Borisevich1, Craig A. Bridges1 and Sheng Dai1,2; 1Oak Ridge National Laboratory, United States; 2The University of Tennessee, Knoxville, United States

Recently high-entropy oxides were proposed as promising materials for lithium battery anodes, with reports showing improvements in the storage capacity and cycling ability of the rock-salt type materials attributed to entropic stabilization due to random distribution of metal cations within the lattice (see e.g. [1]). However, multiple further studies suggested that these materials are not behaving as a homogenous mix of cations: in situ XAS investigation showed that Li-delithiation follows a multistep path, with some irreversible processes taking place [2], and recent localized spectroscopy results showed nanoscale segregation and differential movement of the constituent cations during charging and discharging [3]. It is therefore very important to evaluate the compositional stability of these materials at different elevated temperatures, given that charge/discharge processes can be highly exothermic.

In this study we are exploring the elemental distribution in the equimolar rock-salt high-entropy oxide of Li, Mg, Mn, Co, Ni, Cu and Zn using compositional mapping with Electron Energy Loss spectroscopy in a Scanning Transmission Electron Microscope in situ Protochips Aduro platform to heat the powders to temperatures ranging from 500°C to 950°C. The initial powders are either the mixture of initial oxides or pre-annealed ex situ, ball-milled before the in situ heating experiment. Our results suggest that, even with a highly homogenized precursors, the most uniform distribution of cations is only achieved at high anealining temperatures, such as 950°C, and thermal treatment much lower than this temperature results in Li segregation to form Cu rich clusters. This is, however, not observed in the Li enriched cathodes, which show Cu segregation. We also find that the reducing vacuum atmosphere inside the microscope contributes to the driving force for the segregation; while the powders annealed at 950°C inside the microcscope from the precursors are the most homogeneous, they still show some segregation compared to powders annealed ex situ at the same temperature which do not.

These results confirm our earlier findings about differential behavior of cations in these materials as they undergo thermal treatment and chemical transformations and suggest that controlling heat distribution within these anodes during anode charging and discharging can be very important for cycling stability.

References:

This work was supported by the DOE office of Science, Basic Energy Sciences, Materials Science and Engineering Division.

3:00 PM BREAK

SESSION SF01.03: Novel Magnetic and Electronic Properties of High Entropy Materials
Session Chairs: Alannah Hallas and Alessandro Mazza
Tuesday Afternoon, April 23, 2024
Terrace Suite 1, Level 4, Summit

3:30 PM *SF01.03.01
Accessing Novel Phase Space by the High Entropy Approach
Alessandro R. Mazza; Los Alamos National Laboratory, United States

Disorder and defects often dictate emergent phenomena in materials – such as electronic phase, magnetic ordering, and mechanical strength. Traditional thought pushes our understanding of phase order to rely on the idea of uniformity in materials, with disorder and defects resulting in lower ordering temperatures and prevention of long-range percolation. However, high entropy materials are challenging this understanding and disorder is emerging as a parameter which drives the local microstates into globally ordered behaviors. We demonstrate that this seemingly counterintuitive statement is not only true but that it simplifies the prediction of predominant functional phase in high entropy oxides. As a result, we design, grow, and characterize high entropy perovskite oxide films demonstrating the utility of this predictive materials approach.

We present these theoretical and experimental results on two classes of single crystal epitaxial films. Magnetism and charge disorder of the high entropy ABO3 perovskite La(Co0.2Mn0.8)2O3, by varying the population of the A-site, is a representative case, demonstrating how a seemingly chaotic landscape of spin and charge disorder can yield an ordered state. Second, to explore electronic phase, we demonstrate realization of extreme A-site cation disorder in (Y0.2La0.8NdxSm0.2Gd0.8)2O3, whose parent ternary oxides each have a large range of electronic (metal to insulator transition) and structural phase transition temperatures. These results suggest cation variance disorder, such as that accessible only in high entropy oxides, can be a critical order parameter in the design of correlated oxides, and that this parameter can more broadly provide continuous tunability to emergent phenomena.

4:00 PM SF01.03.02
Engineering The Spin Transition and Carrier Type with High-Entropy Lattice Distortions in Rare Earth Cobaltates
Alan Zhang1, Timothy D. Brown1, Sangheon Oh1, Catalin Sputaru1, Eli Kinigstein2, Jinghua Guo2, Joshua D. Sugar1, Arantzazu Mascaraque3, Enrique G. Michel4, Alison Shad1, Jacklyn Zhu1, Matthew Witman1, Suhas Kumar1, Alec Talin1 and Elliot J. Fuller1; 1Sandia National Laboratories, United States; 2Lawrence Berkeley National Laboratory, United States; 3Universidad Complutense de Madrid, Spain; 4Universidad Autónoma de Madrid, Spain

There is growing interest in material candidates that provide knobs to tune their properties beyond traditional limits. Compositionally complex oxides, often called high entropy oxides, are excellent candidates, wherein a lattice site shares more than four cations, forming single-phase solid solutions with unique properties. Here, we demonstrate compositional complexity as a tunable parameter in a spin-transition oxide semiconductor La1-x(Nd,Sm,Gd)1-x/3CoO3, by varying the population of rare earth cations. As the compositional complexity increases with x, localized and uniform lattice distortions occur that have profound effects on the material’s semiconductor-to-metal spin transition and carrier type. Experimental measurements, together with first-principles calculations, demonstrate that atomic-range distortions from the varying rare earth radii induce a crossover from hole-majority to electron-majority conduction at x = 0.8 without the introduction of electron donors. Thus, we show that control of localized lattice distortions through compositional complexity is a facile knob to tune oxide semiconductors and spin transitions beyond traditional means.
Magnetic-Electric Properties of High-Entropy Oxides

Haihong Huang1,2, Rameshwari Naorem, Prashant Singh and Nicolas Argibay; Ames Laboratory, Ames, Iowa, USA; 2National Tsing Hua University, Taiwan

The quest for artificial, heterostructured magnetoelectrics is driving the search for new magnetic materials that can exhibit enhanced sensitivity to external stimulation. In principle, the system of choice for this purpose can be the new class of materials known as High Entropy Oxides (HEOs). HEOs are single phase solid solutions consisting of five or more elements in equatomic or near-equatomic proportions incorporated into the cationic sub-lattice(s). What sets HEOs apart is their remarkable chemical complexity, encapsulated within a single crystallographic structure, often resulting in unique functionalities. From a local structure standpoint, HEOs exhibit an exceptionally large number of distinct metal-oxygen-metal pairings. Consequently, the magnetic correlations in HEOs, influenced by the coordination geometry, valence, spin state, and type of hybridized metal cations, are naturally influenced by an extensive variety of neighboring ionic configurations. These conditions give rise to a complex magneto-electronic free-energy landscape within HEOs, potentially leading to the stabilization of unconventional spin-electronic states. This form of inherently imbalanced magnetism has the potential to be influenced by external stimuli, such as voltage, presenting opportunities for the development of artificial magnetoelectrics. Examples of these systems, including perovskites and spinels, will be discussed in the context of their magneto-electronic properties, which are a consequence of the extreme local chemical disorder.

5:00 PM SF01.04.02

The Investigation of Electrical Properties Using High-Entropy Spinel-Oxide as an Anode for Lithium-Ion Batteries

Chia-Chien Ma, I-Han Lee and Tri-Rung Yew; National Tsing Hua University, Taiwan

The global demand for lithium-ion batteries (LIBs) is increasing, primarily because they can be used for various applications. To improve the energy density of LIBs, transition metal oxides are potential candidates for anodes owing to their high capacity and earth abundance. However, the issues such as low ionic conductivity, low Coulombic efficiency, and structural degradation during charge/discharge cycles limit the development of transition metal oxides in LIBs applications.

High-entropy oxides exhibit new chemistries and outstanding cycling stability for developing electrode materials. Nevertheless, they often contain expensive raw materials, and their effects on the application of LIBs are still unclear. In this work, a novel spinel-structure AMFCZ-based high-entropy oxide with five cost-effective and non-toxic oxides consisting of aluminum, manganese, iron, copper, and zinc ions is synthesized using a solid-state method with an ideal capacity of ~1000 mAh/g. Its cycling performance, electrochemical properties, and reaction mechanisms are investigated, showing good rate capability.

The slurries containing the AMFCZ-based active materials, carbon black (Super P), carboxymethyl cellulose (CMC), and styrene-butadiene rubber (SBR) are coated on a copper foil by using a doctor-blade process to form an electrode. After that, the electrode is dried in a vacuum oven, followed by assembling half-batteries in a glove box. The crystal structure of AMFCZ-based anode is characterized by X-ray diffraction (XRD) analysis. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDX) are used to analyze the morphology and composition distribution of AMFCZ-based anodes. Galvanostatic charge/discharge (GCD), electrochemical impedance spectroscopy (EIS), and X-ray photoelectron spectroscopy (XPS) are used to analyze the cycling performance and electrochemical properties. This work reveals a novel high-entropy oxide as an anode and demonstrates its electrochemical properties as an anode for LIBs.

5:00 PM SF01.04.03

Inhibition Effect of Segregation and Chemical Order on Grain Boundary Migration in NbMoTaW Multi-Principal Element Alloy

Xiao-Tong Li, Xiaozhi Tang and Ya-Fang Guo; Beijing Jiaotong University, China

Wide-range applications of high entropy materials (HEA) requires their superior mechanical properties, which essentially relies on grain boundary (GB) stability for sustaining plastic deformation. While the fundamental mechanisms of GB migration in HEA differs from the ones in conventional materials due to lattice distortion and local chemical environments. Particularly the GB segregation in HEA always accompanies local chemical order (LCO) variations. To quantitatively and efficiently investigate the impacts of solute segregation and chemical order on GB migration, we applied atomistic simulations for the NbMoTaW multi-principal element alloy. Assisted by a contrived Nb-rich model, it is found that solute segregation and chemical order synergistically inhibit GB migration. Nb segregation increases the critical stress for GB migration, and the presence of chemical order further enhances the resistance of GB to plastic deformation. The destruction of local ordering structures is responsible for the difficult GB migration. Transition pathway analyses show that GB modified with both Nb segregation and chemical order requires high migration barrier, and the prior migration of GB sites tend to avoid regions with heavier chemical order. These results provide new insight into how chemical complexity affects elementary GB motion and contribute to manipulating the stability of MPEAs.

5:00 PM SF01.04.04

Theory-Guided Searching for Ductile Single-Phase Refractory Multi-Principle-Element Alloys

Hailong Huang, Rameshwari Naorem, Prashant Singh and Nicolas Argibay; Ames Laboratory, Ames, Iowa, USA

The global demand for lithium-ion batteries (LIBs) is increasing, primarily because they can be used for various applications. To improve the energy density of LIBs, transition metal oxides are potential candidates for anodes owing to their high capacity and earth abundance. However, the issues such as low ionic conductivity, low Coulombic efficiency, and structural degradation during charge/discharge cycles limit the development of transition metal oxides in LIBs applications.

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A Phonon-Unfolding Based Method for Quantitative Assessment of Thermal Conductivity of High Entropy Ceramics

Yuxuan Wang, Guoqiang Lan and Jun Song; McGill University, Canada

Thermal barrier coating materials have been extensively used in fields of aerospace and power industry. It can protect the underlying substrate against hot gas streams while effectively isolating the heat flow. High entropy ceramics, with their unique disorder structure, exhibit ultra-low thermal conductivity and good high temperature stability, which make them promising candidate materials for next generation thermal barrier coatings (TBCs). Unlike the conventional ceramic materials where the intrinsic thermal resistance largely comes from phonon-phonon interactions, the thermal resistance in high entropy ceramics predominantly arises from phonon-disorder scattering. In this study, we propose a new method based on the supercell phonon unfolding (SPU) technique to predictively assess the thermal conductivity of high entropy ceramics, focusing on the high entropy rocksalt oxide group as the representation. We demonstrated that our method could obtain an indicator in direct correspondence to the thermal conductivity, thus allowing quantitative comparison of the thermal conductivities of different high entropy ceramics. A good agreement has been found between our model predictions and the experimental measurements, confirming the validity of our method. The method provides a valuable predictive tool for screening and design of high entropy ceramics for TBCs.

Development of High Entropy Perovskite Oxide Electro catalysts for the Oxygen Evolution Reaction: A Combined Experimental, Density Functional Theory (DFT) and Machine Learning Approach to Predicting Oxygen Vacancy Formation Energies

Panesan J. Tukur, Jianjun Wei, Yirong Mo, Hanning Chen, Wei Yong and Yinning Zhang; 1UNC Greensboro, United States; 2The University of Texas at Austin, United States; 3High Point University, United States; 4University of West Georgia, United States

This research explores the design and development of high entropy perovskite oxide electro catalysts for the oxygen evolution reaction (OER) using a comprehensive approach that integrates experimental investigations, density functional theory (DFT) calculations, and machine learning techniques. By harnessing the potential of high entropy materials, we aim to enhance the electrocatalytic activity of perovskite oxides for the critical OER process. We investigate the formation energies of oxygen vacancies and molecular adsorption energies on these catalyst surfaces using state-of-the-art DFT simulations. Additionally, machine learning models are employed to predict these critical properties, providing insights into catalyst performance across a wide compositional space. The synergistic combination of these methods promises to accelerate the discovery of advanced OER electro catalysts with improved efficiency and sustainability, contributing to the advancement of renewable energy technologies.

Ultra-Fast Synthesis of High Entropy Boride Layers and Their Characterization

Merve Uysal Komurlu and Ali Erdemir; Texas A&M University, United States

In this study, we used an ultra-fast boriding process to quickly and uniformly produce thick boride layers on high entropy refractory alloys consisting of W, Re, Nb, Zr, Ta, and V. Boriding is performed at 1000°C and for 1 hour. Chemical, structural, and mechanical characterization of the boride layers was carried out using relevant test methods and confirmed that W and Re-containing alloys were among the very best in terms of boride layer thickness of 40 µm and hardness. While, Nb, Ta, and V containing alloys attained thickness values of around 3 µm. Nano hardness profiles across the boride layers revealed that W and Re-containing alloys possessed exceptional hardness, i.e., around 40 GPa. In the cases of other alloys, hardness values of boride layers fell between 18.5 GPa and 8 GPa. Such significant variations in thickness and hardness highlight the need for a more systematic and predictive modeling approach that can provide critical information on the selection of constituent refractory metals in high entropy alloy systems as well as desirable boride phases with superior mechanical, thermal, and oxidative properties.

Microwave Plasma Synthesis of MoNbTaVW High Entropy Alloy: A Novel Approach

Bria C. Storr and Shane A. Catledge; University of Alabama at Birmingham, United States

We investigate a novel approach for synthesis of the high entropy alloy MoNbTaVW from metal oxide precursors via microwave-induced plasma. The process involves ball milling of the metal-oxides, followed by microwave plasma annealing at 1800°C for a duration of 1 hour. Hydrogen is used as the plasma feedgas for efficient reduction of metal-oxides. Analysis through X-ray diffraction, scanning electron microscopy/energy dispersive x-ray analysis, and Vickers hardness testing has revealed the characteristic structure/properties of high-entropy alloy. This includes a single-phase body-centered cubic structure with a uniform distribution of all five metals, and measured hardness of 6.8 ± 0.9 GPa. This hardness aligns closely with findings reported in literature for high entropy alloys sharing the same five-metal configuration. In addition to rapid volumetric heating enabled by interaction of microwaves with the dielectric precursors, the microstructure exhibits clear evidence of localized microwave sintering. The outcomes highlight the promising potential of microwave plasma as a rapid, cost-effective, and versatile processing tool for the production of high entropy alloys.

The Crystal Chemistry in Two Families of Compositionally Complex Oxide Electro catalysts

Katharine Page; 12The University of Tennessee, Knoxville, United States; 2Oak Ridge National Laboratory, United States

Integration of renewable feedstocks into the current energy infrastructure drives the development of electro catalysts that can maintain high surface areas and selective electrocatalytic activities under a variety of challenging chemical and environmental conditions. Recently, several compositionally complex oxides (CCOs) have been reported with intriguing and tunable electrocatalytic properties. We present recent studies on compositionally complex Rare Earth cerate oxygen evolution reaction (OER) electro catalysts and bifunctional OER and oxygen reduction reaction (ORR) spinel ferrite electrocatalysts. A combination of local to long-range electron, x-ray and neutron scattering probes are employed to investigate their complex configurational diversity and associated structure-property trends. Relationships are explored between the cation site preferences, chemical-short-range order, and promising electrocatalytic properties achieved in the families through compositional tuning and variation in synthesis/processing conditions. Experimentally derived models are supported by Density Functional Theory
High temperature decomposition of entropy-stabilized oxide (MgCoNiCuZn)O

11:15 AM

find that the liquid copper phase is essential to the development of a single phase. We propose the possibility that engineered, selective melting may be utilized to realize and design other ESO constituent particles remain inactive until 1020 °C, where it then dissolves the liquid phase to form an entropy stabilized oxide. Modifying the composition and phase of the binary mixture, we predict reaction dynamics leading to entropy stabilization. We investigate (MgCoNiCuZn)O and establish the importance of kinetics in single phase formation. Rapid movement and diffusion of ions within the oxidic phase can facilitate the development of stable, single-phase materials.

High entropy oxides (HEO) are characterized through the effects of configurational disorder. The wide combinatorial space offered by complex materials, however, challenges our ability to evaluate electrocaloric performance accurately. In this work, we explore the potential of HEOs as candidates for high entropy refrigerants. We investigate the electrocaloric performance of (Na,Bi,Sr,Ba,Ca)TiO3 and (Na,Bi,Sr,Ba,Ca)TiO3. A pivotal parameter in evaluating electrocaloric performance is the dependence of adiabatic electrocaloric temperature change as a function of temperature, which is intricately linked to the change of polarization with respect to temperature under a constant electric field [3]. To predict this parameter, we develop models for the temperature-dependent polarization P(T) of high-entropy oxides taking into account chemical disorder and local distortions.

The electrocaloric effect holds significant promise for advancing sustainable solid-state refrigeration technologies. High-entropy oxides [1] are potentially advantageous due to their high thermal stability of their polar phases. In this work, we evaluate the phase stability and electrocaloric performance of the high-entropy perovskite (Na,Bi,Sr,Ba,Ca)TiO3. A pivotal parameter in evaluating electrocaloric performance is the dependence of adiabatic electrocaloric temperature change as a function of temperature, which is intricately linked to the change of polarization with respect to temperature under a constant electric field [3]. To predict this parameter, we develop models for the temperature-dependent polarization P(T) of high-entropy oxides taking into account chemical disorder and local distortions.


Funding: The Center for Nanoscale Science at the Pennsylvania State University is a Materials Research Science and Engineering Center (MRSEC) supported by the National Science Foundation (DMR-2011839)

9:45 AM SF01.05.04

Ion Beam Modification of High-Entropy Oxides

William J. Weber1, Candice Kinsler-Fedon1, Lauren Nuckols1, Brianna L. Musico1, Anamul H. Mir3, Ritesh Sachan4, David Mandrus4, Yanwen Zhang1, Veerle Keppens1; 1University of Tennessee, United States; 2Los Alamos National Laboratory, United States; 3University of Huddersfield, United Kingdom; 4Oklahoma State University, United States; 5Idaho National Laboratory, United States

High-entropy oxides (HEOs) have recently gained recognition for their low thermal conductivity and tunable mechanical capabilities, but little is known about their response to high energy heavy ion beams. In this work, the heavy-ion irradiation response of HEOs with the pyrochlore and perovskite structures has been investigated. The damage accumulation behavior at 300 K due to 4 MeV Au ion irradiation of a 100°-oriented HEO titanate pyrochlore single crystal has been investigated by Rutherford backscattering spectrometry in channeling geometry and transmission electron microscopy (TEM). In addition, in situ TEM irradiation using 600 keV Xe ions has been employed to reveal the dose and temperature dependence of amorphization in a HEO pyrochlore with the same composition. In another single-crystal HEO titanate pyrochlore composition, amorphization due to 23 MeV Ni ions has been characterized by Raman spectroscopy, which indicates a much higher dose for amorphization, suggesting significant athermal recovery during irradiation due to the high electronic energy loss of the Ni ions. Ion tracks formed in a HEO perovskite structure irradiated with 774 MeV Xe ions have been characterized by TEM, and the stability of these ion tracks under electron beam irradiation has been evaluated. The results obtained on these HEO structures are compared to those of their single-component counterparts.

10:00 AM BREAK

SESSION SF01.06: Formation and Stability of High Entropy Oxides

Session Chair: Alannah Hallas
Wednesday Morning, April 24, 2024
Terrace Suite 1, Level 4, Summit

11:00 AM SF01.06.02

Reaction Pathway in The Formation of Rocksalt Entropy-Stabilized Oxides

Avery-Ryan E. Ansbro1, AkiraMiura2, Wenhao Sun2 and John T. Heron1; 1University of Michigan, United States; 2Hokkaido University, Japan

High entropy oxides (HEO) are characterized through the effects of configurational disorder. The wide combinatorial space offered by complex materials, however, challenges our ability to predict reaction dynamics leading to entropy stabilization. We investigate (MgCoNiCuZn)O and establish the importance of kinetics in single phase formation. Rapid movement and diffusion of ions within the oxidic phase can facilitate the development of stable, single-phase materials. In this work, we explore the potential of HEOs as candidates for high entropy refrigerants. We investigate the electrocaloric performance of (Na,Bi,Sr,Ba,Ca)TiO3 and (Na,Bi,Sr,Ba,Ca)TiO3. A pivotal parameter in evaluating electrocaloric performance is the dependence of adiabatic electrocaloric temperature change as a function of temperature, which is intricately linked to the change of polarization with respect to temperature under a constant electric field [3]. To predict this parameter, we develop models for the temperature-dependent polarization P(T) of high-entropy oxides taking into account chemical disorder and local distortions.

11:15 AM SF01.06.03

High Temperature Decomposition of Entropy-Stabilized Oxide (MgCoNiCuZnO)

Matthew J. Webb1, Mike Gerhardt2, Avery-Ryan E. Ansbro1, Peter Meisenheimer3, Tony Chiang1, Christina Rost2, Susan B. Sinnott1,1 and Jon-Paul Maria1; 1University of Michigan, United States; 2James Madison University, United States; 3University of California, Berkeley, United States; 4Virginia Tech, United States

Entropy-stabilized oxides represent a unique class of single-phase, multicomponent oxides that achieve stability through a substantial configurational entropy, ∆Sconf, which counters a positive, unfavorable enthalpy. Although it is generally postulated that entropy-stabilized oxides will exhibit robust thermal stability due to the presence of the -T∆Sconf term in Gibbs' free energy, their behavior at high temperatures remains largely unexplored. In this presentation, I will discuss the stability of the prototypical entropy-stabilized oxide, rocksalt (MgCoNiCuZnO), in the 1300-1700 °C range in air. As temperatures exceed 1300 °C, a gradual reduction in the Cu and Zn content within the rocksalt phase is observed. We pose that the correlated partial loss of these elements is mediated by local distortions and defects that facilitate greater diffusion rates for these ions at elevated temperatures.

11:30 AM SF01.06.04

High-Entropy Layered Double Hydroxides as Precursors for High-Entropy Oxides

Suqiong Lee1, Juwahn Noh2 and Ho Jin Ryu1; 1Korea Advanced Institute of Science and Technology, Korea (the Republic of); 2Korea Research Institute of Chemical Technology, Korea (the Republic of)
Layered double hydroxides (LDHs) consist of positively charged metal cation layers with anion interlayers and water molecules, as following by formula, $M_{x+y}^{2+}M_{y}^{3+}(OH)_{2[A^x]_y[A^{2x-y}]_{3x-y}}\cdot 2H_2O$. This material has advantages such as tunable metal composition layers, exchangeable interlayer anions, and memory effect, actively applying to the research fields of catalysts, batteries, drug delivery, and adsorption. Through the flexible design of tunable metal layers, LDHs can be expanded to a high entropy system. The reported high entropy system exhibits a lower adsorption activation in energy in comparison to conventional systems. This resulted from the various adsorption activation energy spectrums and the availability of multiple binding sites because of the mixing of multiple elements. Furthermore, high-entropy LDHs can be easily transformed into high entropy layered double oxides (LDOs) through calcination. Nevertheless, there is a scarcity of research on high-entropy LDHs and high-entropy LDOs. To address this gap, 120 binary, and ternary LDHs were synthesized through co-precipitation, serving as a database for expanding to the quaternary and quinary systems with a machine-learning-based approach. Out of the 120 LDHs, 47 cases were successfully formed as LDH crystal structures, while 10 cases showed mixed phases with less than half consisting of the secondary phases, and the remainder failed to crystallize as LDHs. The thermal stability of synthesized 57 cases was conducted and the evaporation temperature of the parent interlayer anions varied depending on the combination of metal elements. Lastly, the order of iodate adsorption capacity within the ternary system was as follows: Mg-based, Mn-based, Co-based, and Ni-based. Furthermore, 70% of the ternary system showed an improvement in adsorption capacity compared to simple binary cases, underscoring the importance of expanding the high entropy LDH system. Moreover, the exploration of high entropy LDHs might be the role of precursors for expansion into the high entropy oxide research area.

11:45 AM SF01.06.05

Growth of High-Entropy Oxide Single Crystals by means of Floating Zone Technique

Dongjeon Song and Alannah Hallas; The University of British Columbia, Canada

The high-entropy materials (HEMs) have been dealt with as a new play ground of the material engineering, since the functionality of the materials is expected to enhance by controlling the new degrees of freedom. Also, the field flips traditional condensed matter physics paradigms on their head by seeking to understand what properties arise in the presence of profound configurational disorder. However, the fundamental physics governing these materials, including the true degree of configurational entropy, its role in stabilizing the structure, and its effect on other physical properties such as magnetism and electrical transport remain open questions. A key roadblock towards achieving a deeper understanding of HEMs has been the inability to study these materials in single crystal form. Although the imperative to study HEMs in single crystal form are clear, many crystal growth methods are excluded because the synthesis of HEMs requires high levels of both thermodynamic and kinetic control. We suggest that floating zone growth is the optimal method to unlock this new frontier. In this talk, we will report several high-entropy oxide single crystals grown by the floating zone technique and discuss the advantages of this method in achieving high quality crystals of HEMs.

SESSION SF01.07: Machine Learning and Data Driven Approaches

Session Chairs: Scott McCormack and Simon Schweidler

Wednesday Afternoon, April 24, 2024

Terrace Suite 1, Level 4, Summit

1:45 PM SF01.07.01

Accelerating Material Discovery of New High-Entropy Materials through High-Throughput Synthesis, Characterization and Machine Learning Methods

Simon Schweidler, Anurag D. Khandelwal, Jan Schütze, Leonardo V. Valesco, Pascal Friederich, Markus Reischl, Ben Breitung, Horst W. Hahn, and Jasmin Aghassi-Hagmann;

Karlsruhe Institute of Technology, Germany; Universidad Nacional de Colombia Sede La Paz, Colombia

New materials are synthesized and optimized with the explicit intention of enhancing current state-of-the-art materials in various fields of application, addressing the continually growing societal demands. In this context, high-entropy materials (HEMs) offer a huge research area for the development of novel material compositions and potential applications, e.g., as electrodes in batteries or fuel cell or in the field of electrochemical catalysis.[1] Unlike classical materials, HEMs intentionally maximize configurational entropy by increasing the number of elements to reduce free formation energy and stabilize a single-phase crystal structure. In addition, the "cocktail effects" describing the interactions between different elements often lead to partially unexpected properties, which may affect potential application areas. Therefore, the advantage of using HEMs lies in the possibility of influencing their elemental composition and electronic structure through the choice of design parameters. This flexibility offers the possibility to create materials with unique surface properties by changing the size of the e.g. catalytic centers and/or the electronic structure, as well as by selectively creating defects (e.g. oxygen vacancies). However, exploring the vast compositional space of high-entropy materials in a conventional approach, i.e., one experiment at a time is prohibitive in terms of cost and time. Consequently, the development of high-throughput experimental methods supported by machine learning and theoretical predictions will facilitate the search for HEMs in their compositional diversity. This talk will therefore focus on the establishment of automated high-throughput methodologies in the field of synthesis and characterization for metallic and non-metallic (ceramic) HEMs, allowing the creation of material libraries of material properties.[2–4] This facilitates the analysis of material properties in terms of the overall composition, the effect of individual elements, morphological and/or structural differences. Machine learning-based data analysis and theoretical approaches also provide opportunities for virtual development of new materials for functional and structural applications.

2:15 PM SF01.07.03

Data-Driven Design of High-Entropy Ceramics for Extreme Environments

Md T. Islam and Scott Broderick; University at Buffalo, United States

High-entropy ceramics present a promising material class but represent a design challenge due to the massive compositional design space. Through the use of machine learning approaches, design rules linking compositions, for example, of CeO2, Y2O3, and Eu2O3 components, with mechanical properties for accelerated selection of compositional refinement. These machine learning techniques identify optimal compositions and reveal underlying relationships by capturing the intricate multidimensional relationships between composition, processing conditions, microstructure, and mechanical performance. Our findings present a set of promising compositions that exhibit enhanced mechanical properties, ideal for extreme environment applications, such as hypersonic applications.

2:30 PM BREAK

SESSION SF01.08: Functional Properties of High Entropy Materials III—Electronics

Session Chairs: Jasmin Aghassi-Hagmann and T. Zac Ward

Wednesday Afternoon, April 24, 2024

Terrace Suite 1, Level 4, Summit

3:30 PM SF01.08.01

High-Entropy Oxides for Electronic Applications: Present and Future

Jasmin Aghassi-Hagmann, Ben Breitung, Yuevue He, Hongrong Hu and Anurag D. Khandelwal; Karlsruhe Institute of Technology, Germany

HEMs represent a class of materials characterized by the incorporation of a minimum of five distinct elements within a single-phase lattice structure. This incorporation serves to elevate configurational entropy, a measure of entropy arising from the mixing of dissimilar elements, thereby engendering the emergence of unique material properties. There exist various subtypes, with high-entropy alloys and high-entropy ceramics being the most prominent among them. While alloys are typically unified within a single lattice structure, ceramics exhibit a more complex
Research on entropy stabilized oxides (ESOs) has primarily focused on exploring new structures, chemistries, dislocations [1], or unique properties. However, few studies discuss the impact of secondary phases on functionality. Here, electronic transport mechanisms in the canonical ESO (Co,Cu,Mg,Ni,Zn)O were assessed as a function of secondary phase content [2]. When single-phase, the oxide is a small polaron electronic conductor. After heat treatments, Cu-rich tenorite particles form at grain boundaries, which enhances the grain interior rocksalt oxide electronic conductivity due to increased Cu cation vacancies and compensating small hole polarons. While Cu depletion tailors grain interior the conduction mechanism, Cu-rich tenorite grain boundary phases create a pathway for Cu$^{2+}$Cu$^{3+}$ small hole polarons after longer heat treatment times. The ability to selectively grow secondary phases nucleated at grain boundaries enables tuning of electrical properties in entropy-stabilized and complex concentrated oxides using microstructure design, nanoscale engineering, and heat treatment, paving the way to develop many novel materials.

References:
[1] Xin Wang, Justin Cortez, Alexander Dupuy, Julie Schoenung, W.J. Bowman (2023) “High entropy oxide (Co,Cu,Mg,Ni,Zn)O exhibits grain size dependent room temperature deformation” Materials Research Letters

"Enhanced Electrical Conductivity caused by Phase Transformation and Interfacial Segregation in an Entropy Stabilized Oxide" Hasti Vahidi, Alexander Dupuy, Benjamin Lam, Justin Cortez, Pulkit Garg, Timothy Rupert, Julie Schoenung, William J. Bowman and Huiming Gao; University of California, Irvine, United States

In this talk, I will give an overview of the electronic and magnetic properties of various systems studied in our group, and discuss the perspective they open for applications.

Although no clear link has been made to date between these properties and the possible role of entropy-stabilization (or even high-entropy nature), cocktail effects have been reported in some cases with functional properties of the multicomponent compounds significantly different from that of their single-cation counterparts.

In this talk, we will give an overview of the electronic and magnetic properties of various systems studied in our group, and discuss the perspective they open for applications.

Functional High Entropy Oxides: From Electronic to Magnetic Properties David Berardan, Adrien Moll, Claudia Decorse and Nita Dragoe; University Paris-Saclay, France

Since their first report by Rost et al. in 2015 [1], Entropy Stabilized Oxides and High Entropy Oxides (HEOs) have become a hot topic in the field of functional oxides, with many papers devoted to the synthesis of new compositions and structures and to the study of various functional properties. In the past few years, many compositions have been obtained with different crystal structures, with both entropy-stabilized and thermodynamically stable compounds. Some of them exhibit promising functional properties, among other: superionic Li conductivity or fast ionic conductivity, colossal dielectric constants, photocatalytic properties, unexpected magnetic ordering, (...). Although no clear link has been made to date between these properties and the possible role of entropy-stabilization (or even high-entropy nature), cocktail effects have been reported in some cases with functional properties of the multicomponent compounds significantly different from that of their single-cation counterparts.

In this talk, we will give an overview of the electronic and magnetic properties of various systems studied in our group, and discuss the perspective they open for applications.

Element Sensitive Characterization of High-Entropy Oxide Perovskite Thin Films Alan Farhan, Baylor University, United States

Employing the entropy-driven stabilization concept into the perovskite structure showed first promising results demonstrating the potential unlimited freedom in designing ferroic properties in high-entropy oxide perovskite (HEOP) thin films [1]. Here, I will show how element-sensitive characterization with x-ray absorption spectroscopy (XAS), employing x-ray magnetic circular and linear dichroism (XMCD and XMDL) can shed light into how each transition metal element contributes to the overall ferroic order in HEOP thin films with a primary focus on rare-earth-based R$\text{Ni}_3\text{Co}_2\text{Fe}_0\text{Mn}_2\text{Cu}_0\text{O}_2$ (R: Tb, Lu and Dy). The results highlight the important role of elevated Co$^{3+}$ concentrations, likely induced via strain, in introducing long-range ferromagnetic order [2, 3] and the occurrence of spin-reorientations in Dy-based HEOPs [4].

References:
An Insight into The Functional Properties of High-Entropy Perovskite Oxides


In this study, we report a combined experimental and computational investigation on the mixing behavior of cations in this system. Remarkably, we find ultra-low enthalpic costs to cation mixing, resulting in entropy dominance and ideal mixing behavior. This facilitates the room-temperature and low-temperature synthesis of high-entropy materials (high-entropy semiconductors) from these compounds, as demonstrated experimentally by Folgueras et al in 2023.5 We elucidate the underlying structural and electronic origins of this facile cation miscibility in these systems, and analyze the resulting optical, thermodynamic and structural changes upon cation mixing.

Our work demonstrates that vacancy-ordered perovskites present an exciting new class of high-entropy semiconductors, synthetically at much milder conditions than typical high-entropy materials. Moreover, we elucidate the origins of this behavior, allowing the extraction of general design rules for high-entropy semiconductors with tailored properties.

In recent years, there has been a surge of research interest in high entropy materials, driven by the potential to engineer their functional properties. High entropy materials, with their diverse elemental compositions, exhibit distinctive characteristics compared to conventional materials due to the intricate interplay of inter-elemental interactions, some of which cannot be predicted. Among these materials, oxide perovskites stand out as a versatile material class with applications ranging from catalysis and solid-state fuel cells to oxide solar cells, rendering them particularly captivating for high-entropy investigations. Noteworthy studies have already shown the exceptional performance of high-entropy perovskite oxides in critical applications such as electrochemical catalysts, high-energy-density capacitors, and thermoelectric systems. The extensive array of perovskite systems, coupled with the immense spectrum of high-entropy cation combinations within them, opens up a vast domain of possibilities for such diverse applications.

In this talk, a comprehensive study of lanthanum-based perovskite-type oxides containing various compositions of transition elements (Co, Cr, Cu, Fe, Mn, Ni and Zn) at the B site is given, with the aim of studying the effects of the different cations on the properties of these materials. Various analysis techniques are used to characterize the optical and electronic behavior of these materials and thus enable further optimization for specific applications.
High-Pressure Synthesis of High-Entropy Spinel-Type Semiconducting Manganates and Perovskite-Type Ferroelectric Niobates

Avakyo Yamamoto1, Haruka Yokoyama1, Tomoki Nakayama1, Riki Maeda1, Kimitoshi Murase1, Anna Laila1, Yann-Andre Kemerer2 and Nita Dragoc1; 1Shibaura Institute of Technology, Japan; 2Université Paris-Saclay, France

We have studied high-entropy (HE) chalcogenides1 and oxides prepared at high pressure. The high-pressure method has several advantages in stabilizing HE compounds; for example, it can form the volatile elements and quickly form high-temperature phases. Here, we report our recent study on HE spinel-type manganates as a thermistor and HE perovskite-type niobates, possibly as ferroelectric relaxors.

We focused on NiMn2O4 as a pristine that is a typical NTC (Negative Temperature Coefficient) thermistor compound. NiMn2O4 and partially (minor component) substituted ones show proper resistivity for monitoring temperatures between 300–500 K in various electric devices. The efficiency of a thermistor is evaluated with the B constant (corresponding to sensitivity) in general. Most commercial ones show B ≥ 3,000–4,000 K. Our objective of this HE-spinel project is to expand the temperature range up to 700 K while keeping B > 3,000–4,000 K by controlling temperature dependence of resistivity with the HE techniques.

Two types of crystal systems appear in AMn2O4 (A=Mg, Co, Ni, Cu, and Zn) spinel: cubic in A=Ni and Co and orthorhombic in A=Mg, Cu, and Zn. It is interesting to see which structural variation to be adopted in the spinel structure with the HE stabilized if we were starting from TIO with divalent in a closed golden cell of high-pressure synthesis assembly. We prepared a single phase of tetragonal spinel (Mg, Co, Ni, Zn, Ti)Mn2O4 with sintering at high pressure (4 GPa) and quenched from ca. 1250 K to 350 K in several seconds. In contrast, samples sintered in the air were a mixture of tetragonal and cubic phases or two sets of tetragonal phases, whether quench (liquid nitrogen) or slow cooling. The temperature dependence of resistivity showed semiconducting behavior with ΔB=5,000–5,500 K at 300–700 K. In addition, resistivity's absolute value is higher than conventional ones, an advantage in sensitivity at higher temperatures. Ti may be located in the B site, and part of Mn moved to the A site. The Cu version (Mg, Co, Ni, Zn, Cu)Mn2O4 showed lower B=3,000 K at 300–700 K and lower resistivity. The properties look sensitive to cooling processes and oxygen deficiency. We are also preparing A and B double sites' HE spinel.

Another HE project is to obtain a ferroelectric relaxor in perovskite-type niobates. ANbO3 (Li, Na, K, and Ag) are well-known ferro(antiferro)electric compounds. Structure types and or distortion types of these compounds differ depending on the A element; however, they all show partial substitution of each other. For example, in KNbO3, Li and Ag could be substituted 5-10% of K, and NaNbO3 makes a complete solid solution with KNbO3. In this study, we adapted KNbO3 as a pristine and prepared HE niobates with equal molar selected 2–5 elements among Li, Na, K, Ag, and others in A site at ambient and high pressure. The high-pressure method effectively suppresses alkaline metals' vaporization (Li, Na, and K). We found LiNbO3 is more stable in a LiNbO3-type structure at high pressure. Therefore, equal molar HE compounds may be challenging in this system. Once it stabilized in a single phase, even if Li concentration is lower than other metals, it expected a ferroelectric relaxor in the temperature dependence of dielectric constant.

We also present our progress in XAS and XPS studies in HE pyrite (Fe, Co, Ni, CuX2 (X = S and Se)). It investigates a local configuration and interaction difference by comparing A element in a single metal AX2 (A=Fe, Co, Ni, and Cu).


11:00 AM SF01.10.02 Influence of Synthesis Method on The Properties of The Spinel High Entropy Oxide Mario Ullses Gonzalez Rivas1, Solveig S. Aamlid1, Megan R. Rutherford1, Edgar E. Villalobos-Portillo2, Hiram Castillo-Michel2, Ronny Sutarto2, Ning Chen2, Robert J. Green3 and Alannah Hallas3; 1University of British Columbia, Canada; 2European Synchrotron Radiation Facility, France; 3Canadian Light Source, Canada; 4University of Saskatchewan, Canada

Understanding and controlling sample dependence is a critical step towards any material achieving widespread use in applications. High entropy oxides (HEOs) are a class of materials with immediate potential for an array of applications but whose sample dependence has the potential to be significantly profound due to their high degree of configurational disorder. In this work, we seek to clarify the extent of sample dependence in HEOs by directly comparing the structural, magnetic, and electronic properties of an HEO with the spinel structure synthesized by five distinct methods. These methods (solid state, high pressure, hydrothermal, molten salt, and combustion) each provide distinct levels of kinetic and thermodynamic control in the growth process. The spinel HEO's ferrimagnetic structure was determined from neutron diffraction, whilst the site distribution of the cations in each sample was calculated using x-ray absorption spectroscopy. We conclude that this overall robustness to synthesis method make HEOs excellent candidates for a variety of industrial processes.

11:15 AM SF01.10.03 Rapid Synthesis of Entropy Stabilized Oxides Using Radio Frequency Heating Aniruddh Vashisth; University of Washington, United States

Entropy-stabilized oxides (ESOs) represent an exciting new category of hybrid materials and single-phase metal oxides, composed of multiple ions, exhibiting material characteristics that lie between those of their constituent oxides or occasionally showcasing entirely novel properties. One drawback of ESOs is their energy expensive manufacturing process, which has hindered the pace of their development and scaling. In this study, we introduce an innovative, energy-efficient method for synthesizing ESOs. This approach leverages the rapid heating capability of carbonaceous materials when exposed to radio frequency (RF) fields within the 1–200 MHz range. By employing carbon fibers and graphene as RF susceptors, we successfully achieved the synthesis of (MgCoNiCuZn)O through RF-triggered combustion synthesis, achieving heating rates of 203°C/s with a 20 W input power. This technique reduces the ESO formation time to less than a minute, significantly enhancing fabrication efficiency. The morphology and composition of the resultant ESO-carbon fiber and ESO-graphene composites were comprehensively examined using spectroscopy and characterization techniques. Moreover, single carbon fibers coated with ESO underwent testing for tensile strength and modulus, revealing minimal changes in mechanical properties compared to pristine fibers. In this study, for the first time, a new method for producing ESO-carbon composites has been demonstrated using out-of-oven electromagnetic heating using radio frequencies in the range of 1–200 MHz at low input power (less than 25 W).

11:30 AM SF01.10.04 High-Entropy Spinel Ferrite Nanoparticles via Low-Temperature Synthesis for The Oxygen Evolution Reaction Judith Zander, Julia P. Wölfel and Roland Marschall; University of Bayreuth, Germany

High-entropy oxides are a material class that is currently receiving rapidly increasing attention due to the large variety in composition and adaptable properties. Cooperative effects between different metal cations in the crystal structure in addition to entropic phase stabilisation have proven beneficial for electrocatalytic applications. Most synthesis methods, however, require high synthesis temperatures and long synthesis times, and often only yield selected samples in good phase-purity. We herein present for the first time a microwave-assisted low temperature synthesis of earth-abundant high-entropy oxide nanoparticles. Phase-pure spinel ferrites (AFe2O4) of various compositions ranging from one to seven different A-cations were successfully obtained after only 30 min synthesis time at 225 °C. A detailed characterisation of their properties in relation to their composition was performed, and they were also employed for the alkaline oxygen evolution reaction (OER). A partial replacement of Fe by Co moreover shows the high versatility of the synthesis that also allows for the simultaneous variation of the B-ion.


11:45 AM SF01.10.05 Designing Nanostructure Evolution-Self-Assembly in a Complex Concentrated Oxide Huangming Guo1, Christopher Mead2, Marquez Balingit1, Soham Shah3, Xin Wang1, Mingjie Xu4, Ich Tran4, Toshihiro Aoki4, Jack Samaniego1, Kandis Abdul-Aziz3, Lincoln J. Lauhon2 and William J. Bowman1,4; 1University of California, Irvine, United States; 2Northwestern University, Illinois, United States; 3University of California, Irvine, United States; 4Northwestern University, Illinois, United States

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SESSION SF01.11: High Entropy Materials—Catalysis and Beyond
Session Chairs: Ben Breitung and Sheng Dai
Thursday Afternoon, April 25, 2024
Terrace Suite 1, Level 4, Summit

1:30 PM *SF01.11.01
Entropy-Maximized Materials for Catalysis Applications
Sheng Dai1,2; 1Oak Ridge National Laboratory, United States; 2The University of Tennessee, Knoxville, United States

Until recently the design and synthesis of synthetic catalysts have been dominated through enthalpic factors (e.g., charge-charge interactions, charge-transfer interactions). With emergence of high entropy materials (HEMs), another avenue to design and synthesize catalytic materials has opened up. The definition of HEMs is any material that consists of the solid solution of more than five components that allows great flexibility in tuning surface compositions and interfacial functionalities. Here we present the synthesis of high entropy electrocatalysts that potentially outperform the traditional catalysts in energy-related catalysis reactions. The synthesis strategies through entropy maximization will be discussed.

2:00 PM SF01.11.02
Sol-Gel-Derived Ordered Mesoporous High Entropy Spinel Ferrites and Assessment of Their Photoelectrochemical and Electrocatalytic Water Splitting Performance
Marcus Einert, Arslan Waheed1, Stefan Lauterbach1, Maximilian Mellin1, Marcus Rohnke2, Lysander Wagner2, Julia Gallenberger1, Chuanmu Tian1, Bernd Smarsly2, Wolfram Jaegermann1, Franziska Hess1 and Helmut Schlaad3; 1Technical University of Darmstadt, Germany; 2Justus-Liebig-Universität Giessen, Germany; 3Technical University Berlin, Germany; University of Potsdam, Germany

With the introduction of high-entropy oxides (HEO) as a novel class of materials, unexpected and interesting properties have emerged and are currently under investigation. A HEO consists of five or more ionic oxides occupying a single crystallographic site and inducing a high degree of configurational disorder, which increases the entropic contribution to the Gibbs free energy of formation. This extra gain of energy stabilizes the formation of single-phase structures unique and, so far, unpredictable properties. Significant efforts have been devoted to the development of new HEO phases; however, the large majority of synthetic approaches are based on solid-state, rather than sol-gel chemistry allowing only the preparation of micrometer-sized, low-surface-area particles.

With respect to sol-gel synthesis, the precise control of hydrolysis and condensation reactions of the complex precursor is important in order to form uniform structures. The whole reaction system becomes even more complex when an additional component—such as a structure-directing agent—is added. This intricate interplay of reactants, such as control of reaction kinetics, is system becomes even more complex when an additional component—such as a structure-directing agent—is added. This intricate interplay of reactants, such as control of reaction kinetics, is approach has not been reported yet.

For the first time the design of periodically ordered high-entropy-assisted (CoNiCuZnMg)Fe2O4 spinels prepared by dip-coating and EISA process is reported. A synthetic route was developed, utilizing the unique diblock copolymer (poly(ethylene-co-butylene)-block-poly(ethylene oxide), known as KLE, in order to obtain periodically ordered and 15−18 nm sized mesopores within the high-entropy ferrite (HEF) network. The mesostructured HFE electrodes were found to be a direct coating of the nano- and macroscale. Time-over-flight secondary ion mass spectrometry (ToF-SIMS) and electron microscopy analysis verified a homogeneous distribution of all elements within the thin film structure. The mesoporous HFE electrodes were used to study the fundamental impact of a nanoscale framework on the electrocatalytic and photoelectrocatalytic properties. Hence, the HFE electrodes were investigated as an oxidation electro-catalyst and n-type photoanode for solar water oxidation. For both applications the near-metallic electric conductivity, which was related to an electron hopping mechanism induced by the interaction of 3d-states of the inserted transition metals, was found to improve the performance. The photoreponse of HFE photoanodes is limited to owe severe surface recombination as evidenced by intensity-modulated photocurrent spectroscopy.

This novel high entropy oxide class can be considered as interesting candidate and nanostructure for energy applications where high surface-area offerings a large number of (catalytically) active reaction sites are advantageous. [1]


2:15 PM SF01.11.03
Size Controlled Monodisperse Alloy Nanocrystals via Colloidal Synthesis, from Medium to High Entropy and Their Excellent Catalytic Properties
Jasper Clarysse, Yunhua Xing and Vanessa Wood; ETH Zürich, Switzerland

High entropy alloy (HEA) nanocrystals (NCs) are solid solutions of 5 or more elements, while medium entropy alloy (MEA) NCs are solid solutions of 2 to 4 elements. Entropy alloy nanocrystals are an emerging class of materials which show intriguing properties such as enhanced resistance to oxidation and mixing of immiscible elements within nanocrystals. Furthermore, HEA NCs have recently been demonstrated as catalysts in various important reactions (e.g., water splitting and oxygen reduction reaction) with record or near-record activities, attributed to...
synergistic” and “cocktail” effects originating from the combination of multiple metals within the NCs. Yet, the exact structure-activity relationships, leading to the excellent performance of high-entropy alloys in applications such as catalysis remain poorly understood. Furthermore, no synthesis method for highly monodisperse and size-controlled medium and high entropy alloy NCs exists yet. Here we show the colloidal synthesis of highly monodisperse entropy alloy NCs [1-2], employing oleylamine as a suitable reaction solvent and non-poisoning L-type ligand. Furthermore, we extend our synthetic method to achieve MEA NCs constituting of non-precious, environmentally benign metals (e.g., Ni-Zn) and we report the first size-tunable synthesis of HEA NCs (e.g., 1.8 nm, 2.5 nm, and 3.5 nm HEA NCs) [3]. The synthesis method is facile and easily scalable. We demonstrate that the resulting nanocrystals possess size-dependent catalytic properties and exhibit better catalytic performance compared to monometallic nanocrystals. We achieve MEA and HEA nanocrystals with excellent catalytic properties and study these for different reactions (e.g. semihydrogenation of alkenes and hydrogen-evolution reaction). We understand the crystallographic and electronic structure of the nanocrystals using a range of advanced characterization techniques (high resolution transmission electron microscopy and synchrotron-based X-ray diffraction, total X-ray scattering and X-ray absorption spectroscopy) and using density functional theory calculations and reveal the relationships between catalytic performance and structure of the MEA and HEA NCs.

Rapid Down-Selection of Novel High-Entropy Materials and Insights into their Characteristic Energy Scales from Temperature-Dependent Elastic Properties

**SESSION SF01.11: Computational and Experimental Techniques to Study the Mechanical and Thermal Properties of High-Entropy Alloys**

**4:00 PM SF01.12.02**

Rapid Down-Selection of Novel High-Entropy Materials and Insights into their Characteristic Energy Scales from Temperature-Dependent Elastic Properties

**Christopher Mizzi**, Tannor Munro1, Osman El-Atwami2, Saryu Fensin3 and Boris Maiorov3; 1Los Alamos National Laboratory, United States; 2Pacific Northwest National Laboratory, United States

High-entropy materials have generated much interest owing to their exceptional performance and high tunability. However, there are significant challenges in optimizing high-entropy compositions for tailored applications, such as in nuclear reactors, stemming from the immense size of the high-entropy design space. There is a pressing need for rapid, quantitative property assessments to identify promising high-entropy candidates, down-select compositions for further study, and provide experimental inputs to facilitate model development. One enticing property to examine in this context is elasticity. Elastic constants describe the extent to which materials resist elastic deformation, providing important information on mechanical performance as well as microscopic details about the nature of bonding and characteristic energy scales in materials. These features mean elastic constants naturally connect experiment and theory, making them prime candidates to serve as a benchmark for materials design, model development, and model validation.

In this talk, I will share elastic constant measurements on a range of refractory high-entropy alloys at ambient conditions to exemplify how elastic constants and ultrasonic attenuation can be used to rapidly identify promising high-entropy compounds for further study. Then, I use elastic constant determination down to 2K to explore the effects of composition on characteristic phonon energy scales (e.g., Debye temperature), anharmonicity, and mechanical performance. These results are compared with theoretical predictions. Resonant ultrasound spectroscopy (RUS) is used for these experiments because of its ability to non-destructively determine the entire elastic constant tensor from a single measurement with high accuracy and precision. This approach, which entails extracting elastic constants from mechanical resonant frequencies, is amenable to all high-entropy materials, from metals to ceramics, compatible with any amount of crystalline anisotropy or texture, and capable of providing rapid feedback on novel high-entropy materials. As such, elastic constant determination with RUS is ideal to rapidly identify promising high-entropy materials, examine their functional properties, and determine key energy scales to incorporate in predictive models.
Critical Assessment of Mass and Lattice Disorder in Thermal Conductivity Prediction for Medium and High Entropy Ceramics

Yuyuan Wang, Guoqiang Lan and Jun Song; McGill University, Canada

Medium and high entropy ceramics, with their distinctively disordered structures, exhibit ultra-low thermal conductivity and high temperature stability. These properties make them strong contenders for next generation thermal barrier coating (TBC) materials. However, predicting their thermal conductivity has been challenging, primarily due to their unique phonon scattering mechanisms. Apart from the conventional phonon-phonon scattering mechanism, the phonon-disorder scattering, comprising both mass and force disorder, are also expected to make significant contribution in determining the thermal conductivity of medium and high entropy ceramics. However, it remains challenging to quantify the phonon-disorder contribution, particular in the aspect of force disorder. Here we demonstrated a relationship between the lattice disorder, a quantity more readily calculable, with force disorder, rendering it possible to substitute the force disorder by lattice disorder. Based on this relationship and drawing inspiration from Klement’s equation of static imperfection, we have developed a model that quantitatively assess the connection between disorder and thermal conductivity. Applying our model to the medium/high entropy rocksalt and pyrochlore oxides as the representative, we found good alignment between the theoretical predictions and experimental measurements of thermal conductivities, confirming the validity of our model. The model developed offers a critical predictive tool for rapid screening of TBC materials based on medium and high entropy ceramics.

Local Chemical Fluctuation and Lattice Thermal Conductivity of High-Entropy Thermoelectric Materials

Wu Wang, Shixuan Liu, Yan Wang and Jiaqing He; Southern University of Science and Technology, China

High-entropy materials, which consist of multiple elements occupying the same crystallographic site, have emerged as the promising materials for a variety of applications [1,2]. With the mutual interaction of different elements, local chemical fluctuation arises in high-entropy structures and largely enhances the properties of various materials including metallic alloys [3], Li-ion batteries [4], and catalysts [5]. Recently, this high-entropy strategy has also been applied to enhance the performance of thermoelectric materials with the combination of multiple elements [6,7]. The local chemical fluctuation could dampen the propagation of heat-carrying phonons and thus largely reduce lattice thermal conductivity of thermoelectric materials.

HiPIMS deposition of high-entropy alloy films for applications in tribological coatings

Yilu Chang; Tokyo Institute of Technology, Japan

The deposition of high-entropy alloy (HEA) films by plasma immersion ion implantation and superfusion (HiPIMS) is studied for tribological applications. HEAs are known for their excellent mechanical properties, such as high hardness and wear resistance, which are beneficial for applications in tribology. However, the deposition of HEA films by conventional sputtering techniques often results in poor adherence and low mechanical properties due to the complex phase compositions.

In this work, HEA films are deposited by HiPIMS and their microstructure, compositional profile, and mechanical properties are characterized. The effects of deposition parameters, such as power, gas flow rate, and substrate temperature, on the film properties are investigated. The results show that HiPIMS deposition enables the fabrication of dense and adherent HEA films with tailored mechanical properties. The wear properties of the deposited films are tested using a pin-on-disc tribometer, and the results indicate improved tribological performance compared to conventionally sputtered films.

References


Investigating High Temperature Thermal Properties of Rare Earth Oxides for Thermal Barrier Coatings

William T. Riffle, Hunter Schonfeld, Kristyn Ardrey, Prasanna Balachandran, Beth Opila, Patrick E. Hopkins and Saman Zare; University of Virginia, United States

Rare earth oxides (REOs) show promising thermal properties required for next generation thermal barrier coatings (TBCs) for ultrahigh temperature applications (~1500 °C). TBCs mitigate conductive heating between hot components by reducing thermal conductivity through increased phonon-phonon scattering. New research aims to explore the fundamental mechanisms for this reduction and explore other properties of interest such as melting temperature and emissivity.

In this work, we perform a series of thermal and optical studies via pump-probe thermoreflectance, laser radiometry, and spectroscopic ellipsometry to elucidate temperature-dependent thermal properties of REOs. With a novel laser-based metrology, thermal conductivities, melting temperatures and emissivities of ceramics over 2000 °C can be measured nondestructively. Understanding these trends is of utmost importance in choosing REOs that can endure cycling to operating temperatures. Additionally, through ellipsometry, the lifetimes of optical phonons can be understood. Anharmonic scattering dominates thermal transport at high temperatures so measuring lifetimes with changing temperature is important to understand fundamental energy transport in REOs. By investigating pertinent physical scattering mechanisms at relevant temperatures, we deconvolute key design considerations for next generation TBCs.

FIRST-PRINCIPLES CALCULATIONS OF STRUCTURAL TRANSITIONS WITHIN MULTI-PRINCIPAL COMPONENT TRANSITION METAL CARBIDES

Theresa Davey1,2 and Ying Chen1; Bangor University, United Kingdom; 2Tohoku University, Japan

High-entropy or multi-principal component ultra-high temperature ceramics (UHTCs), such as rocksalt structured MC1-x, where the cation M is an equiatomic or non-equiatomic mixture of metallic elements including Ti, Zr, Hf, Nb, and Ta, and the anion C is carbon, have recently generated significant interest due to their potential improved or tuneable properties such as melting point, hardness, ductility, and oxidation resistance. The single metallic element UHTC carbides, such as zirconium carbide, are known to have a wide range of stoichiometry facilitated by significant numbers of carbon vacancies (up to around 50% of the carbon atoms), where in different parts of the phase space, the vacancies exhibit long-range ordering, short-range ordering, or are randomly distributed. Until now, there have been no systematic investigations varying carbon stoichiometry in multi-principal cation carbides, either experimentally or theoretically.

Individually, all the MC1-x carbides have a tendency to form long-range vacancy-ordered phases at low temperature, although these are extremely challenging to experimentally synthesise. In single cation transition metal carbides (e.g. ZrC1-x, HfC1-x), the short- and long-range carbon vacancy ordering is driven by different local bonding surrounding different vacancy cluster configurations. However, similar but slightly different trends are observed in group IV and group V transition metal carbides, resulting in different symmetries, for example low temperature M2C (M = Ti, Zr, Hf) has a cubic Fd-3m structure, whereas M6C (M = Ta) has a trigonal P-3n1 structure.

This work uses first-principles calculations to explore multiatomic mixing (binary, ternary, quaternary, and quinary) on the metallic element lattice at different carbon stoichiometries. Within this, disordered vacancies, and various vacancy-ordered structures were considered. Special Quasirandom Structures (SQS) were generated for each composition, to provide a supercell approximation of random mixing. Density functional theory (DFT) calculations were used to obtain the ground state energy and structural and electronic properties. The atomic bonding is investigated, and trends are identified by considering the local atomic environments and cluster configurations.

The effects of the multi-principal cation lattice has on the carbon vacancy ordering on the anion lattice are explored, at absolute zero and considering finite temperature effects. The most stable crystal structures are identified for various multi-cation actions at different carbon stoichiometries. Miscible and immiscible mixtures are identified, where approximate temperatures of miscibility gaps are determined using the Bragg-Williams configurational entropy approximation for ideal mixtures. The tendency for phase separation is compared in equivalent composition

SESSION SF01.13: High Entropy Carbides, Borides, and Silicates

Session Chairs: Theresa Davey and Scott McCormack

Friday Morning, April 26, 2024

Terrace Suite 1, Level 4, Summit

8:30 AM SF01.13.01

First-Principles Calculations of Structural Transitions Within Multi-Principal Component Transition Metal Carbides

Theresa Davey1,2 and Ying Chen1; Bangor University, United Kingdom; 2Tohoku University, Japan

High-entropy or multi-principal component ultra-high temperature ceramics (UHTCs), such as rocksalt structured MC1-x, where the cation M is an equiatomic or non-equiatomic mixture of metallic elements including Ti, Zr, Hf, Nb, and Ta, and the anion C is carbon, have recently generated significant interest due to their potential improved or tuneable properties such as melting point, hardness, ductility, and oxidation resistance. Single metallic element UHTC carbides, such as zirconium carbide, are known to have a wide range of stoichiometry facilitated by significant numbers of carbon vacancies (up to around 50% of the carbon atoms), where in different parts of the phase space, the vacancies exhibit long-range ordering, short-range ordering, or are randomly distributed. Until now, there have been no systematic investigations varying carbon stoichiometry in multi-principal cation carbides, either experimentally or theoretically.

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multi-cation vacancy-disordered and vacancy-ordered carbides. Approximate order-disorder transition temperatures are obtained for mixed-cation substoichiometric carbides and compared with the miscibility gaps in the same system. On this basis, the possibility of synthesising certain vacancy-ordered multi-principal cation compounds is revealed, alongside the required range of synthesis temperatures.

9:00 AM SF01.13.02
Computational Investigation into Synthesis of Transition Metal Borides Himanshu Shekhar and Aravind Krishnamoorthy; Texas A&M University, United States

Borides of transition metals and high-entropy alloys offer novel opportunities to design materials that demonstrate phase stability, high strength, and thermal oxidation resistance at high temperatures and under extreme conditions. Identifying mechanically strong and chemically inert transition metal borides requires an understanding of the synthesizability of different transition metal borides, as well as their mechanism of growth during boriding of such metals. We performed ab initio Density Functional Theory simulations to quantify phase stability, formation energies of point and extended defects, and point defect migration barriers in crystalline borides of transition metals and their alloys. A point defect model based on the computed defect concentrations and ionic mobilities was used to explain the experimentally observed thicknesses of boride films formed by the boriding of different transition metals and alloys. Thermodinamic (formation energies and stability) and kinetic (energy barriers and mobilities) data from these ab initio simulations were also used to create a graph neural network model for the screening of compositional phase space of high-entropy borides to identify promising candidates with high phase stability and synthesizability.

9:15 AM SF01.13.03
Predicting The Synthesizability and Properties of Disordered Materials from First-Principles Cormac Toher; The University of Texas at Dallas, United States

The successful development and manufacturing of new materials, for applications ranging from wear resistant coatings for cutting tools and thermal protection barriers in aerospace engineering to new catalysts and photovoltaics, as well as materials for batteries and electronics, depends on computational thermodynamics to predict synthesizability and stability. Thermodinamic models for synthesizability must incorporate entropy, which is particularly important at high temperature for multi-element materials [1, 2]. Descriptors and thermodinamic models have been developed based on the thermodinamic density of states extracted from ensembles of ordered calculations in the AFLOW repository [3, 4] to predict the synthesizability of new disordered materials such as high entropy carbides [5, 6]. Similar methods are now being combined with machine-learning to investigate high-entropy rare-earth silicates for thermal and environmental barriers in gas turbines [7].


10:00 AM BREAK

SESSION SF01.14: High Entropy Intermetallics and Alloys

Session Chairs: Alannah Hallas and Cormac Toher
Friday Morning, April 26, 2024
Terrace Suite 1, Level 4, Summit

10:30 AM SF01.14.01
Boron Intersitial and Boride Strengthened Grain Boundary for Toughening Refractory High-Entropy Alloys Ping-Hua Ko, Ya-Jing Lee and Shou-Yi Chang; National Tsing Hua University, Taiwan

Refractory high-entropy alloys exhibit a high mechanical strength and an excellent structural stability at elevated temperatures, and are of great potential for applications to aerospace and nuclear power components. However, the drawback of poor grain boundary cohesion and consequent early brittle intergranular fracture renders their practical applications limited. According to the literature, boron interstitials (or borides) have been verified to improve the cohesion strength of grain boundaries and thus the ductility of some intermetallic compounds such as nickel aluminide(s). Introducing boron interstitials (or forming multicomponent borides) particularly at grain boundaries was hence considered in this study for enhancing grain boundary cohesion and toughening refractory high-entropy alloys. A very small amount (0.1 at.%) of boron was added in arc-melted Hf0.5Mo0.5Nb0.5Ti0.5Zr0.5 refractory high-entropy alloys, and the microstructure, compositions and crystallographic orientations of the alloys were characterized. Macroscale compressive tests were conducted for measuring the stress-strain response of the alloys, and micropillar compressive tests and indentations were carried out for measuring the strength of grains and grain boundaries. Microstructure observations indicated that elemental boron was uniformly distributed in the refined single-phase, solid-solution grains, while some nanosized boride particles were dispersed at the grain boundaries. With the addition of boron, the hardness of weak grain boundaries (about 5.0 GPa) was markedly improved to the equivalent level of grain interiors (about 6.2 GPa). While the yield strength of the boron-added alloys did not change (about 1450 MPa), the ultimate compressive strength effectively increased from 1690 to 2240 MPa at a higher work hardening rate. The compressive strain increased from 20-25% to 35-40%, attributable to the inhibited boundary decohesion-caused brittleness as the distinct transition of intergranular-to-transgranular fracture. Micropillar compression tests suggested that the grain boundaries of the alloys without boron early decohered at a stress of below 700 MPa, whereas those with boron did not fracture even after the adjacent grains yielded. Owing to the high charge-density-enhanced grain boundary cohesion, the boron-added alloys also showed a high structural stability at elevated temperatures, with a retained strength of 1190 and 990 MPa at 600 and 800°C, respectively.

10:45 AM SF01.14.02
Predictive Modelling of The Structure and Phase Stability of High-Entropy Materials: Case Study of Al0.5Cr0.5Fe0.5Co0.5Ni Christopher D. Woodgate1, Laura H. Lewis2,2 and Julie Staunton1;
1University of Warwick, United Kingdom; 2Northeastern University, United States

Advancing both fundamental understanding and technological application in the rapidly developing field of high-entropy materials, computational-forward modelling approaches are an important tool to help guide experiment. Starting from a given combination of constituent elements, we would like to be able to predict a material’s crystal structure, its thermodynamic stability, as well as the nature of emergent atomic short- and long-range order, as this will enable us to go on to predict subsequent macroscopic materials properties. Here we present results from a first-principles-based, all-electron Landau theory which has previously been used with success to study the Cantor alloy and its derivatives [1, 2], as well as the refractory high-entropy alloys [3]. We study the Al0.5Cr0.5Fe0.5Co0.5Ni system for 0 ≤ x ≤ 2 and demonstrate successful reproduction of the experimentally observed crystal structure and phase behaviour of this material. We successfully predict the A1+B2 coexistence region of the phase diagram, explain the lack of observation of an atomically disordered A2 phase, and give insight into the preferred low-temperature atomic arrangements. As the methodology is first-principled, we are able to explain ordering tendencies in terms of materials’ underlying electronic structure, and pull out qualitative rules to explain ordering tendencies in these complex systems.

Acknowledgements
We gratefully acknowledge the support of the UK EPSRC, Grant No. EP/W021331/1. C.D.W. is supported by a studentship within the UK EPSRC-supported Centre for Doctoral Training in Modelling of Heterogeneous Systems, Grant No. EP/S022848/1. This work was also supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences under Award Number DE SC0022168 (for atomistic insight) and by the U.S. National Science Foundation under Award ID 2118164 (for advanced manufacturing aspects).

References

11:00 AM SF01.14.03

Final_Abstract_Book_PF_Sessions_mrsspring2024_20-Jun-2024-14-29-03 (1).html[6/20/2024 2:34:09 PM]
Combinatorially sputtered thin films can be leveraged as a rapid, materials discovery process in mechanical alloy design. Ta₆Ti₅Hf₂Zr₂ thin films were synthesized via combinatorial sputtering from pure Ta, Ti, Hf, and Zr targets. The substrate was not rotated to generate compositional gradients where 12.4±w=71.6, 6.40−c=55.6, 4.22−c=58.8, 7.25−c=48.9 over a 100 mm diameter substrate. The crystal structure, phase fraction, film morphology, mechanical (i.e. modulus and hardness), optical (i.e. n and k), thermal (i.e. phase stability, CTE, and thermal conductivity), and corrosion properties (i.e. corrosion current and rates) are all correlated to the Ta₆Ti₅Hf₂Zr₂ composition. Temperature dependent x-ray diffraction (TDXRD) reveals the thermal stability of the material system. TDXRD has shown the as-deposited material library is primarily stable in a single HCP phase below 60 at. % Ta at room temperature but will form increasing amounts of a BCC phase at elevated temperatures. Nanoindentation of as-deposited films shows good agreement between experimental, solid solution estimations of hardness via a simple rule of mixtures from bulk elements, and correlated to a few up-scaled bulk samples. Thin film modulus shows good agreement with bulk rule of mixture estimations after accounting for thin film substrate effects via King's correction. As-deposited and annealed film properties are compared. Compositions with an optimal combinations of the aforementioned properties were then upscaled to bulk materials for further investigation.

11:15 AM SF01.14.04
Accelerated Discovery of Structural Materials for Harsh Environments Rameshwari Naorem1,2, Hailong Huang1, Gaoyuan Ouyang1, Prashant Singh1, Duane D. Johnson1,2, Jun Cui1, Ryan T. Ort1, Iver E. Anderson1,2, Nicolas Arigbay1 and Brandon Krick1; 1Ames Laboratory, United States; 2Iowa State University of Science and Technology, United States; 3Florida A&M University, United States

Multi-principal-element alloys (MPEA) have emerged as a promising group of advanced materials with unprecedented combinations of mechanical properties compared to conventional alloys. Materials that can tolerate harsh environments and retain high strength at elevated temperatures are needed to enable greater efficiency in applications including nuclear reactors, hydrogen combustion turbines, bearings, and hypersonic vehicles. We will present results from materials design efforts focused on refractory alloys that rely on high-throughput synthesis and characterization methods like additive manufacturing, tribology-based mechanical testing, and electronic-structure modeling. Discussion topics will include rapid screening of thermomechanical properties using surface (scratch)-based techniques to assess hardness, fracture toughness, and tensile ductility. We will also present preliminary results from composition tailoring of MPEA to understand and control the impacts of hydrogen exposure on selected refractory MPEAs and to develop alloy design criteria for mitigating hydrogen embrittlement.

11:30 AM SF01.14.05
Bridging the Gap between Modeling and Characterization to Unravel Short-Range Order and Properties of Si-Ge-Sn-Pb Alloys Shunda Chen, Xiaochen Jin and Tianshu Li; George Washington University, United States

Group IV concentrated alloys composed of Si-Ge-Sn-Pb are promising candidates for mid-infrared photonics owing to their tunable band gaps, low-cost, and CMOS-compatibility. Although group IV alloys have been long conceived as a random solid solution, our recent ab initio-based statistical sampling predicted substantial short-range order (SRO) behaviors in group IV alloys 1-4. The structural complexity was further shown to yield a substantial impact on the underlying electronic 1-3, topological 4, and transport properties of group IV alloys. Although SRO may have a complicated implication on material properties, it also opens an emerging opportunity for engineering SRO to harvest new functionalities that are challenging to achieve through traditional heterojunctions. Emerging characterization evidence based on EXAFS5, Raman6, AP7 and 4D-STEM support our prediction of SRO, but important questions need to be addressed regarding the actual structures, spatial domain size, and its distribution, and corresponding changes in the properties of SRO, before a practical strategy can be employed. The explicit answers to these questions require synergistic efforts from both characterization and modeling. Here I will discuss our ongoing theoretical effort to close the gap between theory and characterization to enable deciphering the fine structural details of complex alloys. We have developed a highly accurate, highly efficient machine-learning potential (MLP) based on neuroevolution potential framework for group IV systems. The developed MLP is shown to reach a DFT-level accuracy by exhibiting a root mean squared error of energy < 1 meV/atom with respect to the DFT training data set and more importantly, enables a side-by-side comparison with AP and 4D-STEM on the same scale. Using this development, we discovered the spatial structural heterogeneity in group IV alloys. In particular, we show that structural details at a fine level, as reflected by the distributions of both atomic SRO parameter and spatial SRO domains, are vital for the underlying electronic structures of group IV concentrated alloys.

This work is supported by Department of Energy, Office of Basic Energy Sciences under Award No. DE-SC0023412.


11:45 AM SF01.14.06
Fabrication and Characterization of Two-Dimensional High-Entropy Sulfides and Tellurides Yingchao Yang; University of Missouri, United States

Since the discovery of graphene monolayers by mechanical exfoliation in 2004, many other two-dimensional (2D) materials have been synthesized, such as transition metal dichalcogenides (TMDs), hexagonal boron-nitride (h-BN), black phosphorous. Another category of materials, high entropy alloys (HEAs) are constructed by the combination of multiple principal elements at an equimolar or near-equimolar fraction. HEAs offer an extensive combinatorial space facilitating superior functionalities that are generally lacking in conventional alloys composed only of one or two principal elements. The combination between 2D materials and HEAs results in new 2D high-entropy materials (2D HEMs). Even though 2D HEMs have significant potential towards catalysis and energy storage, the rationale and criterion for designing 2D HEMs and demonstration of feasibility in synthesized 2D HEMs are still missing.

In this presentation, we will demonstrate the successfully synthesized five-metal-element sulfide and tellurides. Sulfides have been synthesized through chemical vapor deposition (CVD) method and tellurides have been obtained via the conventional solid-state reaction (SSR) approach. Advanced characterization techniques have been performed to confirm that uniform elemental distribution and single phase 2D HEM have been achieved. The designed and fabricated 2D HEMs adds an exceptional family member to the fast-growing field of 2D materials.

SESSION SF01.15: Virtual Session: High Entropy Materials
Session Chairs: Ben Breitung, Scott McCormack and T. Zac Ward
Tuesday Morning, May 7, 2024
SF01-virtual

10:30 AM **SF01.15.01
High-Throughput Experimentation for The Exploration of High Entropy Materials: From Alloys to Oxides and Nitrides Alfred Ludwig1,2,1; Ruhr-University Bochum, Germany; 2Ruhr-Universität Bochum, Germany

Discovery of new materials is a key challenge in materials science. New materials for sustainable production/storage/conversion of energy carriers are necessary to improve existing and to enable future energy systems. Compositionally complex materials, frequently called high entropy materials, offer a vast multidimensional search space, which provides opportunities for discovering new materials. Next to alloys compounds such as oxides and nitrides are of interest. However, efficient methods for the exploration and exploitation of this multidimensional search space are necessary, especially as oxides and nitrides need more sophisticated synthesis methods such as reactive sputter deposition. Here, the integration of high-throughput thin-film combinatorial materials science methods with simulation and materials informatics (1) is presented as an effective means to produce large datasets on new materials, which enables mastering of
Micro-Focused X-Ray Absorption Spectroscopy Studies of Plutonium Materials
Sarah Hickam
10:30 AM
*SF02.01.01

Electrospun High-Entropy Spinel Oxides as Catalysts for as Electrocatalysts for Oxygen Evolution in Alkaline Environment
Saveria Santangelo; Mediterranea University, DICEAM, Italy

The generation of H₂ via the electrochemical splitting of water is a promising and sustainable technology. Nonetheless, the oxygen evolution reaction (OER) still represents the bottleneck of the process. Spinel-structured transition metal (TM) oxides have shown great potential as an alternative to platinum group metal-based electrocatalysts as they are Earth-abundant, inexpensive and stable. Among them, those based on the high-entropy concept, benefiting from the synergy among their multiple-metallic components, are in focus due to their interesting performance in various energy applications [1,2], including the OER in alkaline environment.

This contribution focuses on the case of electrospun spinel-type high-entropy oxide (HEO) nanofibers (NFs), which thanks to their granular architecture are suitable to the preparation of ink-jet printable OER electrocatalysts [3]. It presents the results of the evaluation of a large set of HEO NFs with oxygen-deficient surface as electrocatalysts in alkaline medium. HEO NFs based on different equimolar TM combinations, are prepared under different calcination conditions and characterized by a combination of benchtop analytical techniques to investigate the complex and interdependent changes in the morphology of the fibers, crystallinity and inversion degree of the spinel oxide, concentration of the oxygen-vacancies, cation distribution in the lattice produced through the formation of H₂O, and the relationships with the different electrochemical properties of the fibers. The electrocatalytic performance of HEO NFs are discussed in terms of the most common descriptors, namely outer 3d-electron number, e_g filling and occupation of 16e sites.


SYMPOSIUM SF02

Actinide Materials
April 23 - April 25, 2024

Symposium Organizers
Edgar Buck, Pacific Northwest National Laboratory
Sarah Hernandez, Los Alamos National Laboratory
David Shuh, Lawrence Berkeley National Laboratory
Evgenia Tereshina-Chitrova, Czech Academy of Sciences

SESSION SF02.01: Spectroscopy/Advanced Characterization
Session Chairs: Liane Moreau and David Shuh
Tuesday Morning, April 23, 2024
Terrace Suite 2, Level 4, Summit

10:30 AM *SF02.01.01
Micro-Focused X-Ray Absorption Spectroscopy Studies of Plutonium Materials
Sarah Hickam¹, Arjen van Veenelen¹, Daniel Olive¹, Kasey Hanson¹, Raymond Atta-Fynn¹, Nicholas Edwards² and Samuel Webb²; ¹Los Alamos National Laboratory, United States; ²SLAC National Accelerator Laboratory, United States

Synchrotron X-ray absorption spectroscopy (XAS) is an established technique for studying the local structure of plutonium materials, including oxides and metals. Modern imaging and high-resolution techniques provide detailed information that may elucidate questions regarding the fate of impurities with different Pu oxidation conditions and may also find utility in nuclear forensics investigations. Combining XAS with x-ray fluorescence (XRF) mapping provides the ability to quickly locate particles or areas of interest with up to 1 μm spatial resolution and then obtain local structure information from individual points. In this work, we apply micro-focused XRF-XAS techniques to the study of common impurities in plutonium oxides, such as gallium,
The Auger Parameter and Plutonium
Paul Roussel; AWE, United Kingdom

The Auger parameter, $\alpha$, the sum of the binding energy of the most prominent core level transition and the kinetic energy of the Auger transition, as measured in a single X-ray Photoelectron Spectrum, can afford chemical state / chemical fingerprinting, non / local screening and initial / final state information. The use of the Auger parameter and the related chemical state plot offer advantages. [1] Specifically, the chemical state / environment determination over $\alpha$, the Auger parameter, indicates the state of the system with electrons being moved from the occupied 4d states to unoccupied 5f states. For soft X-rays, the peak separations are small, allowing the doublet peaks to be collected together, in a single spectrum. The intensity calibration is intrinsic, within some small variations such as those due to storage ring beam current decay and fluctuations and other higher order effects. For tender and hard X-rays, the peak separations tend to be larger, often requiring two separate spectra and some sort of new normalization, especially for High Energy Resolution Fluorescence Detection (HERFD) XAS spectra. It will be shown that the step heights in the EXAFS regime can be used as a cross calibration between the $M_4$ and $M_5$ spectra. If two well characterized cases can be used as controls. (EXAFS is Extended X-ray Absorption Fine Structure, typically about 20 eV or more above the white-lines (sharp, intense peaks) at threshold, e.g. the 5f peaks.) Thus, a quantitative analysis method has been developed that allows the cross calibration of separate Uranium $M_4$ and $M_5$ X-ray absorption spectra (XAS), in particular those collected with the new High Energy Resolution Fluorescence Detection (HERFD) method. With this method, it is now possible to generate experimental Branching Ratio (BR) values from the $U$ $M_4$ XAS HERFD data.

1. J. G. Tobin, S. Nowak, S.-W. Yu, R. Alonso-Mori, T. Kroll, D. Nordlund, T.-C. Weng, Dimosthenis Sokaras; 2University of Wisconsin-Oshkosh, United States; 3SLAC National Accelerator Laboratory, United States; 4Lawrence Livermore National Laboratory, United States

Historically, Branching Ratio measurements with X-ray Absorption Spectroscopy (XAS) and related techniques have played a key role in the advancement of the understanding of 5f electronic structure. [1] Specifically, the chemical state / environment determined $\alpha$, and the Auger parameter in the Auger transitions over $\alpha$, of the actinide elements with electrons being moved from the occupied 4d states into unoccupied 5f states. For soft X-rays, the peak separations are small, allowing the doublet peaks to be collected together, in a single spectrum. The intensity calibration is intrinsic, within some small variations such as those due to storage ring beam current decay and fluctuations and other higher order effects. For tender and hard X-rays, the peak separations tend to be larger, often requiring two separate spectra and some sort of new normalization, especially for High Energy Resolution Fluorescence Detection (HERFD) XAS spectra. It will be shown that the step heights in the EXAFS regime can be used as a cross calibration between the $M_4$ and $M_5$ Spectra, if two well characterized cases can be used as controls. (EXAFS is Extended X-ray Absorption Fine Structure, typically about 20 eV or more above the white-lines (sharp, intense peaks) at threshold, e.g. the 5f peaks.) Thus, a quantitative analysis method has been developed that allows the cross calibration of separate Uranium $M_4$ and $M_5$ X-ray absorption spectra (XAS), in particular those collected with the new High Energy Resolution Fluorescence Detection (HERFD) method. With this method, it is now possible to generate experimental Branching Ratio (BR) values from the $U$ $M_4$ XAS HERFD data.


Site-Specific Morphological and Chemical Analysis of Nuclear Materials
Brandon W. Chung1, Alexander A. Baker1, Scott Donald2, Tian Li2, Rachel Lim2, Uday Mehta2, Debra L. Rosas3, Donya Servando-Williams3, Vanna Son3, Nicholas Cicchetti3, Alexander Ditter4 and David K. Shuh3; 1University of Nevada, Las Vegas, United States; 2University of Nevada, Las Vegas, United States; 3University of Nevada, Las Vegas, United States; 4Lawrence Berkeley National Laboratory, United States

Nuclear forensics requires accurate identification of distinguishing material characteristics to delineate the material’s origin-to-interdiction information. We developed the focused ion beam (FIB) methodology to reveal entraped material such as internal morphological and chemical features within the surface/subsurface and bulk of nuclear materials. Our recent effort also established the capability of using the FIB-based micromanipulation technique to select, isolate, and extract a site-specific microscopic feature from bulk plutonium (Pu) and uranium (U) materials. Using a combination of scanning electron microscopy (SEM), transmission electron microscopy, three-dimensional (3D) spatial modeling, and synchrotron-based X-ray spectromicroscopy, we identified distinguishing morphological and chemical characteristics that are attributable to the material’s provenances. Variations in the internal chemical composition and morphological structure were found to distinguish materials from different origins, processing, and environmental exposures. The information is of potential use in identifying material characteristics related to the provenance, process, and pathways of interdicted nuclear materials.

In order to clarify accident progression scenarios in the Fukushima NPP accident, it is essential to evaluate the behavior of fuel heated to high temperatures, and information on fuel behavior in the "ultra-high temperature region (around melting point)" is required. However, there is little information on the structural and electronic properties of actinides in this high temperature region. In this study, we developed a new measurement cell that enables high-temperature heating and constructed an in-situ observation system using synchrotron radiation XAFS and XRD to obtain information on the structure and electronic state of materials around the melting point. The validity of machine learning was also verified by comparison with the structural and electronic state information predicted by theoretical calculations using NN potentials. In this study, we mainly report the results obtained by synchrotron radiation analysis of yttrium-stabilized zirconia around the melting point as first step. The measurements were performed at the JAEA beamline BL22XU at SPring-8. The incident light intensity was measured with an ion chamber placed just in front of the sample, a CCD detector and imaging unit for X-ray diffraction, and a silicon drift detector for XAFS, each of which was placed horizontally displaced from the optical axis downstream or upstream of the sample, taking into account the position of the window in the measurement chamber. The heating system was a pulsed current heating furnace using W as the electrode, which is capable of performing structural analysis experiments up to ~3500K. In the radial structure function by XAFS, the distance of the first peak originating from Zr-O tends to shorten as the temperature increases, especially around 2000 K. This indicates a phase transition of zirconia, corresponding to the phase transition of zirconia from Tetragonal to Cubic. On the other hand, the second peak originating from Zr-Zr shows a trend of increasing distance as a whole, and the peak became so small that its order is almost unobservable near the melting temperature. The energy of the absorption edge also showed a tendency to shift to the lower energy side with the structural change due to the temperature increase.

1:30 PM | SF02.02.01
Application of Ultra-High Temperature XAFS Measurement System for Actinide Materials
Yuichiro Yaita; Japan Atomic Energy Agency, Japan
The small absorption cross sections ($\varepsilon < 10 \text{ M}^{-1} \text{ cm}^{-1}$) characteristic of Laporte-forbidden transitions in the f-elements have limited the practical implementation of lanthanide and actinide nanoparticles in devices for applications ranging from solar capture to sensing. While various strategies designed to circumvent the problems of low f-f oscillator strengths have been investigated, comparatively little work has explored the utility of organic ligands with high absorption coefficients ($\varepsilon \approx 10^{2} - 10^{3} \text{ M}^{-1} \text{ cm}^{-1}$) in sensitizing excited states in f-element macromolecules and nanocrystals. Our approach investigates actinide hybrid architectures, in which sensitization is achieved with aromatic antenna functioning as terminal light absorbers to convert light into luminescence with unusually high external quantum yields. In addition, chiral constructs allow for luminescence circular polarization for sensing applications and forensic determination. Energy transfer mechanisms in these actinide compounds and particles will be discussed, with an emphasis placed on the generality of this material architecture for realizing ligand-pumped, photon conversion and polarization.

2:30 PM SF02.02.03
Elastic Properties of Pu Alloys using Resonant Ultrasound Spectroscopy
Boris Maiorov; Los Alamos National Laboratory, United States

Determining the elastic properties of Pu alloys and their changes as a function of temperature and time is a powerful tool to study thermodynamic and dynamic changes. Temperature dependence informs the nature of the free energy of the different phases, as elastic moduli are fundamental thermodynamic susceptibilities and connect directly to thermodynamics, electronic structure, and mechanical properties. Changes occurring as a result of self-irradiation change the elastic moduli and affect thermodynamic phase transitions. In turn, these changes are translated to changes in the hardness and brittleness of the compound. Similarly, sound attenuation provides information about dynamic processes such as dissipation associated with defect movement, annealing or re-crystallization. Thus, measurements of elastic moduli and sound attenuation help determine the origin of the phenomena found in $^{235}$Pu and its Ga alloys.

By measuring the mechanical resonance frequencies of a sample, the Resonant Ultrasound Spectroscopy (RUS) technique can extract with extreme precision and accuracy the elastic moduli without corrections. Using RUS we perform time- and temperature-dependent measurements of the mechanical resonance frequencies of polycrystalline Pu with different Ga concentrations. From these measurements, elastic moduli and the sound attenuation can be extracted. I will show the changes in elastic moduli and sound attenuation with time for samples with different ages and Ga concentrations.

2:45 PM SF02.02.04
Soft and Tender X-Ray Synchrotron Radiation Spectromicroscopy for Nuclear Forensics
David K. Shah, Alexander Ditter, Nicholas Ciechetti, Joe Brackbill, Artem Gels, Rachel Lim, Shohini Sen-Britain, Debra L. Rosas, Alexander A. Baker, Scott Donald and Brandon W. Chung; Lawrence Berkeley National Laboratory, United States; University of Nevada, Las Vegas, United States; University of California, Berkeley, United States; Lawrence Livermore National Laboratory, United States

The development of new methods and signatures is crucial for nuclear forensics activities remain effective. Synchrotron radiation analysis offers one way to extend the scope of nuclear forensics investigations in elemental, chemical, and structural analysis which all can be done in imaging modes that in some cases, reaches to the nanoscale. X-ray techniques are particularly useful because of their elemental specificity and non-destructive nature. The ability to use tunable, focused beams makes synchrotron radiation sources a potentially key tool for addition into the array of characterization techniques currently employed, particularly when it comes to the investigation of particles or areas of interest in very small specimens.

There have been recent efforts at the Advanced Light Source (ALS) conducting tender and soft spectromicroscopy using primarily x-ray fluorescence and chemical speciation coupled with selective x-ray absorption near-edge structure (XRF and XANES; Beamline 10.3.2); and with a scanning transmission x-ray microscope (STXM; Beamline 11.0.2). The tender XRF/XANES measurements provide elemental analysis at the low-single micron scale, whereas the STXM can probe electronic structure with ligand K-edge spectroscopy and chemical speciation via XANES with a spatial resolution of better than 25 nm. Several uranium, plutonium, and along with other relevant specimens, from both particle-based systems and monoliths fabricated by focused ion beam (FIB) methods, have been investigated utilizing these specific aforementioned techniques. The potential signatures obtained from this data, as well as the significance of the results, will be presented and discussed. The outlook for synchrotron radiation within nuclear forensics including the strengths and drawbacks of these techniques will also be discussed.

3:00 PM BREAK
This presentation will showcase the capabilities of relativistic quantum chemistry approaches in exploring the electronic structure of actinide-containing compounds. The focus will be on luminescence properties and core-level spectroscopic observables of the uranyl moiety (UO22+) within both linear and bent uranyl complexes. Given the challenges associated with nuclear waste management and the environmental impact of fission products, efficient extraction and characterization methods for actinide-containing compounds are of great societal importance.

The electronic structure of actinide compounds remains poorly understood compared to other elements in the periodic table. Valence- and core-level spectroscopic techniques offer valuable insights into this complex subject. The presentation will demonstrate how luminescence spectroscopy and X-ray spectroscopies serve as sensitive tools for probing the electronic structure and bonding nature between the uranyl moiety and its coordinated ligands.

Specifically, the talk will cover the application of relativistic Time-Dependent Density Functional Theory (TDDFT) with the CAM-B3LYP functional. This method has proven effective in providing accurate excitation/emission energies and vibronic progressions for linear uranyl complexes (UO2Cl42-, UO2F52-, UO2(CO3)32-, UO2(NO3)2-, enabling the assignment of experimental data [1]. Additionally, the impact of bending the uranyl moiety on spectroscopy and observed vibronic progressions will be discussed [2].

The presentation will also delve into TD-DFT simulations of the core spectra of the uranyl tetrachloride dianion (UO2Cl42-) in the Cs2UO2Cl4 crystal. These simulations align with previously reported angle-resolved near-edge X-ray absorption spectroscopy (NEXAFS) at the oxygen K-edge and high-energy resolution fluorescence detected (HERFD-XANES) at the uranium L-edge [3].


### 8:30 AM *SF02.04.01
**Ab Initio Spin-Fluctuation Hamiltonian for Delta-Pu at Finite Temperatures**

**Babak Sadigh**, Kyoung Kweon, Per Söderlind, Michael Surch, Lorin Benedict and Fei Zhou; Lawrence Livermore National Lab, United States

Spin/orbital-polarized density functional theory has been used extensively in the past years to explore materials properties of the Pu metal, from its polymorphic phase diagram to energetics of formation and migration of lattice defects and impurities in the various Pu phases. Calculations to date have been conducted using one or other static low-energy spin configuration. The effect of allowing for non-collinear spin/orbital fluctuations is yet largely unexplored. We have thus developed a novel technique that allows for efficient calculations of adiabatic non-collinear spin/orbital excitations within spin-constraint density-functional theory. We use this technique to extensively explore the potential energy landscape of adiabatic spin fluctuations in delta-Pu. Several families of low-energy non-collinear spin configurations are found. We construct an effective Hamiltonian for thermal spin fluctuations in delta-Pu and study its statistical mechanics via Monte Carlo simulations. We report the impact of spin/orbital fluctuations on the structure and magnetic susceptibility of delta-Pu at finite temperatures.

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

### 9:00 AM SF02.04.03
**Ab Initio Studies of The Interaction of H with Pu6Fe**

**Raymond Atta-Fynn** and Sarah Hernandez; Los Alamos National Laboratory, United States

The corrosion of plutonium (Pu) by hydrogen (H) is rapid, however the mechanisms which dictate the hydride formation process is not fully understood. Iron (Fe) is a common impurity in Pu and segregates to the grain boundaries and triple points to form the intermetallic compound Pu6Fe. To understand the role played by Pu6Fe in the hydride formation process, density functional theory was employed to compute the energetics and electronic structure of H in interstitial and vacancy sites in Pu6Fe. H binding was exothermic, with binding energies around -0.4 to -0.2 eV/H atom. With the aid of ab initio molecular dynamics, the interstitial diffusion of H was modeled and the crystal structure for bulk Pu6Fe hydride was predicted. The role played by the Pu 5f electron states in the hydride formation process will be elucidated.

### 9:15 AM *SF02.04.04
**Ab Initio Heavy Element Composite Methodologies**

**Bradley Welch**, 1, Sasha North, 2, Nuno Almeida 1 and Angela K. Wilson 1; 1Michigan State University, United States; 2Adrian College, United States

Providing the correct qualitative description much less achieving quantitative accuracy for the prediction of energetic properties can become challenging for the lanthanides and actinides due to increasing computational costs and, typically, increasing complexity of the methodologies required. Developments by our group and applications that have provided insight about both energetic predictions for species of the lower part of the periodic table and the theoretical strategies used for the predictions will be highlighted. Specifically, we will discuss the heavy element correlation consistent Composite Approach (f-ccCA) and the super correlation consistent Composite Approach (s-ccCA), which have been designed for elements of the lower periodic table. These methods are build upon the main group and transition metal correlation consistent composite approaches, which have been effectively utilized for many hundreds of species. Successes and challenges in describing heavy elements will be overviewed.

### 10:00 AM BREAK

### 10:30 AM *SF02.05.01
**Piezomagnetism in Uranium Dioxide: Actinide Science at High Magnetic Fields**

**Krzysztof Grofzyk** 1, Marcelo Jaime 2, Daniel Antonio 1, Zahir Islam 1, Myron Salamon 4, Andres Saul 5, Rico Schönemann 6 and James Smith 6; 1Idaho National Laboratory, United States; 2Physikalisch-Technische Bundesanstalt, Germany; 3Advanced Photon Source, United States; 4National High Magnetic Field Laboratory, United States; 5Centre Interdisciplinaire de Nanoscience, France; 6Los Alamos National Laboratory, United States

The spin-lattice coupling in uranium dioxide remains an unsolved puzzle resulting from the lack of a thorough understanding of the strong coupling between 5f-electron magnetism and lattice vibrations. Besides being the main nuclear fuel material, UO2 is a Mott-Hubbard insulator with well-localized 5f electrons (U4+ electronic configuration) and its magnetic state is characterized by a non-collinear antiferromagnetic structure of 3k type and multidomain Jahn-Teller distortions. In the magnetic state, a UO2 single crystal subjected to strong magnetic fields exhibits the...
Strain-Driven Switching between Distinct Antiferromagnetic States in Frustrated Antiferromagnet UO₂

Eugenio Tershchita-Chitrova, Leonid Povorozni4, Sergiu Kimelevskyi4, Lukas Horak4, Thomas Goude4 and Roberto Caciuffo4; 1Institute of Physics, Czech Academy of Sciences, Czechia; 2École Polytechnique, Institut Polytechnique de Paris, France; 3Collège de France, Université PSL, France; 4Vienna Scientific Cluster Research Center, Vienna Technical University, Austria; 5Faculty of Mathematics and Physics, Charles University, Czechia; 6European Commission, Joint Research Centre (JRC), Germany; 7National Institute for Nuclear Physics, Italy

In materials containing magnetic atoms arranged in geometrically frustrated lattices, various magnetically ordered states can possess comparable energies with respect to the inter-site antiferromagnetic (AFM) exchange interactions. The concept of geometric frustration often intersects with broader phenomena in condensed matter physics, such as quantum spin liquids, topological states, and critical behaviour [1]. In recent decades, there has been a growing interest in intentionally manipulating magnetic states in collinear antiferromagnets, motivated by advancements in AFM spintronics [2]. In our study, we demonstrate the fundamental potential to control spin orientations in frustrated antiferromagnets, paving the way for their utilization in spintronics.

Our research focuses on the interplay of magnetic and exchange anisotropy effects in artificial heterostructures based on a canonical frustrated 3-4 antiferromagnet, UO₂. We demonstrate that effective switching between the AFM states of different symmetries can be achieved by stretching the lattice of UO₂. The phenomenon is probed experimentally using the exchange bias (EB) effect in stoichiometric UO₂Fe₂O₄ bilayers. By employing many-body first-principles calculations based on the charge self-consistent Hubbard-I approximation [3,4] we identify magnetic configurations in the UO₂ layers. We show that a minor tetragonal distortion induces a transition between antiferromagnetic states of different symmetries, driven by appearance of a robust single-ion anisotropy. This impact the arrangement of magnetic moments at the UO₂Fe₂O₄ interface and thus influences the magnitude of exchange bias. Our findings showcase how epitaxial strain enables the manipulation of antiferromagnetic states in frustrated antiferromagnets by controlling single-site anisotropy.

We acknowledge the support of Czech Science Foundation under the grant no. 22-19416S. The samples were prepared in the framework of the ERL project of the European Commission Joint Research Centre, ITU Karlsruhe. Experiments were performed in MGML (mgml.eu), which is supported within the program of Czech Research Infrastructures (project no. LM2023065).

These radiation-induced processes cannot simply be switched off, as they are as fundamentally inherent to plutonium as the impact of relativistic effects on its atomic structure. Plutonium plays a key role in global actinide research and nuclear fuel cycle technologies, and yet, our fundamental understanding of its inherent radiation-induced chemical behavior is limited. Recovery in Stabilized Delta Pu and its Effects on Thermophysical Properties of Plutonium Oxide Solid Solutions.

Defect Chemistry and Radiation Stability of (Gd & Zr) Co-Doped UO2 Solid Solutions.

For a more complete picture of the poorly understood “aging” processes of defect accumulation and damage evolution in δ-phase 239Pu-Ga alloys, we need to consider the radiation dose rate and thermal history, and composition of the materials. This talk will present experimental results on the evolution of the average structure of δ-phase 239Pu-Ga alloys when exposed to repeatedly alternating-temperatures between ambient and cryogenic values, investigated by time-of-flight neutron diffraction.
While actinide materials have seen an enormous swell of interest in recent years due to the surprising and fascinating quantum properties of materials such as UTe$_2$, this interest has largely been confined to a small set of compounds. The intrinsic obstacles to research the actinides present has greatly limited broader explorations into novel materials, novel analytical methods, and manipulation of actinide isotopics. Savannah River National Laboratory, in light of its unique position ameliorating many of the difficulties of actinide research, has pursued a research effort to begin those broader explorations.

Utilizing primarily chemical vapor transport and flux synthesis methods, SRNL has generated a number of actinide-based quantum materials, both subject to contemporary mainstream interest and those which have been neglected for decades with insufficient characterization. High-quality crystals of materials such as UTe$_2$ have been prepared and characterized at much higher levels of fidelity than possible at the time of their discovery, clarifying disagreements in the existing literature and revealing new and compelling magnetic features. SRNL also plans to prepare a series of UTe$_2$ samples with tailored uranium isotopics, including the use of highly enriched uranium, enabling an unprecedented investigation of the impact of nuclear spin on the unusual quantum properties of that material.

Most importantly, this work results from the establishment of an actinide-based material synthetic capability which will allow the synthesis of entirely new materials, including with actinides other than uranium. The richly complex correlation effects endemic to actinide species will no doubt lead to novel and intriguing quantum properties, offering a whole new realm of investigation.
However, it was not clear from the SEM-EDS, how these elements were incorporated into the Pu-phase. We used Scanning Electron Microscopy, (SEM), Scanning Transmission Electron findings of Reynolds and co-workers with the observation of similarly large 5 to 10 micrometer particles of Pu-bearing particles that also appeared to contain bismuth and phosphorus.

USA. This concern was bolstered by the apparent discovery of a bismuth-plutonium phase in the wastes by Reynolds et al. Initial analyses of TX-118 solids with SEM-EDS matched the accumulation of plutonium particles in waste tanks has been suggested as a process that could lead to a nuclear criticality event during the processing of wastes at the Hanford site, WA, Laboratory, United States.

Highly Stable and Hierarchical Porous Ce-Based MOF for Efficient Uranium Extraction from Seawater Muhammad Asim, Bhupendra K. Singh and Wooyong Um: Pohang University of Science and Technology (POSTECH), Korea (the Republic of)

In this work, we have developed a highly stable hierarchically mesoporous Ce-based MOFs with an efficient uranium extraction performance in harsh seawater conditions and proposed as an extraction efficiency in simulated seawater conditions, CeHMMOF displayed robust uranium removal efficiency (>50% of 100 µg/L initial U concentration in 12 minutes), surpassing reported extraction efficiency as well as chemical and structural stability in ocean water.

To ensure the practical utilization of CeHMMOF on commercial scale, our research is ongoing and in the subsequent phases of this study, firstly, we will comprehensively evaluate the stability test conducted in simulated seawater conditions (Na+ = 23,000 mg/L, Cl- = 35,500 mg/L, Cu = 100 µg/L , pH = 8.0) revealed promising chemical stability and structural resilience size; 1.5 - 2 µm) was successfully synthesized via one pot solvothermal approach. The synthesized MOF was systematically characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscope (SEM) to ascertain its structural, chemical, and morphological attributes. The stability test conducted in simulated seawater conditions (Na+ = 23,000 mg/L, Cl- = 35,500 mg/L, Cu = 100 µg/L, pH = 8.0) revealed promising chemical stability and structural resilience of CeHMMOF during prolonged exposure to simulated seawater up to 21 days, signifying its potential for practical deployment of UES at a larger scale. In terms of affinity for uranium and extraction efficiency in simulated seawater conditions, CeHMMOF displayed robust uranium removal efficiency (>50% of 100 µg/L initial U concentration in 12 minutes), surpassing reported materials concerning the extraction efficiency, and thus affirming the outstanding capability and considerable scope of synthesized Ce-based MOF sorbent for UES application.

In this work, we have developed a highly stable hierarchically mesoporous Ce-based MOFs with an efficient uranium extraction performance in harsh seawater conditions and proposed as an emerging candidate material for a high-throughput and sustainable UES, aligning well with ongoing global efforts to develop a clean and renewable energy resource. To ensure the practical utilization of CeHMMOF on commercial scale, our research is ongoing and in the subsequent phases of this study, firstly, we will comprehensively evaluate the irradiation stability of synthesized MOF to assure its material stability and structural integrity under induced irradiation for long term onshore UES applications. Thereafter, uranium removal mechanism will be investigated in conjunction with other parameters impacting UES performance, including regeneration rate and selectivity of fabricated MOF for uranium extraction in natural seawater.

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amorphous. We propose a particle-particle attachment mechanism for the formation of the plutonium agglomerates in TX-118 wastes. Low solubility Pu-bearing solids formed in the highly alkaline tank waste conditions would have had extremely low particle growth rates through Ostwald ripening or similar mechanisms. We performed precipitation experiments and examined the resulting agglomerates with STEM showing a possible particle attachment mechanism of formation.

### SESSION SF02.11: Chemistry II
Session Chairs: Marisa Monreal and Tsuoshi Yaita
Thursday Afternoon, April 25, 2024
Terrace Suite 2, Level 4, Summit

1:30 PM *SF02.11.01*
**Exploring The Photochemistry and Bonding of Trivalent Americium within Metal–Organic Constructs**
Robert G. Surbella III, Ana Arteaga, Aaron Nicholas, Michael Sinnwell, Bruce K. McNamara and Edgar C. Buck; 1Pacific Northwest National Laboratory, United States; 2The University of Iowa, United States

Metal-organic frameworks (MOFs) are suitable platforms for studying the fundamental properties of the transuranium (TRU) elements. While the material properties that are common to MOFs, (e.g., structural variability, high surface area, and permanent porosity), are often exploited for their functionality, our motivations for studying TRU-MOFs are fundamental in nature. These robust, crystalline constructs are attractive hosts for immobilizing the scarce and often, highly radioactive isotopes of the TRU elements, providing both structural stability and a platform to explore structure–property relationships. The trivalent lanthanide (Ln(III)) containing MOF-76 family is of particular interest in this regard, given its high thermal stability and unique optical properties, which have been explored for use in color tuning and analyte sensing. The MOF-76 family is constructed from Ln(III) ions (where Ln = Eu, Sm, Tb, N...) and 1,3,5-tricarboxylic acid (BTC) ligands, forming a porous, three-dimensional architecture. Perhaps more importantly, the synthetic routes for preparing MOF-76(Ln(III)) are robust, being able to accommodate nearly all the 4f elements, and as such, is an ideal entry point for studying the trivalent actinides, like americium. An overview of this synthetic strategy and the crystal structure of MOF-76(An) will be presented. Moreover, the utility of this platform for studying the optical properties of Am(III) will be highlighted. To this end, the focus will be in differentiating 4f vs. 5f element behavior with respect to ligand-to-metal resonance energy transfer and photoluminescence quenching.

2:00 PM *SF02.11.02*
**Protein Crystallization Provides Insight into Actinide Coordination**
Jennifer N. Wacker, Peter B. Rupert, Marc Allaire, Roland K. Strong and Rebecca Abergel; 1Lawrence Berkeley National Laboratory, United States; 2Fred Hutch Cancer Research Center, United States; 3University of California, Berkeley, United States

The diverse implications in understanding the biological chemistry of the actinides are profound, demonstrated in both the decontamination efforts of individuals after a nuclear accident and the remedial use of radionuclides for cancer treatments and diagnostics. Underpinning these efforts aimed to address critical societal challenges is a thorough understanding of f-element binding and coordination behavior in the presence of biologically-inspired systems. Despite advances in probing the fundamental properties of the actinides through methods such as X-ray Absorption Spectroscopy, opportunities to expand our current understanding at the interface between small molecule actinide complexes and natural systems can be further aided by the use of macro-molecular hosts. By combining hard oxygen-donor chelators that bind actinides with high-sensitivity and utilizing a protein called siderocalin, which has been shown to selectively bind a diverse range of actinide complexes, these ‘actidine-chelator-macro-molecule’ constructs can be crystallized to reveal the fundamental bonding of even the rarest of actinide elements. Protein crystallographic measurements collected at the Advanced Light Source (Beamline 5.0.2) enable actinide coordination to be revealed in the solid-state, and more broadly can help probe the interactions between biological scaffolds and actinide materials.

### SESSION SF02.12: Fuels, Environmental and Forensics
Session Chairs: Brandon Chung and Lingfeng He
Thursday Afternoon, April 25, 2024
Terrace Suite 2, Level 4, Summit

3:00 PM *SF02.12.01*
**Room Temperature Oxidation Kinetics of a U-Nb Alloy**
Scott Donald; Lawrence Livermore National Laboratory, United States

The reaction of atmospheric gases with metal surfaces plays a crucial role in driving many beneficial and detrimental processes such as heterogeneous catalysis, corrosion, protection from degradation, and environmental dispersal. The chemistry and kinetics of the oxide formed on uranium metal alloyed with 14 at.% Nb was investigated following exposure to dry and ambient air environments. Using a combination of x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS), the evolution of the oxide as a function of time and oxygen partial pressure were determined. Segregation of the solute element was found to occur, resulting in the formation of a niobium rich oxide interfacial layer between the UO2 surface and bulk metal. The potential role of this segregation on passivating the material against further oxidation will be discussed and comparisons will be made to the oxidation mechanism of unalloyed uranium under similar environments.

This work was prepared by LLNL under Contract DE-AC52-07NA27344. This support does not constitute an express or implied endorsement on the part of the government.

3:30 PM *SF02.12.02*
**From Conversion to Fabrication and Fine Characterization of MOX Fuel**
Laure Ramond, Florent Lebroton, Julie Simeon, Paul estevenon, Anna Hautecouverture and Guillaume Bernard-Granger; 1,2Commissariat à L’Énergie Atomique et Aux Energies Alternatives, France; 3Université de Montpellier, France

MOX fuel is an intimate mixture of PuO2 in a uranium oxide matrix, with plutonium content ranging from a few percent (light water reactor fuel) to several dozen percent (fast reactor fuel). In addition to conventional powder metallurgy processes, CEA Marcoule is studying other innovative ways of preparing MOX, such as advanced thermal denitration, SCS (solution combustion synthesis) and freeze granulation. The sintering of these different types of powder is being studied at the CEA, with the development of sintering maps and activation energy calculations. A combination of SEM, XRD, and chemical analysis will be used to provide a comprehensive understanding of the sintering process and to identify the most suitable material for the preparation of MOX fuel.

3:45 PM *SF02.12.03*
**Multimodal Analysis of UO2 Corrosion enabled by a Microfluidic Electrochemical Cell**
Jennifer Yao, Eugene S. Ilton, Bianca Schacherl, Bruce K. McNamara, Tonya Vitova and Edgar C. Buck; 1PNL, United States; 2Karatruhe Institute of Technology, Germany

Understanding the corrosion kinetics and mechanisms of spent nuclear fuel (SNF) is crucial for accessing the long term risks associated with the geologic storage of SNF. Experimental approaches have posed serious challenges, given the need for substantial resources and access to shielded hot cell facilities to protect researchers from the intense radiation field. One response is to work with depleted UO2, a close but ultimately unsatisfactory analogue to SNF. An alternative would be to downsize the amount of SNF required such that the need for shielded hot cell facilities would be diminished.

Indeed, an innovative solution has emerged—the Particle-attached Microfluidic Electrochemical Cell (PAMEC)—which has the proven potential to work with microgram quantities of material. Central to the PAMEC is the electrochemical method, which is widely employed for studying corrosion processes. With respect to UO2 corrosion, the PAMEC electrode is a composite of micromgram quantities of UO2 powder, polyvinylidene fluoride (PVDF), and carbon black. The PAMEC has already proven effective in studying UO2 redox behavior, providing consistent results with those from traditional bulk electrochemical studies.
In more detail, the PAMEC is a vacuum-compatible microfluidic platform that provides precise control over experimental conditions (e.g., flow rates, dissolved volatile concentrations such as H2), minimal resource utilization, and the ability to observe redox reactions in real-time and in situ. PAMEC’s in situ and real-time analytic and imaging capabilities, made possible by an ultra-thin 50 nm detection window, include scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS). The same setup allows for operando high-resolution X-ray absorption near-edge structure (HR-XANES) spectroscopy, which we used to track U oxidation states during multiple cyclic voltammetry scans of UO2. The compact nature of the PAMEC simplified shipping the loaded device to the Karlsruhe Institute of Technology (KIT) synchrotron facility CAT-Act beamline in Karlsruhe, Germany for operando HR-XANES analysis.

Our research has showcased the ability of the PAMEC using UO2 corrosion as an example. We envision this approach can greatly reduce the risk associated with studying the corrosion of SNF under conditions that reassemble repository environments, as well as allow for multimodal analyses for acquiring complementary characterization and more in-depth understanding of the corrosion process.


**4:00 PM *SF02.12.04 Improvement of The Fission Track Analysis Methods for Nuclear Forensics Simulation and Tools**

Irshak Halevy1, Rami Babayew2, Yaacov Yehuda zada2, Galit Katarivas Levy3, Jan Lorincik4, Izhak Orion1, Noam Elgad1 and Aryeh Weiss5; 1Ben-Gurion University of The Negev, Israel; 2NRCN, Israel; 3Ben-Gurion University of the Negev, Israel; 4Research Centre Rez, Czechia; 5Bar Ilan University, Israel

In order to address inquiries pertaining to nuclear forensics, our research endeavors involve the formulation of novel methodologies and strategies aimed at enhancing the dependability and precision of this analytical process.

At now, the analysis of microscope pictures is limited to individuals who have received formal training in research methodologies. Given that this analysis relies on the researcher’s own aptitudes and competencies, it is evident that several researchers will yield slightly divergent outcomes. At now, the analysis of microscope pictures is limited to individuals who have received formal training in research methodologies. Given that this analysis relies on the researcher's own aptitudes and competencies, it is evident that several researchers will yield slightly divergent outcomes.

The simulation of fission tracks was conducted using the Monte-Carlo software, GEANT4. This software incorporates various aspects of nuclear fission tracks, including thermal neutron flux, fission cross-section, radiation time, particle size, enrichment, and other relevant physics. The present investigation involves the utilization of Trainer2.0 software to compute the trajectories on our LXen detector, as well as their corresponding projections. These calculations are based on many physical parameters, including neutron flux, particle size, and radiation duration. The outcome manifests as a "star" that is positioned at the center of the simulated particle. The entirety of our software is implemented using MatLab programming language.

The simulation of harsh conditions allows for the exploration of novel aspects inside the fission track technique. The simulation provides insights into determining the appropriate sample size for the FTA procedure.

The simulation has the capability to make predictions and may be compared to both the mini-bulk and micro-bulk analyses.

The novel concept of employing penetrating fluorescent colors provides the capability to perform three-dimensional (3D) scanning with our detector, as opposed to the conventional two-dimensional (2D) scanning. In this particular instance, the Dapi marker was employed as an initial approach. It is widely recognized in the field of biomedical research.

This new idea to investigate the FT Star more than just by his projection.

The determination of the source isotope in a given element can be achieved by analyzing the length and distribution of its tracks. This analysis involves examining the shape of the "fission products distribution" as well as the density of impurities present in the source.

**4:30 PM *SF02.12.05 Examining Actinide-Molten Salts Across Length Scales: Local Structure, Thermal Properties**

Marisa Monreal, J. M. Jackson, Scott Parker, Alexander Long and Sven C. Vogel; Los Alamos National Laboratory, United States

Actinide-molten salts are complex systems central to pyroprocessing for actinide metal purification and recovery, to molten salt reactors (MSRs)—a next-generation nuclear reactor concept currently in rapid growth, and also to a growing number of new energy-related applications. There are gaps in the literature concerning the chemistry and thermal properties of these systems, especially in data collected with well-documented methodology and experimental detail, using salts with analytical data confirming purity, and reported with thorough error analysis and quantified uncertainty. With the overarching goal to contribute to a better understanding of these complex systems, enabling prediction of their behavior, a suite of advanced characterization techniques is being developed at Los Alamos National Laboratory for the accurate and precise measurement of actinide-molten salt thermochemical and thermophysical properties, and for the study of their local structure. The high-quality empirical data collected using these capabilities supports the optimization of pyroprocesses, the development of MSRs, and the validation and refinement of models. Efforts to examine actinide-molten salts across length scales will be described, including recent results from studies both on local structure and on thermal properties of uranium- and plutonium-bearing chloride salts. A selection of techniques and results will be detailed, with a focus on pulsed neutron characterization at the Los Alamos Neutron Science Center (LANSCE), including progress using pair distribution function (PDF) analysis to gain insight into uranium-molten salt local structure, and recent results from measurements of the liquid density of uranium- and plutonium-molten chloride salts as a function of temperature and composition using neutron radiography.

**SYMPOSIUM SF03**

Ion Insertion—Fundamentals Processes and Applications to Switching
April 23 - April 25, 2024

Symposium Organizers
Iwnetim Abate, Stanford University
Judy Cha, Cornell University
Yiyang Li, University of Michigan
Jennifer Rupp, TU Munich
We demonstrate an intercalation chemistry for titanium, hafnium, and zirconium in the highly oxidized state (Zr⁴⁺, Hf⁴⁺, Ti⁴⁺) into 2D layered materials through formation of a soluble, molecular bis-tetrahydrofuran (THF) metal halide complex. This method overcomes challenges distinct to intercalation of highly oxophilic group 4 metals through creation of a molecular species that is highly soluble in organic solvents and is kinetically competent in reactivity. Metal intercalation is demonstrated in several layered hosts including MoO₃, Bi₂Se₃, Si₂Te₃, and GeS. This strategy intercalates, on average, 3 atomic % or less of HF, Ti, and Zr, limited by the high oxidation state and charge transfer with the host. MoO₃ is chemochromically switched from transparent white to dark blue through Zr⁴⁺, Hf⁴⁺, Ti⁴⁺ intercalation. Contrast with methods for intercalation of zero-valent metals in 2D layered materials is demonstrated. We believe that this bis-THF chemistry offers a unique way to ionically switch properties of 2D layered materials and achieves a route to intercalate otherwise elusive guests.

Carbon dioxide levels (CO₂) in the atmosphere continue to rise exponentially as fossil fuels remain a primary energy source for many industrial processes. Consequently, alternative energy technologies, such as solar and wind, must be harnessed to convert CO₂ into liquid fuels through the development of electrocatalytic materials that exhibit high selectivity and efficiency for CO₂ reduction (CO₂R). One such class of materials that have shown promise for CO₂R are Chevrel phase sulfides (CPs), due to their ability to host a wide variety of metal cations that can alter the structural and electronic properties of the crystal framework and in turn CO₂ binding motifs. CPs with the general formula MₓMo₆S₈ (M = transition, alkali, or alkaline metal) are excellent materials to investigate ion (de)insertion mechanisms due to the high ionic mobility of these CPs. The mobility of these protons determines the degree of structural change that occurs during Li⁺ insertion. To investigate these phenomena, we utilized electrochemical cycling to not only co-insert two or more metal cations into the CPs framework for CO₂R studies but to further understand the thermodynamics and kinetics of chemical and electrochemical processes occurring during co-insertion. Furthermore, insertion methods, such as open circuit potential (OCP) mechanism, can be used to investigate the synergistic movement of metal cations throughout the channels formed in the extended Mo₅S₈ solid and their effect on the electronic properties of the crystal structure that could prove beneficial for understanding product selectivity in CO₂R and other catalytic reactions. Aside from electrochemical co-insertion in aqueous electrolytes, medium temperature solid-state synthesis can also be utilized as a synthesis pathway to CPs materials with multiple metal cations inserted. In this work, control of composition and stoichiometry of co-inserted transition metal CPs was achieved through OCP and cyclic voltammetry (CV) electrochemical synthesis techniques, as well as medium temperature solid synthesis methods. Materials were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), x-ray photoelectron spectroscopy (XPS), and x-ray absorption near edge structure spectroscopy (XANES).

Bulk Proton Acidity Modules Structural Transformations in Hydrogen Titanates during Li⁺-Insertion Coupled Electron Transfer Saeed M. Saeed1, Takeshi Kobayashi2, Noah Holzapfel1, Eugene Mamontov3, Naresh Osti1 and Veronica Augustyn1; 1North Carolina State University, United States; 2Iowa State University, United States; 3Oak Ridge National Laboratory, United States

Nanostructured TiO₂-based materials are of interest for energy storage and conversion applications due to their high abundance, low toxicity, and chemical tunability. Lithium titanum oxides, such as spinel-type Li₂Ti₃O₇ and ramafeldite-type Li₂Ti₅O₁₂, have been extensively studied as electrode materials for Li-ion batteries. The synthesis of nanostructured metal oxide materials with high surface area has been a promising path for achieving high specific capacity for electrochemical energy storage. As such, it is important to expand the materials design strategies to synthesize titania oxide materials for high Li-ion energy storage applications. Here we explore a series of layered hydrogen titanates (HTOs), H₂Ti₅O₁₂ₓ•ₓH₂O (n = 3, 4, and 5), with varying degrees of structural protonation and interlayer water. These HTOs are metastable materials prepared via acid etching of alkali titanates. The complexity of the interlayer environment motivated us to understand the role of water content and structural protons on Li⁺-insertion coupled electron transfer from a non-aqueous electrolyte. We hypothesized that structural protons are necessary for high Li⁺ intercalation capacity, while the mobility of these protons determines the degree of structural change that occurs during Li⁺ insertion. To investigate these phenomena, we utilized electrochemistry as well as operando electrochemical XRD, ex situ solid-state NMR, and acid-base titrations. By employing these techniques, we correlated the relative acid strengths of the structural protons to the degree of structural change during Li⁺ intercalation. Our findings show that HTOs with more acidic protons undergo rapid, irreversible structural changes due to hydrogen evolution of bulk protons. Long term electrochemical cycling reveals reversible structural transformations of the HTOs to lithiated titanates. This work provides a comprehensive understanding of the relationship between bulk proton acidity and structural transformations during electrochemical Li⁺ intercalation into titanates. In doing so, it informs the structural design of next generation ion-insertion coupled electron transfer materials for energy storage and conversion.

Medium Temperature Intercalation (MTI) through Microwave Irradiation to Access Catalytically Relevant Metastable Chevrel Phases, MMO₆X₈ (M = Ag, Sn; X = S, Se) Rose Smiley and Jesus M. Velazquez; University of California, Davis, United States

The demand for large scale sustainable energy solutions for an energy landscape evolving posthaste calls for the development of transformative materials with the ability to mediate sustainable energy conversion. Chevrel phases (CPs), MₓMo₆S₈ (M = alkali, alkaline, transition, post-transition, and lanthanide metals; X = S, Se, Te) have shown promise as electrocatalysts for the hydrogen evolution reaction (HER), the reduction of carbon dioxide (CO₂R), and the oxygen reduction reaction (ORR). However, efficient, and selective electrochemical conversion is hindered by achieving controlled bonding affinity of key intermediates. CPs offer a unique platform to probe structure function relationships between active sites and key intermediates in part to their highly tunable framework. While classical high temperature synthesis methods can be used to access thermodynamically stable CPs, the same methods can yield impure material for metastable CPs. Medium temperature intercalation (MTI) can be used to diffuse cations of interest into existing MₓMo₆S₈ framework to access pure phase metastable CPs. This work reports a facile synthesis procedure developed using a commercial microwave to synthesize SnMo₆S₈ and AgMo₆S₈ (X = S, Se), full characterization of the materials, and highlight X-Ray Absorption Near Edge Structure (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS) data to gain insight on local electronics and structure.
Toward Tunable Conductance States in Layered Materials for Neuromorphic Computing using Metal Intercalation

Knoxville, United States; 2Center for Nanophase Materials Sciences, United States

TaOx chemistries have been widely studied as candidates for memristive switching memory and computation due to the non-linear conductance state transitions observed in these materials. In this talk, I will highlight a novel hardware implementation of the well-established backpropagation algorithm that progressively updates each layer using in situ stochastic gradient descent, thus avoiding this storage requirement. We experimentally demonstrate the in situ error calculation and the proposed progressive backpropagation method using a multi-layer hardware implemented neural network based on organic EC-RAM, and confirm identical learning characteristics and classification performance compared to conventional backpropagation in software.

2:30 PM SF03.02.03

Tuning Resistive Switching in ZrTaOx Devices Matthew Flynn-Hepford1, Reece Emery1, Jack Lasseter1, Anton Levelev2, Olga Osvchinikova1 and Philip D. Rack1, 4University of Tennessee-Knoxville, United States; 3Center for Nanophase Materials Sciences, United States

ZrTaOx alloys offer promising properties for stable resistive switching devices due to tantalum’s mixed oxide states and zirconium’s flexible 5S outer valence bonding orbital. To explore this system, we have employed a combinatorial magnetron reactive sputtering of this ZrTa2O7 alloy system over a 100 mm diameter substrate and achieved a composition gradient such that 0.15<x<0.9. We confirm the composition via energy dispersive x-ray spectroscopy and generate a series of Pt/ZrTa2O7/Pt memristors along the gradient and correlate the resultant I-V to the composition as-deposited and as a function of annealing temperature. To gain insight into the switching mechanisms of the effective chemistries we leverage a workflow that couples conductive scanning probe microscopy (SPM) and spatially resolved time-of-flight secondary ion mass spectrometry (ToF-SIMS). Additional defects can then be introduced to these oxide systems, in the form of He, Ne and Si focused ion beams, in order to further understand how intentionally induced defects affect the oxygen motion that drives these devices.

2:45 PM SF03.02.04

Toward Tunable Conductance States in Layered Materials for Neuromorphic Computing using Metal Intercalation Michelle A. Smeaton, Katherine L. Jungjohann and Lance M. Wheeler; National Renewable Energy Laboratory, United States

As computing needs and accompanying energy costs continue to rise exponentially, neuromorphic (brain-inspired) computing has the potential to provide crucial improvements to computing speed and efficiency over traditional CMOS technology. Metal-intercalated, layered van der Waals materials present a promising strategy for tuning conductivity and insulator-metal transitions in devices for neuromorphic computing. Ion-insertion materials have been well studied for energy storage applications; however, the field is slow and energy-expensive due to the transfer of weight data between digital memory and processor chips. Neuromorphic systems can accelerate neural networks by performing multiply-accumulate operations in parallel using non-volatile analogue memory. However, the backpropagation training algorithm in multi-layer (deep) neural networks requires information - and thus storage - on the partial derivatives of the weight values, preventing easy implementation in hardware.

In this talk, I will present a novel hardware implementation of the well-established backpropagation algorithm that progressively updates each layer using in situ stochastic gradient descent, thus avoiding this storage requirement. We experimentally demonstrate the in situ error calculation and the proposed progressive backpropagation method using a multi-layer hardware implemented neural network based on organic EC-RAM, and confirm identical learning characteristics and classification performance compared to conventional backpropagation in software.
Today's semiconductor devices continue to make remarkable progress, supported by technological developments in miniaturisation and integration, but there are fears that this progress will slow down in the near future. In order to evolve into the next generation information society, it is necessary to actively develop high-performance devices and new functional devices that operate on different principles from conventional semiconductor devices. Among these, solid-state ionic devices, which operate by utilising local ion transfer in solids, are expected to be very promising candidates. To date, we have developed ionic nanorachitectonics methods that combine ions and nanotechnology to create novel ionic devices with various unique functions and performances [1,2]. The ionic nanorachitectonics controls the transport of ions, which are much larger in mass and size than electrons, and thus can control not only the electronic state of materials but also the crystal structures of surfaces and interfaces. As a result, it has been found that various functions and performances can be realised that could not be achieved by conventional electronic transport control in semiconductor devices. This talk will focus on the development of memristive, neuromorphic and artificial intelligence related devices such as artificial synapses, artificial vision and physical storage devices created by the ionic nanorachitectonics.

Reference

4:30 PM SF03.02.07
Exploring Bioinspired Information Pathways: Bridging The Gap Between Science and Technology with The Intercalation of Alkaline-Ions in 3D-Aeromaterial of MoS2
Pia Pooker, Soeren Kaps and Rainer Adelung; University of Kiel, Germany

The human brain works with an exceptionally low power consumption but high information output. Understanding the intricate information pathways found in nature, particularly in the human brain, has emerged as a pivotal source of inspiration for revolutionary technological advancements. This exploration into bioinspired information pathways has led to the development of artificial neurons, a key element in unraveling the mysteries of neural processes. This exploration extends its reach to various domains, including energy efficiency, information storage, and neurimristive systems, where the integration of bioinspired concepts promises transformative breakthroughs.

As the brain functions with a decentralized energy supply, there are some striking similarities to alkaline batteries as both function with a liquid electrolyte based electrochemical system and are able to store energy with different kinds of charge transport carriers. In order to mimic spatial arrangement of a neuron inside the brain, a 3D network with a spatially and highly scalable structure, inspired by the intricate architecture of the brain, is designed in this study. Moreover, to mimic the function of the brain, researchers have turned to two-dimensional materials to display the working function of ion channels, an integral aspect of bioinspired information pathways. The application of (non-)equilibrium dynamics allows these materials to serve dual roles. They function not only as energy-efficient batteries but also as information storage devices, thus bridging the gap between energy and data storage.

Among the intriguing materials of bioinspired information pathways are Transition Metal Dichalcogenides (TMDs), such as molybdenum disulfide (MoS2). As part of the broader bioinspired research, TMD materials enable not only efficient energy storage but also serve as a cornerstone for developing innovative information processing technologies. TMDs like MoS2, with their atomically thin structure and tunable bandgap, play a pivotal role in the quest to mimic the remarkable capabilities of the human brain.

In this contribution, an aeron material consisting of the exfoliated 2D-TMD MoS2 and exfoliated graphene (EG) is used as the functional material. For the realization of the battery-like electrodes, the 3D-network is infiltrated with a dispersion of both, exfoliated MoS2 and EG, before etching ZnO away, to have a light, mechanically stable and 3D shaped TMD. In a quest to advance traditional lithium-ion batteries, we are exploring sodium (Na) as well as potassium (K) as a viable alternative as the intercalated species to expand the horizons of layered materials. This shift opens new possibilities for energy storage technologies and fosters sustainability in energy solutions. For testing equilibrium dynamics with both, Li and Na, the battery-like aeron material is incorporated as the anode material with metallic Li as the cathode. The electrolyte is varied with different conducting salts containing Na⁺ and K⁺-ions. The different ion-radii lead to an expansion of the interlayer spacing and hence to higher capacities. For testing non-equilibrium conditions, a tuning of the intercalation pathway of the alkaline ions and hence a tuning of the resistivity of certain pathways can be reached, by contacting several points of the 3D structure and applying different measurements. With this data, a measurement of the network can be achieved.

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 434434223 – SFB 1461

4:45 PM SF03.02.08
Phase-Field Modeling of 3-Terminal Protonic Transistor Switching Dynamics
Michael L. Li and Martin Z. Bazant; Massachusetts Institute of Technology, United States

The need for increased computational efficiency for deep learning applications has led to interest in in-memory computing. One example, three-terminal synaptic transistors with ion or proton intercalation mechanisms [1,2], have been recently studied for their CMOS compatibility and relatively fast switching time. Given the young nature of this technology, there are fundamental unanswered questions about these devices, which creates a gap between the current available models and tools required to simulate and accelerate material and architecture design. Though intercalation materials have been heavily studied in the context of batteries, the large applied voltages to trigger the resistance state switching and nanoscale structure of these films lead to uninvestigated effects on the material reaction and transport properties. Additionally, the impact of these devices’ design and formation on performance is not fully understood. A fundamental investigation of the relationship between material properties and device performance metrics is needed.

Here we present a new phenomenological phase-field model to describe the resistance switching of WO3 3-terminal protonic transistors [1] by extending multiphase polarization theory outline by Tian and Bazant [3]. Through this process, we determine relationships between the effective surface reaction and material transport parameters and device performance parameters, such as switching time and energy. We address the importance of the underlying model for the surface ion-intercalation reaction, comparing different the phenomenological Butler-Volmer and the coupled ion-electron transfer reaction model [4]. Additionally, we investigate the impact of phase separation on these devices, which, due to the large electric fields needed to switch between resistance states, is shown to occur even when the bulk concentration exists in a single-phase region. Finally, preliminary extensions to 3D device topologies are investigated. This model will be indispensable in predicting the impact of material properties and architecture on device performance, accelerating design of similar synaptic transistor technologies.

References

5:00 PM SF03.03.02
In Situ Studies of SrCoOx Heterostructures for Synaptic Memories
Tadese Billo Reta1, Daniel B. Durham1, Yan Li1, Jill Wenderott2, Hua Zhou1, Supratik Guha1 and Dillon D. Fong3;
1Argonne National Laboratory, United States; 2Drexel University, United States

Varying the oxygen concentration in many transition metal oxides can be used to tailor electronic properties, making oxide heterostructures of great interest in iontronics and novel memory devices. We investigate epitaxial SrCoOx heterostructures, depositing insulating SrCoO2.5 and conducting SrCoO3 layers and bilayers on SrTiO3 (001) substrates. The resistive switching properties of the heterostructures depend on structural and electronic phase transitions as governed by ion insertion and extraction. The volume fraction of the different phases significantly influences switch behavior, affording fine control and revealing distinct traits in low-voltage I-V sweeps, especially during DC forming. We employ coherent synchrotron techniques such as X-ray Photon Correlation Spectroscopy (XPCS) during ionic liquid gating to shed light on the dynamics of oxygen ion insertion and extraction. We will discuss these results and findings from electrical device characterization, emphasizing the reliability and performance of these structures.

SESSION SF03.03: Poster Session
Session Chairs: Judy Cha and Aditya Sood
Tuesday Afternoon, April 23, 2024
Flex Hall C, Level 2, Summit

5:00 PM SF03.03.03
In Situ Studies of SrCoOx Heterostructures for Synaptic Memories
Tadese Billo Reta1, Daniel B. Durham1, Yan Li1, Jill Wenderott2, Hua Zhou1, Supratik Guha1 and Dillon D. Fong3;
1Argonne National Laboratory, United States; 2Drexel University, United States

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Mg2+ and Al3+ has been shown. The versatility and stability of titania chemistry lends itself to tuning of its morphology by simple fabrication methods. In this paper, mesoporous titania-silica hybrid gating schemes as promising avenues for advancing the field of 2D materials and nanoelectronics, offering unprecedented control and functionality in future electronic systems. Switching device. In such device operated under high-bias condition, it is critical to prevent undesirable chemical reactions, and so we introduce a very thin high-k dielectric passivation layer to Ti(III) and oxidation of Ti(III) to Ti(IV) from aqueous and non-aqueous solutions. Interestingly, the results show that next to Li+, also facile reversible ion insertion/deinsertion can be carried out with other monovalent cations and even bivalent cations. The morphology and composition of the thin films were determined before and after the ion insertion process using scanning electron microscopy and transmission electron microscopy, combined with EDS and EELS. These measurements provided insights into the charge-discharge characteristics of the composite material and the charge capacity was determined. Proton intercalation/ extraction was found a competing reaction during the charge/discharge process in aqueous solutions and depend on the pH. The total charge capacity of the material is then the sum of proton and cation insertion charges. The electrochemical characteristics of the material thus can be tuned according to the application.

Innovative approaches in materials and concepts will be key to address the energy transition challenge. A key area involves ion insertion materials which are not only interesting for energy storage but also for energy conversion and low power electronics and optoelectronics. Titanium dioxide (TiO2) is well known ion insertion electrode capable of accommodating lithium ions. A special attention will be paid on controlling the energy barriers at the interface electrode / switching film, where Schottky barrier competes with the energy barrier of the redox reactions. A new switching mechanism will be presented, relying entirely on electrochemical processes of oxidation and reduction and depends on the valence state and thickness of filament. The ohmic memristive devices, demonstrate a number of advantages compared to Schottky-based devices, such as combination of digital and analogue switching in same devices, higher voltage window of stability, lower operating currents, higher OFF to ON ratio, high endurance and retention, high temperature stability. The importance of fundamental research will be highlighted, allowing for new functionalities and opportunities for applications.

Memristive devices significantly developed in the last decade, expanding their application horizon much beyond memory applications. Especially important are their functionalities as artificial neurons and synapses, making them promising building units for the next generation bio-inspired neuromorphic hardware. Despite a lot has been learned about materials design and the operation principles of memristors, recent research has shown that fundamentals can still be significantly amended, demonstrating new operation principles and functionalities. In this contribution, the common electrochemical fundamentals of biological and memristive artificial neurons and synapses will be discussed as well as new aspects on materials design and its influence on the physicochemical processes and resulting functionalities of both ECM (CBRAM) and VCM (OxRAM) devices. The effects of the materials and thicknesses of the capping layer appear of special importance and as well the thicknesses and combination of thicknesses of all involved layers. The selection of different materials is changing the electrochemical nanoelectronic processes and as well the performance of the memristors. For reliable performance the device stack should be considered as a whole, and materials used in the stack and their thicknesses should be coordinated and harmonised.

A special attention will be paid on controlling the energy barriers at the interface electrode / switching film, where Schottky barrier competes with the energy barrier of the redox reactions. A new switching mechanism will be presented, relying entirely on electrochemical processes of oxidation and reduction and depends on the valence state and thickness of filament. The ohmic memristive devices, demonstrate a number of advantages compared to Schottky-based devices, such as combination of digital and analogue switching in same devices, higher voltage window of stability, lower operating currents, higher OFF to ON ratio, high endurance and retention, high temperature stability. The importance of fundamental research will be highlighted, allowing for new functionalities and opportunities for applications.

Memristive devices based on the valence change mechanism are highly interesting candidates for data storage and hardware representation of synapses in neuromorphic circuits. Although long-term retention is often required for data storage applications, a time decay of the resistance is advantageous for several applications where short-term plasticity is required. In this work, we investigate in detail the LRS relaxation of volatile SrTiO3 devices. The decay is analysed in terms of the Schottky-Read-Hall model for the contribution of electron traps and in terms of the Gibbs free energy gradient for the contribution of oxygen ion migration. Based on this, we can exclude trapping effects as origin of the LRS decay. In contrast, we could nicely model the device behaviour by oxygen ion migration considering four reservoirs within the devices, connected by oxygen exchange. Our model serves as a tool for developing guidelines and design rules for future volatile memristive technology based on Schottky barrier mediated electron transport. As an example, we demonstrate the acceleration of the decay over 3 orders of magnitude by modifying the microstructure off he SrTiO3 layer.

Layered van der Waals materials, such as transition metal dichalcogenides (TMDs), are a promising platform for applications as diverse as optoelectronics, energy storage, and quantum information in large part due to the tunability of their electronic, optical, and structural properties. Both ground- and excited-state properties can be sensitively modified both during and after synthesis through methods such as ion intercalation, stacking and twisting, the introduction of defects, and coupling to external fields. In this talk, I will explore three different pathways for switching the properties of layered TMDs. Firstly, I will present our recent first principles work on ion intercalation induced phase transitions in different TMD heterostructures, including an intercalation-induced charge density wave (CDW) phase transition in WTe2. Secondly, we will explore structural defects present in TMDs, routes for passivating these defects, and magnetic order arising from defect complexes. Finally, we will explore how many-body effects modify the nonlinear optical response of 2D materials and the coupling to strong external fields beyond the perturbative regime.

Coupling Diffusion and Finite Deformation in Intercalation Materials

Ananya Renuka Balakrishna, Tao Zhang and Delin Zhang; University of California, Santa Barbara, United States

We present a multiscale theoretical framework to investigate the interplay between diffusion and finite lattice deformation in intercalation materials. In this framework, we couple the diffusion of a guest species (Cahn-Hilliard type) with the finite deformation of host lattices (nonlinear gradient elasticity). We adapt this theory to LiMn2O4 to investigate the delicate interplay between surfaces) that arise from lattice misfit. These findings suggest a potential mechanism for structural decay in LiMn2O4. More generally, we establish a theoretical framework that can be used to investigate microstructural evolution pathways, across multiple length scales, in first-order phase transformation materials.

Tailoring The Optical and Electrical Properties of MoTe2 via Electrochemical Intercalation of Lithium Ions

Alvyssa Shivy Xu; Cornell University, United States

Intercalation of lithium (Li) ions is one of the most effective methods to realize structural transformation and to tune the optical and electrical properties of two-dimensional transition metal dichalcogenides (2D TMDs). Numerous studies have focused on the phase transition from semiconducting 2H phase to metallic 1T (or 1T') phase in MoS2 and WS2 induced by the intercalation of Li ions. However, few reports explore the effects of Li intercalation in other TMDs, such as Mo- or W-ditellurides. In particular, novel electronic and energy devices can be achieved using the Li-intercalated MoTe2 with its intriguing electrical, optical and catalytic properties.

Here, we report electrochemical Li intercalation into 1T'-MoTe2 flakes. The 1T' phase is stable down to 0.9 V of the applied electrochemical voltage, and two new phases are observed at 0.7 V (phase I) and 0.4 V (phase II), respectively. The lightly Li-intercalated phase I is evidenced by the disappearance of the Ag peak at ~77.7 cm⁻¹ and the appearance of a peak at ~86.9 cm⁻¹ in Raman spectroscopy and a 10% increase of electrical resistance in two-terminal measurements. For the heavily Li-intercalated phase II, we observe a lattice expansion of ~7% in (001) direction in single-crystal X-ray diffraction, the emergence of new Raman peaks at 16.8 cm⁻¹, 109.0 cm⁻¹ and 132.8 cm⁻¹ in Raman spectroscopy and increase of electrical resistance for over 8 folds. In situ Hall effect measurements confirm the decrease in conductivity, which also decreases with decreasing temperature for the phase II, suggesting a semiconducting phase. The Hall carrier density falls from 10¹⁵ cm⁻² in pristine 1T'-MoTe2 to 10¹⁴ cm⁻² in phase I and to 10¹² cm⁻² in phase II. Our results highlight the importance of electrochemical intercalation of Li ions as a powerful tool to manipulate phase stability and electron density of 2D TMDs.

I will describe two recent efforts probing the dynamics of ion transport and ion-induced metastable phases as probed by time-resolved optical, x-ray and electron scattering. In Li-intercalated WTe2, we find a new metastable phase featuring an anomalously large in-plane chemical expansion coefficient (expansion per unit lithium inserted). It is common for 2D materials to expand in the out-of-plane direction upon intercalation, but large tunable uniaxial in-plane expansion is much more rare. The unusual actuation of LixWTe2 is linked to the formation of a metastable crystallographic phase, potentially enabling novel means for strain modulation at high frequencies. In the second part of the talk I will describe recent efforts to visualize the dynamics of ion hopping in superionic materials.
Ion exchange in layered materials is one type of special ion transport process, which involves ion insertion and ion extraction simultaneously. This type of bi-directional ion transport requires the rearrangement of interlayer ions and will induce the phase evolution of layered host structures. More importantly, ion exchange is a powerful method to access metastable materials with advanced functionalities for energy storage applications. However, the ion exchange reaction pathways in layered materials remain elusive. Here, using layered oxides as model materials, we tracked the real-time phase evolution during Li-Na ion exchange in layered oxides. An interesting pseudo-charging behavior has been observed. Combining with the chemical composition information, the ion exchange pathway of phase separation between Li-rich and Na-poor phases was revealed. Depending on the chemical potential of exchange ions in the solution side, we identified two different exchange routes, the surface reaction-limited route and the diffusion-limited route. The phase separation behavior accompanied by the charge transfer is general in both oxygen and sulfur containing oxides. Both DFT calculation and experiments point to the co-existence of Li-rich and Na-poor phases governed by thermodynamics. Besides, we demonstrate that structural vacancy level and lithium preference are critical in determining the feasibility of ion exchange. Guided by this understanding, Na$_2$CoO$_2$ was converted from the parent Li$_2$CoO$_2$ for the first time and Li$_{0.94}$CoO$_2$ was converted from Na$_2$CoO$_2$ at 1-1000 Li-Na (molar ratio) with electrochemical assisted ion exchange.

Tuning The Insulator Metal Transition in Rare Earth Nickelates through Dynamic Electrochemical Ion Insertion

Alan Zhang, Catalin Spataru, Joshua D. Sugar, Alec Talin and Elliot J. Fuller; Sandia National Laboratories, United States

The rare earth nickelates have received renewed attention due to the discovery of superconductivity in infinite layered structures under substitutional doping[1] and the observation of widely tunable electronic behavior in perovskite structures for use in analog memory devices[2]. Recent work has demonstrated that interstitial dopants (H, alkali metals) can be introduced into nickelates to change the room temperature resistance by 10$^6$ - 10$^8$. However, the evolution of the bond disproportionation transition as a function of interstitial dopants has not been reported and the doping fraction leading to rich correlated electronic behavior is often unknown. The electronic phase diagram in nickelate compounds as a function of interstitial doping is of interest. Here, we carried out lithium doping of PrNiO$_3$ using a dynamic electrochemical process. We constructed electrochemical cells using epitaxial thin films as electrodes and then insert lithium using an electrolyte. For Li$_2$PrNiO$_3$, we find that increased lithium doping interrupts bond disproportionation causing a reduction in the ground state resistivity at small fractions 0<x<0.25 with a successively smaller ON/OFF ratio. At larger fractions x>0.25 we observe the disproportionation transition to be destroyed and fully insulating type behavior is observed (T<5-300K). Raman spectroscopy reveals that lithium introduces structural changes that affect A1g modes which are a sensitive probe of bond disproportionation. Density functional theory calculations confirm the disruption to bond disproportionation with an initial reduction in the bandgap at small fractions and an increase at larger fractions. The results point to interstitial doping as a powerful method to synthesize new phases in strongly correlated systems and for next generation memory devices.

SESSION SF03.06: Dynamical Switching of Electrons, Spins and Phonons
Session Chairs: Iwnetim Abate and Judy Cha
Thursday Morning, April 25, 2024
Room 339, Level 3, Summit

9:00 AM SF03.06.01
Dynamic manipulation of thermal & structural properties using electrochemical & electrical stimuli
Aditya Sood; Princeton University, United States

Beyond energy storage, ion insertion has emerged as a powerful method to dynamically tune the physical properties of materials[1]. While there have been numerous examples of electrochemical tuning of optical and electronic properties, the dynamic manipulation of thermal and structural properties is relatively less explored. I will first describe our efforts to create “thermal switches” – materials whose thermal conductivity can be tuned in real-time – using ion insertion. We show that the reversible intercalation of Li+ into the van der Waals gaps in MoS2 induces a ~8-10x modulation in the cross-plane thermal conductance[2], opening avenues for dynamic thermal management. Interestingly, we find that micron-scale heterogeneities in ion concentration can be imaged using spatially-resolved measurements of thermal conductance, suggesting that heat current measurements could enable operando microscopy in electrochemical systems. Next, I will briefly discuss how ion insertion can change the crystal structure and symmetry in layered crystals; in particular, we discover intriguing uniaxial in-plane lattice expansion caused by Li+ intercalation in WTe2, a finding that has potential applications in electrochemical actuators[3]. Finally, I will describe our recent efforts to visualize nanosecond-timescale and picometer-lengthscale structural dynamics in materials driven electrically[4]. Such ultrafast operando techniques could provide fundamental insights into field-induced intermediate states, metastable phases, and transport pathways in ionic systems.


9:30 AM SF03.06.02
Unlocking Exotic Charge and Spin States in Layered Materials: A Dynamic Approach via Ion-Insertion
Iwnetim I. Abate; Massachusetts Institute of Technology, United States

Layered two-dimensional (2D) and quasi-2D materials, along with their heterostructures, offer a diverse range of electronic, optical, and magnetic properties. The tunability of charge, spin, orbital, and lattice degrees of freedom in these materials, both through static and dynamic methods, provides numerous avenues for addressing fundamental questions and exploring diverse applications. Electrochemical ion-insertion in these van-der-Waals materials serves as a delicate tool to dynamically adjust their properties, potentially leading to the emergence of exotic electronic and spin states that might not be attainable through traditional synthesis methods. In this presentation, I will share our group's research on layered oxide materials where we induce exotic charge and spin states using electrochemical ion-insertion. These unique states challenge existing theoretical models and experimental observations. I will delve into the novel theoretical framework we have developed, underpinned by rigorous computational formalisms, and the distinctive magnetic, optical, and phonon properties observed experimentally.

9:45 AM SF03.06.03
Operando studies of mixed-conduction polymers: Microstructural effects and carrier-induced ordering
Alberto Salleo; Stanford University, United States

New families of conjugated polymers are being investigated as mixed conductors in applications as varied as biosensing, electrocatalysis and brain-like computing. Great advances are being made in developing materials properties and in device design and integration. A fundamental understanding of “how they work” is however still missing. In this talk I will show how we use a suite of state-of-the-art operando techniques, spectroscopic and diffraction-based implemented during electrochemical biasing to study organic mixed conductors and answer basic questions. In particular, we elucidate the effect of electrolyte and charge density on structure and properties, namely carrier mobility. Most of these materials are semicrystalline and microstructure has an effect on their operation. We find that charge density affects structure, which in turn affects the ability of the semiconductor to conduct charges.