## 2019 CNMS USER MEETING Agenda and Abstracts





#### Cover Image

Clockwise, starting at the top right picture with horizontal layout

- 1. Ferroelectric domains in  $CuInP_2S_6$  made visible by piezoresponse force microscopy. (Nina Wisinger).
- 2. STS map at Fermi surface shows the vortex lattices of superconducting Ni doped BaFe<sub>2</sub>As<sub>2</sub> under a magnetic field of 4T at 4K (Zheng Gai).
- 3. Atomically precise graphene nanoribbons grown on a gold substrate with molecular precursors (An-Ping Li).
- 4. SEM image of exfoliated iron oxide (rust) from a steel plate (Bernadeta Srijanto/Dale Hensley).
- 5. A special aberration correction algorithm shows that Si/SiGe interfacial widths can be accurately measured with a 1Å precision using atom probe tomography (APT) as verified with scanning transmission electron microscopy measurements. The image shows APT atom maps aligned with a STEM-HADDF image of a Si/SiGe interface from the same wafer region (Jonathan Poplawsky). Further details can be found here: <a href="https://science.energy.gov/bes/highlights/2018/bes-2018-08-e/">https://science.energy.gov/bes/highlights/2018/bes-2018-08-e/</a>
- 6. WS<sub>2</sub> crystals grown by chemical vapor deposition amidst lithographically-patterned Si nanopillars. SEM and AFM topography images (lower two panels) indicate triangular monolayer crystals, while intensity maps of second harmonic generation (top) and photoluminescence reveal crystalline domains and defects. (Alex Puretzky/Kai Xiao).
- 7. Helium ion microscope image of milled CVD graphene on SiN. The difference in contrast is a result of helium ion collisions defecting the graphene, which reduces the conductivity. (Jake Swett, Univ. of Oxford)
- 8. The Cu exchanged SSZ-13 zeolite catalyst shows a remarkedly improved lifetime compared to that of ZSM-5 in diesel engine catalytic converters for NOx reduction. Atom probe tomography (APT) revealed both catalysts showed signs of Cu-Al cosegregation after a 135,000 mile simulation, while Cu exchanged ZSM-5 showed a more sever co-segregation with nanoscale detrimental CuAl<sub>2</sub>O<sub>4</sub> phases present in the material (Jonathan Poplawsky). Further details can be found here: https://science.energy.gov/bes/highlights/2018/bes-2018-06-d/
- 9. Helium ion microscopy image of cotton fabric at 125 microns used to determine the longevity and tactile feel of the fabric by studying the level of degradation in the outer layer, seen as "wisps" of material surrounding each fiber (Alex Belianinov).
- 10. Low-frequency Raman spectroscopy measured vibrations between twisted 2D layers that revealed how atoms stack in multiple characteristic patterns. Mutual rotation of two monolayers of transition metal dichalcogenides creates large variety of bilayer stacking patterns depending on a twist angle (Alex Puretzky/Liangbo Liang). Puretzky, et. al. ACS Nano (2016).

### **Table of Contents**

2019 CNMS User Meeting Agenda	<b>0</b> 4
Plenary Session	<b>0</b> 5
Oral Presentations // Track A	10
Energy Storage and Conversion	
Oral Presentations // Track B	17
Quantum Materials	
Oral Presentations // Track C	21
Applied Machine Learning	
List of Posters	<b>2</b> 5
Poster Abstracts	31
*Denotes Student Poster	

#### NOTE:

The Abstract Book is available online only. A printed copy will not be included in the handout material.



Agenda

2019 CNMS User Meeting Oak Ridge National Laboratory Oak Ridge, Tennessee

CEN MAT	TER FOR NANOPHASE ERIALS SCIENCES	Asenad	A	Oak Ridge, Tennessee	
	Monday, August 12	Workshops/Tutori	als available		
4-6p	User Meeting Poster Session and Student Poster Competition - Reception, SNS Lobby				
	Tuesday, August 13				
8-9a	<b>User Group Town Hall Breakfast Meeting</b> - SNS Atrium opportunity for questions/discussions with <b>User Executive Committee</b> members				
9:00	WELCOME AND ANNOUNCEMENTS - SNS Auditorium Sean Hearne, CNMS Director				
9:30	Plenary Lecture I, SNS Auditorium Mitra Taheri, Drexel University Intelligent, Multiscale Microscopy: Predictive Understanding of Materials in Extreme Environments				
10:20	Break				
	TRACK A: Room C-156 Energy Storage and Conversion	on		TRACK B: SNS Auditorium Quantum Materials	
10:30 INVITED: Hanna Cho (Ohio State U.) Recent Advancement of Atomic Force Microscopy and Its Applications to Bio/Energy Material Research		10:30 Liangbo Liang (Oak Ridge National Laboratory) PdSe2: A Pentagonal Layered Material Bridging the Gap between 2D and 3D Materials			
11:10 Yixuan Dou (U. Tennessee) Exploring Photoinduced Dielectric Polarization in Organic- Inorganic Halide Perovskites			<b>10:55 Hanna Terletska</b> (Middle Tennessee State U.) Numerical Studies of Electron Localization in Quantum Materials		
11:35 Jisue Moon (Oak Ridge National Laboratory) Understanding Structure Evolutions over Ru-Loaded 3D Electride during Ammonia Synthesis by in situ Neutron Diffraction		<b>11:20 INVITED: Pinshane Huang</b> (U. Illinois, Urbana Champaign) Characterizing 2D Materials with Picometer Precision with Aberration-Corrected Scanning Transmission Electron Microscopy			
12:00	Lunc	h on your own; Pos	ters available for vie	wing	
12:15	<b>Lunch and Learn</b> How to Win Friends, Influence	with <b>Jacqui Weeks:</b> People, and Write	Special lecture for P Better User Proposals	ostdocs and Students, C-156 (Space limited, pre-registration required)	
TRACK A: Room C-156 Energy Storage and Conversion Continued		TRACK C: SNS Auditorium Applied Machine Learning			
2:00 Matthew Boebinger (Georgia Institute of Technology) In Situ TEM for Understanding Chemo-Mechanical Degradation in Battery Materials		<b>2:00 INVITED: Tess Smidt</b> (Lawrence Berkeley National Lab.) Toward the Systematic Generation of Hypothetical Atomic Structures: Geometric Motifs and Neural Networks			
2:25 Feng-Yuan Zhang (U. Tennessee) MoS <sub>2</sub> Nanosheets with Boosted Catalytic Performance for Hydrogen Evolution Reaction			2:40 Thomas Blum ( Machine Learning for Decomposition	U. California, Irvine) or Challenging EELS and EDS Spectral	
<b>2:50 INVITED: Scott Geyer</b> (Wake Forest U.) Putting Atoms in the Right Place for Catalysis: Atomic Templating of Transition Metals with P and B for Synthesis o Renewable Fuels		Atomic for Synthesis of	3:05 Joshua Agar (Lehigh U.) and Rama Vasudevan (ORNL) Data-Driven Approaches for Experimental Science		
3:30	Break				
3:40	Plenary Lecture II, SNS Auditorium Rampi Ramprasad, Georgia Institute of Technology Polymer Genome: A Machine Learning Platform for Rational Polymer Design				
4:30	Announcement of Student Poster Winners - SNS Auditorium				
4:45	Adjourn				
	Wednesday, August 14 Workshops/Tutorials available				

## Center for Nanophase Materials Sciences

# **Plenary Session**

**2019 User Meeting** 

#### Intelligent, Multiscale Microscopy: Predictive Understanding of Materials in Extreme Environments

Professor Mitra Taheri\* Department of Materials Science & Engineering, Drexel University \*Now at Department of Materials Science & Engineering, Johns Hopkins University, Baltimore, MD

#### ABSTRACT

In his seminal lecture, "There's Plenty of Room at the Bottom," Richard Feynman famously stated, "....The only trouble is that the electron microscope is one hundred times too poor...is there no way to make the electron microscope more powerful?" Decades later, the electron microscope would indeed improve, reaching sub-atomic resolution. While this significant advancement set the stage for understanding crystallography and elucidating atomic-scale material structures that control a wide range of properties, the need for predictive understanding of material response in those applications still existed. Moreover, even though we could now "see" atomic arrangements, what did they DO when pushed or subjected to a voltage? These questions spurred enormous investment in dynamic, or in situ, electron microscopy. In situ microscopy provides a platform for tailoring materials for specific applications and understanding their atomic scale mechanisms, expanding our knowledge of matter ranging from biological molecules to structural metals.

Designing next generation materials requires insight into various uncertainties at defect length scales. Interfaces, such as grain boundaries, domain walls, and even heterostructure interfaces play a particularly important role in property development. The mechanisms by which these interfaces interact point defects, dislocations, and other microstructural features dictate important properties such as strength, radiation tolerance, conductivity, and polarization behavior. With the ability to characterize materials behavior with high temporal and spatial resolution, we can potentially fill in gaps in the current understanding interfacial and defect-driven phenomena that define these critical material properties. Recent technique developments have allowed us to define how we can link length and time scales in critical property-determining materials phenomena. Transmission electron microscopy (or TEM), remains at the heart of these efforts, and in particular, in situ transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) are powerful tools for the observation of real-time materials processes, as probing dynamic phenomena yields a predictive understanding of myriad materials and use this knowledge to tailor future, improved systems. This talk reviews some of the latest advancements in in situ microscopy as well as case studies from my group's recent work in a variety of materials systems, including chemistry-property relationships in emerging 2D materials, semiconducting devices, next generation metallic alloys. Results from systematic studies using in situ TEM imaging and electron energy loss spectroscopy will be presented.

In closing, an outlook on emerging dynamic studies and key challenges for "big data" will be presented. In particular, high-throughput data analysis and artificial intelligence methodologies with next generation detection systems will be discussed.

#### BIO

Mitra Taheri is the Hoeganaes Endowed Chair Professor in the Department of Materials Science & Engineering at Drexel University. She leads the "Dynamic Characterization Group," which focuses primarily on the development and use of cutting edge in situ microscopy to develop and characterize materials for a wide variety of applications, ranging from energy to health. While at Drexel, she has received both the NSF and DOE Early Career awards, an ONR Summer Faculty Fellowship, and has been a visiting faculty scholar at the Politecnico di Milano, in Milan, Italy. Her research has been featured in high profile publications such as Science, Nature Communications, ACS Nano, and Nanoletters, and has delivered roughly 150 invited and keynote presentations and seminars across the world.

Taheri received her PhD in Materials Science & Engineering (MSE) from Carnegie Mellon University. As a PhD student, she received a US Steel Graduate Scholarship, a Materials Research Society Graduate Student Award, a full member to Sigma Xi, and was a visiting scholar at RWTH Aachen University in Germany, the National Center for Electron Microscopy (LBL), and the Northwestern University's Center for Atom Probe Tomography. Following her doctoral studies, Taheri was an NRC Postdoctoral Fellow at the Naval Research Laboratory (NRL) and a Director's Postdoctoral Fellow at Lawrence Livermore National Laboratory (LLNL), where she and her group won an R&D 100 award, a Nano-50, and the Microscopy Society of America's Microscopy Innovation Award.

\*Taheri is moving her group and research to Johns Hopkins University during the 2019-2020 year.\*

#### **Polymer Genome: A Machine Learning Platform for Rational Polymer Design**

Rampi Ramprasad Georgia Institute of Technology ramprasad@gatech.edu http://ramprasad.mse.gatech.edu

The Materials Genome Initiative (MGI) has heralded a sea change in the philosophy of materials design. In an increasing number of applications, the successful deployment of novel materials has benefited from the use of computational, experimental and informatics methodologies. Here, we describe the role played by computational and experimental data generation and capture, polymer fingerprinting, machine-learning based property prediction models, and algorithms for designing polymers meeting target property requirements. These efforts have culminated in the creation of an online Polymer Informatics platform (https://www.polymergenome.org) to guide ongoing and future polymer discovery and design [1-3]. Challenges that remain will be examined, and systematic steps that may be taken to extend the applicability of such informatics efforts to a wide range of technological domains will be discussed. These include strategies to deal with the data bottleneck, new methods to represent polymer morphology and processing conditions, and the applicability of emerging algorithms for design.



[1] C. Kim, A. Chandrasekaran, T. D. Huan, D. Das, R. Ramprasad, "Polymer Genome: A Data-Powered Polymer Informatics Platform for Property Predictions," Journal of Physical Chemistry C, J. 122, 31, 17575-17585 (2018).

[2] A. Mannodi-Kanakkithodi, A. Chandrasekaran, C. Kim, T. D. Huan, G. Pilania, V. Botu, R. Ramprasad, "Scoping the Polymer Genome: A Roadmap for Rational Polymer Dielectrics Design and Beyond", Materials Today, 21, 785 (2018).

[3] R. Ramprasad, R. Batra, G. Pilania, A. Mannodi-Kanakkithodi, C. Kim, "Machine Learning and Materials Informatics: Recent Applications and Prospects", npj Computational Materials 3, 54 (2017).

Prof. Ramprasad is presently the Michael E. Tennenbaum Family Chair and Georgia Research Alliance Eminent Scholar in the School of Materials Science & Engineering at the Georgia Institute of Technology. His expertise is in the virtual design and discovery of application-specific materials using computational and data-driven methods. Among his notable projects are a ONR-sponsored Multi-disciplinary University Research Initiative (MURI) in the past to accelerate the discovery of polymeric capacitor dielectrics for energy storage. He is presently leading another MURI aimed at the understanding and design of dielectrics tolerant to enormous electric fields. Prof. Ramprasad is a Fellow of the American Physical Society, an elected member of the Connecticut Academy of Science and Engineering, and the recipient of the Alexander von Humboldt Fellowship and the Max Planck Society Fellowship for Distinguished Scientists. He has authored or co-authored over 180 peer-reviewed journal articles, 6 book chapters and 4 patents. He has delivered over 150 invited talks at Universities and Conferences worldwide, and has organized several international symposia. Prof. Ramprasad received his B. Tech. in Metallurgical Engineering at the Indian Institute of Technology, Madras, India, an M.S. degree in Materials Science & Engineering at the Washington State University, and a Ph.D. degree also in Materials Science & Engineering at the University of Illinois, Urbana-Champaign.

Center for Nanophase Materials Sciences

# **Oral Presentations**

## Energy Storage and Conversion

## Track A

**2019 User Meeting** 

### Recent Advancement of Atomic Force Microscopy and Its Applications to Bio/Energy Material Research

#### Hanna Cho

Department of Mechanical and Aerospace Engineering, The Ohio State University

#### Abstract:

Since the development in the early 1980s, atomic force microscopy (AFM) has been one of the most useful tools in the field of nano- and bio-science. AFM is capable of imaging and characterizing various materials with nanometer-scale spatial resolution under any environmental conditions including in air and liquid. My research group applied our understanding of cantilever dynamics to advance the state of art AFM by (i) interpreting the signal generated by a cantilever's motion; (ii) designing a new cantilever system to obtain more information about material properties; and (iii) developing new (or advanced) techniques to measure multiphysical properties such as piezoelectricity and IR absorptivity. We recently invented a new AFM probe, so-called the inner-paddled cantilever, which enables two independent transduction channels to extend AFM's capability of material characterization beyond topographic imaging. This talk will highlight the extended capabilities enabled by the new AFM probe. Our advanced capabilities of material characterization using AFM are also actively applied to bio/energy material research. This talk will introduce our recent AFM results of investigating the role of collagen piezoelectricity in bone mineralization and in-situ measurements of battery electrodes.

#### **Exploring Photoinduced Dielectric Polarization in Organic-Inorganic Halide Perovskites**

<u>Yixuan Dou</u>, Miaosheng Wang, Jia Zhang, Hengxing Xu, Bin Hu<sup>\*</sup> Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee, 37996, USA

#### Abstract

Hybrid organic-inorganic perovskites (HOIPs) possess the possibilities of enabling photoinduced dielectric polarization. Photoinduced dielectric polarization plays an important role on suppressing the charge recombination, facilitating charge transport, and even polarizing excited states, which are critically important to the development of optoelectronic functionalities in HOIPs. However, it is difficult to realize whether photoinduced polarization contains an electrical polarization within the dipolar polarization regime in HOIPs due to lacking the mechanism of coupling dipolar and electric polarization. This issue originates from mobile ions in HOIPs, which results in the difficulty of detecting dielectric polarization. Here, we use capacitance-voltage (C-V) measurement to probe the photoinduced dipolar polarization and then confirm it by the magnetocapacitance measurement. The capacitance-voltage (C-V) detect the dipolar polarization by applying a low alternating bias of 50 mV while the mobile ions are continuously drifted by gradually scanning the bias from -0.1 V to 1.5 V. In this manner, continuously drifted ions cannot respond to the low alternating bias, enabling the detection of photoinduced electrical polarization in dipolar polarization regime. Then, to confirm the photoinduced dipolar polarization, magnetocapacitance was used to solely detect the dipolar polarization at 1 MHz in HOIPs (MA<sub>x</sub>FA<sub>(1-x)</sub>PbI<sub>3</sub>, x in the range of 0-0.75) under photoexcitation. Magneto-capacitance measurement is a signature tool to exclude the effects of mobile ions (i.e. surface polarization) as mobile ions do not respond to magnetic fields. It was found that the photoexcitation can substantially increase the magnetocapacitance amplitude, confirming that the photoexcitation indeed induces dipolar polarization in HOIPs. In summary, our studies provide a fundamental understanding of photoinduced dipolar polarization effects on the optoelectronic functionalities of HOIPs.

### Understanding structure evolutions over Ru-loaded 3D electride during ammonia synthesis by *in situ* neutron diffraction

J. Moon, J. Kammert, K. Page, J. Tong, A. J. Ramirez-Cuesta, and Z. Wu

Chemical Science Division and Chemical & Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN and Department of Materials Science and Engineering, Clemson University, Clemson, SC

Electrides are compounds that electrons are trapped in a stoichiometric composition occupying anion sites. It has been attracting increasing attention because of their potential applications such as catalyst for ammonia synthesis and low temperature electron emitters, or thermionics. Especially Ru-loaded mayenite electride which includes 3D structure( $[C_{24}Al_{28}O_{64}]^{4+}(e_{-})^4$ ) has been applied as an efficient catalyst for ammonia synthesis. It showed its superior performance in ammonia synthesis in mild condition (ambient pressure, 350~400°C) due to its efficient activation of N=N bond. This is in clear contrast to the traditional ammonia synthesis conducted under high temperature and pressure (150~250 bar at 400~500 °C)(1). The

significant improvement of reaction condition was attributed to the switching rate determining step from N<sub>2</sub> dissociation to N-H bond formation and the removal of H<sup>-</sup> poisoning of the Ru sites electride-bases over the Despite of catalyst. its outstanding activity, direct mechanism study over electride remains unclear and there is no direct observation of hydride in the cage of  $C12A7:e^{-}(2)$ . Here, we discuss our progress to understand its



**Figure 1** (a) Evolution of the d<sub>112</sub> from *in situ* Neutron diffraction under different reaction condition. Fourier difference map analysis over 2wt% Ru/C12A7:e- under (b) He and (b) N<sub>2</sub>:D<sub>2</sub>=1:3 at 400°C

ammonia synthesis mechanism using *in situ* neutron diffraction including Reitveld refinement and difference Fourier map analysis. Ru-loaded electride was synthesized and analyzed by SEM and XRD at Center for Nanophase Materials Sciences. Through isotope-contrast neutron diffraction, the distribution of deuterium and nitrogen molecules in the C12A7:e- structure were determined under reaction condition (400°C, atmospheric pressure). The result clearly showed that the occupancy of the cage change over the reaction and the gas absorption occurred over the cage wall, especially aluminate site. In addition to neutron diffraction, further analysis including pair distribution function analysis and inelastic neutron scattering will be conducted for better understanding of the ammonia synthesis mechanism over the electride-based catalysts.

Acknowledgements: This research is sponsored by Department of Energy, Laboratory Directed Research Development (LDRD). The neutron studies used resources at the Spallation Neutron Source, and further analysis including XRD and SEM were conducted at the Center for Nanophase Materials Sciences, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

- 1. M. Kitano *et al.*, Essential role of hydride ion in ruthenium-based ammonia synthesis catalysts. *Chem Sci* **7**, 4036-4043 (2016).
- 2. S. E. Siporin, R. J. Davis, Isotopic transient analysis of ammonia synthesis over Ru/MgO catalysts promoted by cesium, barium, or lanthanum. *Journal of Catalysis* **222**, 315-322 (2004).

#### In Situ TEM for Understanding Chemo-Mechanical Degradation in Battery Materials

Matthew G. Boebinger,<sup>1</sup> John A. Lewis,<sup>1</sup> Xiahan Sang,<sup>2</sup> Xiaoming Liu,<sup>2</sup> Miaofang Chi,<sup>2</sup> Raymond R. Unocic,<sup>2</sup> and Matthew T. McDowell<sup>1,3</sup>

<sup>1</sup>School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

<sup>2</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

<sup>3</sup>George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

To engineer less expensive and more energy-dense batteries, new materials must be developed to store and transport active ions beyond the currently used Li-ion materials. Current battery systems make use of liquid-based electrolytes and Li-ion electrode materials that undergo small volumetric changes to achieve higher cyclability and stability at the cost of energy density. To satisfy the growing demand for high energy density batteries, alternative materials and systems are being considered, such as lithium metal anodes, solid-state electrolytes, and high-capacity conversion cathodes. However, little is known about the reaction mechanisms these materials undergo during cycling. In this work, *in situ* transmission electron microscopy (TEM) was used to understand the nanoscale reaction mechanisms and chemo-mechanical degradation of two different materials: a conversion nanocrystal electrode material under reaction with Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>; and a Li-conducting ceramic electrolyte under reaction with pure Li metal. In both cases, the large volume changes have a profound effect on the resulting morphology and stress evolution of the material, sometimes with unexpected results.

In the first set of experiments, *in situ* TEM was used to examine cubic  $FeS_2$  nanocrystals as they reacted with Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>. In each case, the  $FeS_2$  nanocrystals underwent a two-phase conversion-type reaction, but only during lithiation was mechanical fracture observed, despite the much larger volume expansion experienced during sodiation and potassiation. This counter-intuitive behavior was found to be the result of the differently-shaped sharp reaction fronts that were present during reaction with the different ions. The reaction front present during lithiation had sharp corners, while the sodiation and potassiation fronts featured blunted corners. From chemomechanical modeling, it was found that the stress concentrated at these sharp corners to a greater degree and led to particle fracture. This finding indicates that the reaction mechanisms play a key role in determining the chemo-mechanical stability of high-capacity materials and further study into the cycling of these previously unconsidered materials with Na<sup>+</sup> and K<sup>+</sup> should be explored.

Another *in situ* TEM study was performed to investigate reaction mechanisms during the formation of the interphase between the Li-conducting ceramic electrolyte,  $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$  (LAGP), and a Li metal electrode. Little is known about the formation of interfacial phases in solid-state batteries, and their effect on electrochemical stability. The interfacial reaction of LAGP with Li was observed to involve lithium insertion and volume expansion, which results in amorphization of the crystalline LAGP. This formation of the expanded interphase induces mechanical stress within the ceramic solid electrolyte that eventually causes fracture. These experiments showed that the morphological evolution of the interphase controls the chemo-mechanical degradation of SSEs and is the root of the failure of the entire system.

### MoS<sub>2</sub> Nanosheets with Boosted Catalytic Performance for Hydrogen Evolution Reaction

Zhiqiang Xie<sup>1</sup>, Gaoqiang Yang<sup>1</sup>, Shule Yu<sup>1</sup>, David A. Cullen<sup>2</sup>, Zili Wu<sup>2</sup>, Scott T. Retterer <sup>2</sup>, and <u>Feng-Yuan Zhang<sup>1</sup>\*</u>

<sup>1</sup>Nanodynamics and High-Efficiency Lab for Propulsion and Power Department of Mechanical, Aerospace & Biomedical Engineering UT Space Institute, University of Tennessee, Knoxville

> <sup>2</sup>Center for Nanophase Materials Sciences Oak Ridge National Laboratory

The electrocatalytic hydrogen evolution reaction (HER) activities of pristine molybdenum disulfides (MoS<sub>2</sub>) mainly originate from their edge sites and sulfur vacancies (S-vacancies). However, the HER performance of MoS<sub>2</sub> is still largely limited due to insufficient active edge sites and low concentration of S-vacancies within basal planes. In this work, a thorough study of electrochemical performances of defect-rich MoS<sub>2</sub> nanosheets is performed. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) are used to study the defect-rich structures of MoS<sub>2</sub> nanosheets before and after electrochemical measurements.

<sup>&</sup>lt;sup>1</sup> Corresponding author. Tel: +1-931-393-7428; Email address: fzhang@utk.edu

#### Putting Atoms in the Right Place for Catalysis: Atomic Templating of Transition Metals with P and B for Synthesis of Renewable Fuels

#### Scott Geyer Wake Forest University

Solving outstanding challenges in selective electrochemical catalysis such as  $CO_2$  reduction, nitrogen reduction and oxygen reduction will require rational design of all aspects of the catalytic site: atom placement, intermediate coordination, binding strengths, and surface coupling. We have established a framework in which high P and B content is used to isolate transition metals sufficiently to destabilize pocket or bridged binding sites, creating an analogous structure to single atom catalysts but with a key variation: the surrounding P and B can act as a proton reservoir in the essential hydrogenation steps. This concept will first be developed with respect to the role of stoichiometry in the hydrogen evolution reaction where experimental and theoretical results comparing  $Co_2P$ , CoP and  $CoP_2$  show dramatic increase in performance with P content, consistent with removal of overly bound bridge binding sites. The low Tafel slope further suggests a mechanism in which both Co and P are active, given the isolation of Co sites. The final result is  $CoP_2$  NCs with a mass activity that rivals that of Pt NCs.

The role of P is further examined for reactions requiring a high degree of selectivity. We have recently focused on P analogs of model selective catalysts:  $AgP_2$  for  $CO_2$  reduction and  $PtP_2$  for oxygen reduction. Our goal has been to develop a framework in which the effect of P can be grouped into geometric effects (such as reduction in intermediate coordination via metal atom isolation) and electronic effects (such as stabilization of positive oxidation states at reducing potentials).  $PtP_2$  is an excellent example of P playing a dual geometric and electronic role. The increased Pt-Pt distance reduces the stability of the bridged \*OOH binding while also weakening the \*OOH top site through changes to the Pt density of states. This leads to a dramatic switch in selectivity towards  $H_2O_2$  from  $H_2O$  for oxygen reduction, with the key advantage over PtHg systems of being Hg free. We show these particles can be stabilized to produce concentrated  $H_2O_2$  at a large scale in a fuel cell type architecture.

In CO<sub>2</sub> reduction,  $AgP_2$  exhibits a greatly reduced overpotential for CO production compared to Ag, and we find that the overpotential change predicted by density functional theory is in excellent agreement. We believe the templating of Ag by P reduces its coordination to other surface atoms, increasing its activity. We find that the CO/H<sub>2</sub> ratio is widely tunable, allowing for voltage tunable production of syngas as a precursor for Fischer-Tropsch synthesis. Finally, we will discuss future directions in CO<sub>2</sub> and N<sub>2</sub> reduction.

Center for Nanophase Materials Sciences

# **Oral Presentations**

## **Quantum Materials**

## Track B

**2019 User Meeting** 

#### PdSe<sub>2</sub>: a Pentagonal Layered Material Bridging the Gap between 2D and 3D Materials

Liangbo Liang, Kai Xiao, Alexander Puretzky, An-Ping Li, David Geohegan, Bobby Sumpter Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831



**Figure 1:** PdSe<sub>2</sub>, a novel layered material with atoms that tile in the famous Cairo pentagonal pattern. It behaves like a 2.5D material due to the unique atomic structure and stronger-than-vdW interlayer coupling.

PdSe<sub>2</sub> is a new layered material with an in-plane pentagonal network and stronger-than-vdW interlayer coupling. It offers great trade-off between carrier mobility, band gap, and air stability for nanoelectronics [1]. Because of its unique atomic structure and strong interlayer coupling, it behaves like 2.5D material and many of its properties are different from those of commonly known 2D materials, such as graphene and MoS<sub>2</sub>. Here I will highlight how we seamlessly integrated multiple CNMS research capabilities, including synthesis, characterization, device fabrication, and modeling/simulation, to explore the structural, electronic, and vibrational properties of PdSe<sub>2</sub>. Because of strong interlayer coupling, its electronic band gap varies significantly from 1.3 eV (monolayer) to 0.06 eV (bulk), based on our calculations and measurements [1]. For 2D graphene and MoS<sub>2</sub> that have weak interlayer interactions, the layers are quasi-rigid in low-frequency interlayer vibrations, which can be described by a linear chain model (LCM); however, in PdSe<sub>2</sub> the layers are no longer quasi-rigid, according to our Raman scattering calculations and measurements. Therefore, the thickness dependence of the interlayer Raman modes' frequencies in PdSe<sub>2</sub> deviates significantly from the LCM. A revised LCM was developed to account for the layer non-rigidity [2]. Finally, according to our nudged elastic band calculations, the pentagonal structure and strong interlayer coupling lead to low diffusion barriers for defects, and hence both intralayer and interlayer hopping of defects can occur relatively easily in PdSe<sub>2</sub> compared to MoS<sub>2</sub>, as observed by scanning tunneling microscope [3]. Our works on PdSe<sub>2</sub> pave the road for the understanding of 2D materials featuring strong and beyond-vdW interlayer interactions.

- [1] A. Oyedele\*, S. Yang\*, <u>L. Liang</u>\*, A. Puretzky, P. Yu, P. Pudasaini, Z. Liu, B. Sumpter, M. Chisholm, W. Zhou, P. Rack, D. Geohegan, K. Xiao, *Journal of the American Chemical Society*, 139 (2017), 14090. [\*Co-lead author]
- [2] A. Puretzky\*, A. Oyedele, K. Xiao, B. Sumpter, D. Mandrus, D. Geohegan, <u>L. Liang</u>\*, 2D Materials, 5 (2018), 035016. [\*Corresponding author]
- [3] G. Nguyen, <u>L. Liang</u>\*, Q. Zou, M. Fu, A. Oyedele, B. Sumpter, Z. Liu, Z. Gai, K. Xiao, A. Li\*, *Physical Review Letters*, 121 (2018), 086101. [\*Corresponding author]

#### Numerical Studies of Electron Localization in Quantum Materials.

Hanna Terletska<sup>1</sup>, Joseph Paki<sup>2</sup>, Sergei Iskakov<sup>2</sup>, Emanuel Gull<sup>2</sup>, Thomas Maier<sup>3</sup>.

<sup>2</sup> <sup>1</sup>Department of Physics and Astronomy, Middle Tennessee State University, <sup>2</sup> Department of Physics, University of Michigan, <sup>3</sup> Oak Ridge National Laboratory.

Many functional properties of quantum materials are intrinsically tied to localized behavior of electrons. The electron-electron driven metal-insulator transition is one of the fundamental phenomena directly related to electron localization, and despite intensive studies still remains largely unsettled. Various exotic phases of matter with potential functional applications are found in the vicinity of such electron localization, including the superconductivity emerging in Mott insulators under chemical doping. Hence, revealing the origin of emerging quantum states of matter in quantum materials is essential for energy technology applications and materials design.

Because of the non-perturbative nature of the interactions, strongly correlated systems are theoretically very challenging. Due the recent advances in numerical methods [1] and the development of non-perturbative many-body techniques such as dynamical mean field theory (DMFT) [2] and its cluster extensions, e.g., the Dynamical Cluster Approximation (DCA) [3], there has been much progress reached. Particularly, significant progress has been achieved in numerical studies of the Hubbard model, which is one of the commonly used minimal models for description of the electron-electron interactions in such systems.

Our focus here is to reveal the effect of non-local Coulomb interactions on the Mott metal-insulator transition. The Mott metal-insulator transition is one of the fundamental phenomena in strongly correlated electron systems. Nonetheless, few exact results are known, especially beyond the local DMFT approximation.

Recent numerical studies [4] of the two-dimensional (2D) Hubbard model have questioned the very presence of the metal-insulator transition in 2D. Their study shows that strong spatially extended antiferromagnetic correlations lead to insulating behavior at any finite onsite interactions, i.e. no metal-insulator transition occurs.

In this work, we use the DCA for cluster size Nc=4. and show that indeed, once non-local correlations beyond the local DMFT level are taken into account, they have a dramatic affect on the metal-insulator transition in 2D. We find that the coexistence region of the metal-insulator transition as well as the shape of it get significantly modified once non-local effects are taken into account. Our results are consistent with those of Ref. [4] .

To look for the possible routes towards stabilization of the metal-insulator transition in 2D systems, we took into account the non-local inter-site Coulomb interactions (inevitably present in real systems), which are neglected in Hubbard model. We show that these non-local interstice electron-electron interactions can lead to the emergence of charge-ordered phase with checkerboard arrangement of electrons. We also find that non-local interactions decrease the correlation effects via screening, resulting in more metallic behavior of the system. Our results suggest that the non-local electron-electron interactions can be

1. E. Gull et al., Reviews of Modern Physics 83, 349 (2011).

considered as a plausible route towards the stabilization of the metal-insulator transition in 2D.

- 2. A. Georges et al., Rev. Mod. Phys. 63, 13 (1996).
- 3. T. Maier et al., Rev. Mod. Phys. 77, 1027 (2005).
- 4. T. Schäfer et al., Phys. Rev. B 91, 125109 (2015).



Figure 1: V-U phase diagram for extended Hubbard model at T=0.1. Data obtained for Nc=4 DCA cluster. The results show that the metal-insulator transition boundary is pushed to larger U as the strength of inter-site electronelectron interactions V increases. Also, at larger V, a charge order phase emerges with checkerboard arrangement of electrons on lattice sites.

## Characterizing 2D materials with picometer precision with aberration-corrected scanning transmission electron microscopy

#### **Pinshane Y Huang**

Materials Science and Engineering University of Illinois at Urbana-Champaign

Defect and strain engineering of 2D materials is an emerging area of research, where homogeneous or heterogeneous alloying can stabilize exotic electronic phases such as Weyl semimetals or pattern the properties of 2D nanoelectronics and optoelectronics on the nanoscale. Aberrationcorrected scanning transmission electron microscopy (STEM) is an important tool to study how atomic defects such as vacancies and substitutional dopants impact the structure and properties of 2D materials. Yet, high-precision characterization of defects in 2D materials remains challenging because they are irradiation sensitive, making it difficult to achieve high resolution and signal-tonoise ratio (SNR) measurements without modifying the intrinsic structure. Here, we demonstrate methods that use deep learning techniques based on convolutional neural networks (CNNs) to interpret large volumes of atomic-resolution images of 2D transition metal dichalcogenides (TMDCs). CNNs have revolutionized image recognition in fields such as medical diagnosis, weather forecasting, and facial recognition; recently, they have been applied to detect defects in atomic-resolution STEM images. In our work we utilize fully convolutional network (FCN), a variant of CNN, to identify defects in monolayer WSe<sub>2-x</sub>Te<sub>x</sub>. Using the resulting data, we are able to visualize the local picometer-scale strain fields to understand how single-atom defects interact with one another and the surrounding lattice. These results will be important to the design of 2D quantum materials with tailored properties.

Center for Nanophase Materials Sciences

# **Oral Presentations**

## **Applied Machine Learning**

## Track C

**2019 User Meeting** 

#### Toward the Systematic Generation of Hypothetical Atomic Structures: Geometric Motifs and Neural Networks

#### Tess Smidt

#### Lawrence Berkeley National Laboratory

Materials discovery, a multidisciplinary process, now increasingly relies on computational methods. We can now rapidly screen materials for desirable properties by searching materials databases and performing high-throughput first-principles calculations. However, high-throughput computational materials discovery pipelines are bottlenecked by our ability to hypothesize new structures, as these approaches to materials discovery often presuppose that a material already exists and is awaiting identification. In contrast to this assumption, synthesis efforts regularly yield materials that differ substantially from the structures in databases of previously known materials. In this talk, we discuss strategies for generating hypothetical atomic structures using the concepts of geometric motifs (the recurring patterns of atoms in materials) and neural networks that can manipulate discrete geometry (tensor field networks).

#### Machine Learning for Challenging EELS and EDS Spectral Decomposition

<u>Thomas Blum<sup>1,2,\*</sup></u>, Jeffery Graves<sup>3</sup>, Michael Zachman<sup>2</sup>, Ramakrishnan Kannan<sup>3</sup>, Xiaoqing Pan<sup>1</sup>, Miaofang Chi<sup>2,\*</sup>

<sup>1</sup> Physics & Astronomy, University of California, Irvine, Irvine, CA, USA

- <sup>2</sup> Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA
- <sup>3</sup> Computational Data Analytics, Oak Ridge National Laboratory, Oak Ridge, TN, USA
- \* Corresponding Authors: tblum@uci.edu, chim@ornl.gov

Scanning transmission electron microscopy (STEM) is one of the primary methods of characterizing heterogenous catalysts due to its extraordinary spatial resolution and the ability to perform imaging and chemical analysis simultaneously at the atomic scale. For the characterization of heterogenous catalysts that are composed of a metal nanoparticle and oxide support, the atomic configurations are often probed by Zcontrast imaging while the chemical distributions can be revealed by using either electron energy loss spectroscopy (EELS) or energy dispersive X-ray spectroscopy (EDS). However, challenges in characterizing catalysts using STEM lay in detecting the subtle chemical and electronic structure changes on the metal nanoparticle surfaces. Possible overlapping of peaks/edges in EELS and EDS further complicate the analysis, making traditional analysis difficult. Machine learning offers exciting tools for analyzing EELS and EDS spectrum images where traditional analysis techniques struggle. We propose a new procedure for improving the convergence of the non-negative matrix factorization (NMF) dimension reduction algorithm to a meaningful and interpretable result. A weakness of conventional NMF is its sensitivity to local minima during convergence. One way to combat this effect is to impose additional constraints, or costs, on the minimization algorithm to reduce the likelihood of settling at a local minimum. Another approach is to use an improved initial guess, which increases the likelihood of the algorithm reaching the global minimum. Here, we combine both of these techniques to improve the quality of results by using the non-linear "perfect pixel" algorithm, ATGP, to generate initial guesses for the joint-nonnegative matrix factorization algorithm that augments the cost function of NMF and encourages sparsity in the pixels and smooth transitions. Figures 1 and 2 show that Joint-NMF identified the palladium nanocube in the second component and differentiated two carbon components. The first component is the uniform lacey carbon support and the third component builds in thickness a feature characteristic of carbon contamination. The number of components was estimated by selecting the number of components required to capture the most variance as determined with PCA. This work shows that this new machine learning based algorithm is able to detect overlapping components in EELS spectrum image datasets that are challenging for conventional microscopy data analysis methods.



**Figure 1.** Z-contrast STEM image and component maps of palladium on carbon from Joint-NMF. The length of the scale bar is 2 nm.



**Figure 2.** Spectral components from Joint-NMF. (i) lacey carbon support, (ii) palladium component, (iii) carbon contamination

#### Data-Driven Approaches for Experimental Science

Joshua C. Agar,<sup>1</sup> Rama Vasudevan<sup>2</sup>

<sup>1</sup>Lehigh University, Bethlehem, PA 18015, USA <sup>2</sup>Center for Nanophase Materials Science, Oak Ridge National Laboratory, TN 37830, USA

Scientific discoveries are punctuated by new capabilities to reproducibly design, create, stabilize, characterize, and understand the matter which is synthesized, processed, or shaped into functional forms. Despite one-off laboratory successes of "disruptive technological breakthroughs" downstream commercial integration of laboratory discoveries has been underwhelming. One of the key limitations is the inability to reproduce experiments. This "reproducibility crisis" translates to research and development efforts, wherein, it is common for nominally-the-same material produced using different synthesis methods or by different research groups to exhibit marked differences in structure and properties.<sup>2</sup> This, in turn, severely hinders community-driven scientific developments, siloing access to materials and understanding to small interacting groups of researchers who have access to "the secret sauce". Addressing this problem requires a multifaceted approach combining new norms in scientific data management which makes the data FAIR (*i.e.*, findable, accessible, interoperable, and reusable),<sup>3</sup> and intelligent algorithms which turn this data into actionable information. Here, we highlight the importance of data management and provide exposures to community driven projects which can facilitate this effort. We will then discuss how to adapt state-of-the-art machine learning approaches to accelerate the analysis of spectra, images, hyperspectral images, and even use these tools to generate predictive data-driven experiments. We will conclude by highlighting some of the shortcomings of existing algorithms in dealing with problems in nanoscience and provide our perspective on opportunity areas for materials specific algorithm development.

- 1. Baker, M. 1,500 scientists lift the lid on reproducibility. *Nature* **533**, 452–454 (2016). doi:10.1038/533452a
- Zhang, J., Rutkowski, M., Martin, L. W., Conry, T., Ramesh, R., Ihlefeld, J. F., Melville, A., Schlom, D. G. & Brillson, L. J. Surface, bulk, and interface electronic states of epitaxial BiFeO<sub>3</sub> films. *J. Vac. Sci. Technol. B Microelectron. Nanometer Struct. Process. Meas. Phenom.* 27, 2012–2014 (2009).
- Wilkinson, M. D., Dumontier, M., Aalbersberg, I. J. J., Appleton, G., Axton, M., Baak, A., Blomberg, N., Boiten, J.-W., da Silva Santos, L. B., Bourne, P. E., Bouwman, J., Brookes, A. J., Clark, T., Crosas, M., Dillo, I., Dumon, O., Edmunds, S., Evelo, C. T., Finkers, R., Gonzalez-Beltran, A., Gray, A. J. G., Groth, P., Goble, C., Grethe, J. S., Heringa, J., 't Hoen, P. A. C., Hooft, R., Kuhn, T., Kok, R., Kok, J., Lusher, S. J., Martone, M. E., Mons, A., Packer, A. L., Persson, B., Rocca-Serra, P., Roos, M., van Schaik, R., Sansone, S.-A., Schultes, E., Sengstag, T., Slater, T., Strawn, G., Swertz, M. A., Thompson, M., van der Lei, J., van Mulligen, E., Velterop, J., Waagmeester, A., Wittenburg, P., Wolstencroft, K., Zhao, J. & Mons, B. The FAIR Guiding Principles for scientific data management and stewardship. *Sci Data* 3, 160018 (2016). doi:10.1038/sdata.2016.18

#### Center for Nanophase Materials Sciences 2019 User Meeting Poster Session

\*denotes Student Poster

#### Monday, August 12, 2019 4:00 - 6:00p

#### **Poster Locations**

SNS Lobby – 2 Levels: 01-53 Posters will also be available for viewing on Tuesday, August 13

01. Exploring Photoinduced Dielectric Polarization in Organic-Inorganic Halide Perovskites Yixuan Dou, Miaosheng Wang, Jia Zhang, Hengxing Xu, Bin Hu Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA

## 02. The Effect of Surface Curvature on Coalescence-Induced Jumping of Nanodroplets on Superhydrophobic Surfaces

Xukun He, Lei Zhao, and Jiangtao Cheng Department of Mechanical Engineering, Virginia Tech, Blacksburg, VA 24060, United States

#### 03. Electrochemical Reduction of Nitrogen to Ammonia under Ambient Conditions Kui Li,<sup>1</sup> Gaoqiang Yang,<sup>1</sup> Shule Yu,<sup>1</sup> David A. Cullen,<sup>2</sup> Zili Wu,<sup>2</sup> Scott T. Retterer,<sup>2</sup> and Feng-Yuan Zhang<sup>1</sup> <sup>1</sup>Nanodynamics and High-Efficiency Lab for Propulsion and Power; Department of Mechanical, Aerospace & Biomedical Engineering; UT Space Institute, University of Tennessee, Knoxville <sup>2</sup>Center for Nanophase Materials Sciences Oak Ridge National Laboratory

#### 04. \*Theoretical Studies of Electroreduction of N2 in Strong Electric Field Anna Y. Duke, Dillon G. Gagnon, Jacek Jakowski, Adam J. Rondinone, Bobby G. Sumpter, Jingsong Huang Center for Nanophase Materials Sciences, ORNL, Oak Ridge, TN 37831-6493

## 05. \*Carbon polyaniline capacitive deionization electrodes: Application and further insight from neutron vibrational spectroscopy

Samuel F. Evans,<sup>1,2</sup> Zachary D. Hood,<sup>3,4</sup> Yongqiang Cheng,<sup>5</sup> Marko R. Ivancevic,<sup>1</sup> Devin J. Wilson,<sup>1</sup> Shiba P. Adhikari,<sup>6</sup> Amit K. Naskar,<sup>2,6</sup> Costas Tsouris,<sup>7</sup> M. Parans Paranthaman<sup>1,2</sup> <sup>1</sup>Chemical Sciences Division, Oak Ridge National Lab, Oak Ridge, TN 37831 <sup>2</sup>The Bredesen Center for Interdisciplinary Research and Graduate Education, Knoxville, TN 37996 <sup>3</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139 <sup>4</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831 <sup>5</sup>Chemical and Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

<sup>7</sup>Energy and Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

#### 06. \*Neutron Spectroscopic and Thermochemical Characterization of Lithium-Aluminum Layered Double Hydroxide Chloride

Samuel F. Evans,<sup>1,2</sup> Lili Wu,<sup>3</sup> Yongqiang Cheng,<sup>4</sup> Alexandra Navrotsky,<sup>3</sup> Bruce A. Moyer,<sup>1</sup> Stephen Harrison,<sup>5</sup> M. Parans Paranthaman<sup>1,2</sup>

<sup>1</sup>Chemical Sciences Division, Oak Ridge National Lab, Oak Ridge, TN 37831
<sup>2</sup>The Bredesen Center for Interdisciplinary Research and Graduate Education, Knoxville, TN 37996
<sup>3</sup>Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California Davis, Davis CA 95616
<sup>4</sup>Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
<sup>5</sup>All American Lithium, Brawley CA 92227

#### 07. \*Characterizing Chemo-Mechanical Degradation at Solid-State Battery Interfaces

John A. Lewis,<sup>1</sup> Jared Tippens,<sup>2</sup> Francisco Javier Quintero Cortes,<sup>1</sup> Matthew T. McDowell,<sup>1,2</sup> <sup>1</sup>School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, 30332 <sup>2</sup>George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, 30332

\*Ferroic and Ionic Behavior of Photovoltaic Hybrid Organic-Inorganic Perovskites 08. Yongtao Liu,<sup>1,2</sup> Liam Collins,<sup>1</sup> Anton V. Ievlev,<sup>1</sup> Alex Belianinov,<sup>1</sup> Stephen Jesse,<sup>1</sup> Kai Xiao,<sup>1</sup> Mahshid Ahmadi,<sup>2</sup> Bin Hu.<sup>2</sup> Sergei V. Kalinin.<sup>1</sup> Olga S. Ovchinnikova<sup>1</sup> \* <sup>1</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, United States <sup>2</sup>Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, United States \*Determining the Structure and Stability of Thermoelectric La<sub>3-x</sub>Te<sub>4</sub>-Ni Composites using High-Resolution 09. and *In-Situ* TEM M. P. Thomas,<sup>1</sup> A. Ullah,<sup>1</sup> D. Cheikh,<sup>2</sup> S. K. Bux,<sup>2</sup> and B. S. Guiton<sup>\*1</sup> <sup>1</sup>Department of Chemistry, University of Kentucky, Lexington, Kentucky, USA <sup>2</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA Toward a general method for inserting metal atoms in graphene at the atomic scale 10. Ondrei Dvck.<sup>1</sup> Jacob Swett.<sup>2</sup> Cheng Zhang.<sup>3</sup> Philip Rack.<sup>1,3</sup> Jason D. Fowlkes.<sup>1,3</sup> Andrew R. Lupini.<sup>1</sup> Sergei V. Kalinin,<sup>1</sup> Stephen Jesse<sup>1</sup> <sup>1</sup>Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN <sup>2</sup>Oxford University, Department of Materials, Oxford OX1 3PH, UK <sup>3</sup>Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN Localized electrical transport at vertically oriented oxide interfaces 11. Wenrui Zhang, Christopher M. Rouleau, Jong Keum, Zheng Gai, Gyula Eres Center for Nanophase Materials Sciences, Oak Ridge National Laboratory \*Infrared Plasmonic Response and Fluorine-Induced Faceting in Colloidal F:In<sub>2</sub>O<sub>3</sub> Nanocubes 12. Shin Hum Cho,<sup>1</sup> Sandeep Ghosh,<sup>1</sup> Zachariah J. Berkson,<sup>2</sup> Jordan A. Hachtel,<sup>3</sup> Jianjian Shi,<sup>4</sup> Xunhua Zhao,<sup>4</sup> Lauren C. Reimnitz,<sup>1</sup> Clayton J. Dahlman1,<sup>5</sup> Yujing Ho,<sup>1</sup> Anni Yang,<sup>1</sup> Yuanyue Liu,<sup>4</sup> Juan-Carlos Idrobo,<sup>3</sup> Bradley F. Chmelka,\*2 Delia J. Milliron<sup>1</sup> <sup>1</sup>McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin <sup>2</sup>Department of Chemical Engineering, University of California, Santa Barbara <sup>3</sup>Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge <sup>4</sup>Department of Mechanical Engineering, The University of Texas at Austin, Austin <sup>5</sup>Materials Department, University of California, Santa Barbara \*Mixed metal zero-mode guides (ZMWs) for tunable fluorescence enhancement 13. Abdullah Al Masud,<sup>1</sup> W. Elliott Martin,<sup>1</sup> Faruk H. Moonschi,<sup>1</sup> Bernadeta R. Srijanto,<sup>2</sup> C. Patrick Collier,<sup>2</sup> Christopher I. Richards\*1 <sup>1</sup>Department of Chemistry, University of Kentucky, 505 Rose street, Lexington KY 40506 <sup>2</sup>Center for Nanophase Materials Sciences, Oak Ridge National Lab, Oak Ridge TN 37831 \*Epitaxial stabilization of Ruddlesden-Popper iridate series and iridate superlattice 14. Junyi Yang, Lin Hao, Han Zhang, Kyle Noordhoek and Jian Liu Department of Physics and Astronomy, University of Tennessee at Knoxville Toward control of the photonic and phononic quantum state of hBN single-photon emitters 15. Matthew A. Feldman,<sup>1,2</sup> Claire E. Marvinney,<sup>2</sup> Nathan Rosenmann,<sup>3</sup> Tristan Carlson,<sup>4</sup> Yu-Chuan Lin,<sup>5</sup> Yiyi Gu,<sup>3</sup> Kai Xiao,<sup>5</sup> James H. Edgar,<sup>6</sup> Ivan I. Kravchenko,<sup>5</sup> Alexander A. Puretzky,<sup>5</sup> Richard F. Haglund,<sup>1</sup> and Benjamin J. Lawrie<sup>2</sup> <sup>1</sup>Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, USA <sup>2</sup>Quantum Information Science Group, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA <sup>3</sup>Department of Physics, University of Illinois, Chicago, Chicago, IL 60607, USA <sup>4</sup>Department of Physics and Astronomy, University of the South, Sewanee, TN 37383, USA <sup>5</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA <sup>6</sup>Department of Chemical Engineering, Kansas State University, Manhattan, Kansas 66506, USA Combined HREELS, STM, and STS study of Sr<sub>3</sub>(Ru<sub>1-x</sub>Mn<sub>x</sub>)<sub>2</sub>O<sub>7</sub> 16. Yifan Yang,<sup>1</sup> Mingming Fu,<sup>2</sup> Rongyin Jin,<sup>1</sup> Ward Plummer,<sup>1</sup> Gai Zheng<sup>2</sup> <sup>1</sup>Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70803 <sup>2</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory Oak Ridge, TN 37831, USA

#### 17. Assembly of proteins in solution and at the interface

Marek Tatarko,<sup>1</sup> Eric S. Muckley,<sup>2</sup> Ivan Sukuba,<sup>1</sup> Monojoy Goswami,<sup>2,3</sup> Jan-Michael Carrillo,<sup>2,3</sup> Bobby G. Sumpter,<sup>2,3</sup> Tibor Hianik,<sup>1</sup> Ilia N. Ivanov<sup>2</sup>

<sup>1</sup>Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynska dolina, 842 48 Bratislava, Slovakia
<sup>2</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831
<sup>3</sup>Computational Sciences and Engineering Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831

#### 18. \*A Physics-Inspired Representation of Local Atomic Structure for Developing Physically-Informed Machine Learning Based Interatomic Potentials

Matthew C. Barry,<sup>1</sup> Surya R. Kalidindi,<sup>1-3</sup> and Satish Kumar<sup>1</sup> <sup>1</sup>Department of Mechanical Engineering, Georgia Institute of Technology <sup>2</sup>Department of Materials Science and Engineering, Georgia Institute of Technology <sup>3</sup>Department of Computational Science and Engineering, Georgia Institute of Technology

#### 19. \*Laser-induced Carbon base Smart Flexible Sensor Array for Multi Flavors Detection

Yongchao Yu,<sup>1</sup> Lingyue Zhang,<sup>1</sup> David Hu,<sup>3</sup> Zhili Feng,<sup>2</sup> Pooran C Joshi,<sup>2</sup> Jayne Wu,<sup>3</sup> Zili Wu,<sup>4</sup> \*Anming Hu<sup>1</sup> <sup>1</sup>Department of Mechanical, Aerospace and Biomedical Engineering, University of Tennessee, Knoxville, TN37996, USA <sup>2</sup>Division of Materials Science, Oak Ridge National Lab, Oak ridge, TN 37831-6061 USA <sup>3</sup>Department of Electrical Engineering & Computer Science, University of Tennessee, Knoxville, TN37996, USA <sup>4</sup>Center of Nanophase Materials Science, Oak Ridge National Lab Oak Ridge, TN 37831-6061 USA

#### 20. Memory and Learning in biomolecular soft materials for neuromorphic computing

Joseph Najem,<sup>1</sup>Ryan Weiss,<sup>2</sup>M. Sakib Hasan,<sup>2</sup> Graham Taylor,<sup>3</sup> R. Stanley Williams,<sup>4</sup> Garrett Rose,<sup>2</sup> Stephen A. Sarles,<sup>1</sup>C. Patrick Collier<sup>5</sup>

<sup>1</sup>Mechanical, Aerospace and Biomedical Engineering, University of Tennessee Knoxville

<sup>2</sup>Electrical Engineering and Computer Science, University of Tennessee Knoxville

<sup>3</sup>Bredesen Center, University of Tennessee Knoxville

<sup>4</sup>Department of Computer Science and Engineering

<sup>5</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

#### 21. Parametric Study of Modulated Light Transmission Through Nanoscale Hole Arrays

Alaa Adel Abdelhamid, Francis X. Hart, and Eugenii U. Donev

Department of Physics and Astronomy, The University of the South, Sewanee, Tennessee

## 22. From suppressed void growth to significant void swelling in NiCoFeCr complex concentrated solid-solution alloy

Zhe Fan,<sup>1</sup> Tai-ni Yang,<sup>2</sup> B. Kombaiah,<sup>1</sup> Xing Wang,<sup>3</sup> P.D. Edmondson, Y.N. Osetsky,<sup>1</sup> Hongbin Bei,<sup>1</sup> Ke Jin,<sup>1</sup> Chenyang Lu,<sup>2</sup> Lumin Wang,<sup>2</sup> Karren L. More,<sup>3</sup> William J. Weber,<sup>4,1</sup> Yanwen Zhang,<sup>1,4</sup> <sup>1</sup>Materials Science and Technology Division, Oak Ridge National laboratory, Oak Ridge, TN 37831, USA <sup>2</sup>Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI 48109, USA <sup>3</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA <sup>4</sup>Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA

#### 23. 3D Nanoprinting using an Electron Beam

Eva Mutunga,<sup>1,3</sup> R. Winkler,<sup>3</sup> J. Sattelkow,<sup>3</sup> P. D. Rack<sup>1,2,4</sup> H. Plank,<sup>3,5</sup> and J. D. Fowlkes\*,<sup>1,2,5</sup> <sup>1</sup>Bredesen Center for Interdisciplinary Research and <sup>2</sup>Materials Science and Engineering Department, The University of Tennessee, Knoxville, Tennessee 37996, United States

<sup>3</sup>Christian Doppler Laboratory for Direct–Write Nanofabrication of 3D Nano–Probes (DEFINE), Institute of Electron Microscopy, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria

<sup>4</sup>Nanofabrication Research Laboratory, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

<sup>5</sup>Institute for Electron Microscopy, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria

#### 24. Synthesis of Bottlebrushes from PGMA-PVDMA Block Copolymers

Bin Hu, Nikolay Borodinov, Rajeev Kumar, Scott T. Retterer, Bradley S. Lokitz Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

#### 25. Greyscale E-Beam Lithography Revisited: Dynamic Range and Roughness of Patterns on Silicon Ivan Kravchenko, Nickolay Lavrik, Abhijeet Guirati and Tevis Jacobs

<sup>1</sup>Center for Nanophase Materials Sciences Oak Ridge National Laboratory, Oak Ridge, TN, USA <sup>2</sup>Mechanical Engineering & Materials Science, University of Pittsburgh, Pittsburgh, PA, USA

#### 26. Norbornene-based Bottlebrush Polymers: Controlled Synthesis, Characterization, and Solution Behavior

Tianyu Li,<sup>1</sup> Hui Li,<sup>2</sup> Kunlun Hong,<sup>2\*</sup>

<sup>1</sup>Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Knoxville, TN, 37996 <sup>2</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831

#### 27. An *Ab Initio* Description of Electronic Response to Electron Beam Irradiation D. B. Lingerfelt, J. Jakowski, P. Ganesh, and B. G. Sumpter Center for Nanophase Materials Sciences, Oak Ridge National Lab, Oak Ridge TN 37831

#### 28. Systematic Computational Fluid Dynamics Study of the Gas Transport in a Closed Desorption Cell to Combine Atomic Force Microscopy and Atmospheric Pressure Mass Spectrometry in a Multimodal Imaging Platform

Matthias Lorenz,<sup>1,2</sup> Ryan Wagner,<sup>3</sup> Roger Proksch,<sup>3</sup> Olga S. Ovchinnikova<sup>2</sup> <sup>1</sup>University of Tennessee, Knoxville, TN 37996 <sup>2</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831 <sup>3</sup>Oxford Instruments Company, Santa Barbara, CA 93117

#### 29. Investigation of Carbon Nanostructures in Cu Covetics by APT, HIM, and TOF-SIMS

Beihai Ma,<sup>1</sup> Uthamalingam Balachandran,<sup>1</sup> Tae H. Lee,<sup>1</sup> Steve E. Dorris,<sup>1</sup> Jianguo Wen,<sup>2</sup> Yuzi Liu,<sup>2</sup> Jonathan D. Poplawsky,<sup>3</sup> Anton Ievlev,<sup>3</sup> Artem Trofimov,<sup>3</sup> and Alex A. Belianinov<sup>3</sup> <sup>1</sup>Applied Materials Division, Argonne National Laboratory, Argonne, IL 60439 <sup>2</sup>Nanoscience and Technology Division, Argonne National Laboratory, Argonne, IL 60439 <sup>3</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

#### **30.** Tunable quadruple-well ferroelectricity in a van-der-Waals layered material

Sabine Neumayer,<sup>1</sup> John A. Brehm,<sup>2,3</sup> Lei Tao,<sup>3</sup> Andrew O'Hara,<sup>3</sup> Marius Chyasnavichus,<sup>1</sup> Michael A. Susner,<sup>5</sup> Michael A. McGuire,<sup>2</sup> Sergei V. Kalinin,<sup>1</sup> Stephen Jesse,<sup>1</sup> Panchapakesan Ganesh,<sup>1</sup> Sokrates T. Pantelides,<sup>2-4</sup> Petro Maksymovych,<sup>1</sup> and Nina Balke<sup>1</sup> <sup>1</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA

<sup>2</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
<sup>3</sup>Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA
<sup>4</sup>Department of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, Tennessee, 37235, USA
<sup>5</sup>Aerospace Systems Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433 USA

#### 31. Unveiling Nanoscale Information in Zeolites Via Atom Probe Tomography

Jonathan D. Poplawsky,<sup>1</sup> Joel E. Schmidt,<sup>2</sup> Simon R. Bare,<sup>3</sup> and B.M. Weckhuysen<sup>2</sup> <sup>1</sup>CNMS, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA <sup>2</sup>Debye Institute for Nanomaterials Science, Utrecht University, Utrecht 3584, Netherlands <sup>3</sup>SSRL, SLAC National Accelerator National Laboratory, Menlo Park, CA 94025, USA

## 32. Understanding effects of alloy chemical complexity on helium bubble formation by accurate segregation measurements using atom probe tomography

Xing Wang,<sup>1</sup> Hongbin Bei,<sup>1</sup> Yanwen Zhang,<sup>1-2</sup> Jonathan Poplawsky,<sup>1</sup> and Karren L. More<sup>1</sup> <sup>1</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37830 <sup>2</sup>University of Tennessee, Knoxville, TN, 37996

#### **33. \*3D-Printed Carbon Electrodes for Neurotransmitter Detection** Qun Cao, Nickolay V. Lavrik, and B. Jill Venton

#### 34. \*Formation, Migration and Oxidation of Silver Oxide Phase in Au-Ag Core-Shell Nanoparticles at High Temperature

Peifu Cheng,<sup>1</sup> Dmitri Zakharov,<sup>2</sup> Naiya Soetan,<sup>1</sup> Rizia Bardhan,<sup>1</sup> Adri van Duin,<sup>3</sup> and Piran R. Kidambi<sup>1\*</sup> <sup>1</sup>Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee 37235, USA <sup>2</sup>Center for Functional Nanomaterials Brookhaven National Laboratory, Upton, New York 11973, USA <sup>3</sup>Department of Mechanical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

#### **35. \*High** *Q* **factor meridian whispering gallery modes sensing in a water droplet on nano-structured surfaces** Weifeng Cheng,<sup>1</sup> Jiangtao Cheng,<sup>1\*</sup> Meng Zhang,<sup>2</sup> Jiansheng Liu,<sup>2</sup> and Zheng Zheng<sup>2</sup> <sup>1</sup>Department of Mechanical Engineering, Virginia Tech, 635 Prices Fork Road, Blacksburg, VA 24061, USA <sup>2</sup>School of Electronic and Information Engineering, Beihang University, 37 Xueyuan Road, Beijing 100191, China

## **36.** \*Ion transport through and permeability of extended DNA nanotube channels anchored by their ends in synthetic membranes

Naresh Niranjan Dhanasekar, Yi Li, Rebecca Schulman

Johns Hopkins University, Department of Chemical and Molecular Engineering, Baltimore, Maryland 21218, USA

#### 37. \*Bottom-Up Synthesis of Ultrathin PdSe2 Crystals with High Electron Mobility

Yiyi Gu,<sup>1,2,6</sup> Hui Cai,<sup>2</sup> Jichen Dong,<sup>4</sup> Yiling Yu,<sup>2</sup> Anna N. Hoffman,<sup>3</sup> Chenze Liu,<sup>3</sup> Akinola Oyedele,<sup>2</sup> Yu-Chuan Lin,<sup>2</sup> Alexander A. Puretzky,<sup>2</sup> Gerd Duscher,<sup>3</sup> Philip D. Rack,<sup>2,3</sup> Christopher M. Rouleau,<sup>2</sup> Xiangmin Meng,<sup>1</sup> Feng Ding,<sup>4,5</sup> David B. Geohegan,<sup>2</sup> Kai Xiao<sup>2\*</sup>

<sup>1</sup>Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

<sup>2</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
<sup>3</sup>Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, United States
<sup>4</sup>Center for Multidimensional Carbon Materials, Institute for Basic Science (IBS), Ulsan 44919, Republic of Korea
<sup>5</sup>Department of Materials Science and Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea

<sup>6</sup>Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

#### 38. \*Photonic Crystal Design with Mix and Match Unit Cells for Mode Manipulation

S. I. Halimi, Z. Fu, F. O. Afzal, J. A. Allen, S. Hu, and S. M. Weiss Vanderbilt University

#### 39. \*Carbonized Polymer Structures for Electrochemical Sensing

Mohammad Aminul Haque,<sup>1</sup> Nickolay V. Lavrik,<sup>2</sup> Dale K. Hensley,<sup>2</sup> Nicole McFarlane<sup>1</sup> <sup>1</sup>Department of Electrical Engineering and Computer Science, The University of Tennessee, Knoxville, TN 37996, USA <sup>2</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

## **40.** \*First principles analysis of magnetoresistance in tunneling junctions based on 2D materials J.J. Heath and M.A. Kuroda

Department of Physics, Auburn University

41. \*Effective conversion of two-dimensional transition metal dichalcogenides for atomic alloys and vertical heterojunctions by pulsed laser deposition

Yu-Chuan Lin,<sup>1</sup> Yiling Yua Chenze Liu,<sup>2</sup> Alexander Puretzky,<sup>1</sup> Mina Yoon,<sup>1</sup> Christopher Rouleau,<sup>1</sup> Gyula Eres,<sup>1</sup> Gerd Duscher,<sup>2</sup> Kai Xiao,<sup>1</sup> and David Geohegan<sup>1</sup>

<sup>1</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA <sup>2</sup>Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA

#### 42. \*Using Nanomaterials and Advanced Imaging to Discern Plant Peptide Signaling and Trafficking Mechanisms

Jessica Morgan,<sup>1</sup> Dian Liu,<sup>2</sup> Joanna Jelenska,<sup>3</sup> Bozhi Tian1,<sup>1,4</sup> and Jean Greenberg<sup>1,3</sup> <sup>1</sup>Biophysical Sciences; <sup>2</sup>Biocheistry and Molecular Biophysics; <sup>3</sup>Molecular Genetics and Cell Biology, and <sup>4</sup>Chemistry, University of Chicago, Chicago IL

#### **43. \*High-throughput multifunctional materials characterization with real-time analytics and feedback** Eric S. Muckley,<sup>1</sup> Monojoy Gosami1,<sup>2</sup> Bobby G. Sumpter,<sup>1,2</sup> Ilia N. Ivanov<sup>1</sup> <sup>1</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831 <sup>2</sup>Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

#### 44. **\*Nanobrazing of Nickel Superalloys and Advanced Characterization of Nanobrazing behavior** D. Bridges, B. Nielsen, C. Rouleau, J. Poplawsky, K. More, R. Xu, A. Hu Department of Mechanical, Aerospace, and Biomedical Engineering, University of Tennessee, Knoxville Center for Nanoscale Material Sciences, Oak Ridge National Laboratory Rolls Royce Corporation

#### **45. \*High-Throughput Approach to the Characterization of Two-Dimensional Heterostructures** Adam Pfeifle,<sup>1</sup> Panchapakesan Ganesh,<sup>2</sup> and Marcelo A. Kuroda<sup>1</sup> <sup>1</sup>Department of Physics, Auburn University <sup>2</sup>Oak Ridge National Laboratory

## 46. \*Polymeric phosphonium zwitterions: A systematic investigation of the structure-property relationships of novel phosphonium ionomers

Philip J. Scott,<sup>1</sup> Bradley S. Lokitz,<sup>2</sup> and Timothy E. Long<sup>1</sup> <sup>1</sup>Department of Chemistry, Macromolecules Innovation Institute (MII), Virginia Tech <sup>2</sup>Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory

#### 47. \*Carbon nanomaterial enabled ultra conductive Cu composites

Tolga Aytug, Lydia Skolrood, Kai Li, Ilia Ivanov, Mina Yoon, Michael McGuire, Andrew Lupini, Tsarafidy Raminosoa, Chengyun Hua, Annie Stevens, and Burak Ozpineci Oak Ridge National Laboratory, Oak Ridge, TN

### 48. \*Printed flexible silver sensors with electro-deposited TiO<sub>2</sub> nanowires for room temperature CO<sub>2</sub> gas sensing

Lingyue Zhang,<sup>1</sup> Yongchao Yu,<sup>1</sup> Curtis Hill,<sup>2</sup> Zili Wu,<sup>3</sup> \*Anming Hu<sup>1</sup> <sup>1</sup>Department of Mechanical, Aerospace and Biomedical Engineering, University of Tennessee, Knoxville, TN37996, USA <sup>2</sup>National Aeronautics and Space Administration, 300 E St SW, Washington, DC 20546, USA <sup>3</sup>Center of Nanophase Materials Science, Oak Ridge National Lab Oak Ridge, TN 37831-6061 USA

#### **49. \*Spatially extended gap states induced up-conversion photoluminescence** Xixiang Zhu

University of Tennessee

#### 50. Converting lignin into value-added polymer materials

Mengmeng Cui,<sup>1</sup> Logan T. Kearney,<sup>1</sup> Ngoc A. Nguyen,<sup>1</sup> Peter V. Bonnesen,<sup>2</sup> Kunlun Hong,<sup>2</sup> David Uhrig,<sup>2</sup> Jong K. Keum,<sup>3</sup> and Amit K. Naskar<sup>1</sup>

<sup>1</sup>Carbon and Composite Group, Materials Science and Technology Division; <sup>2</sup>Center for Nanophase Materials Science; <sup>3</sup>Neutron Science Directorate, Oak Ridge National Laboratory

#### 51. Interplay of the polydisperse set of crowders in compacting *Escherichia coli* nucleoid

Da Yang,<sup>1</sup> Jaana Männik,<sup>2</sup> Scott T. Retterer,<sup>3</sup> Jaan Männik<sup>1</sup> <sup>1</sup>Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996, USA <sup>2</sup>Department of Biochemistry, and Cellular and Molecular Biology, The University of Tennessee, Knoxville, TN 37996, USA <sup>3</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

#### 52. The Influence of Side-chain Length on Backbone Rigidity for Conjugated Polymers

Zhiqiang Cao<sup>1</sup>, Song Zhang<sup>1</sup>, Luke Galuska<sup>1</sup>, Tianyu Li<sup>2</sup>, Kunlun Hong<sup>2</sup>, and Xiaodan Gu<sup>1</sup> <sup>1</sup>School of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg <sup>2</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge

#### 53. Multimodal detection-enabled analysis of complex protein -enzyme mixtures

A.Vass<sup>1</sup>, G. Papoutsidakis<sup>2</sup>, I. Sukuba<sup>3</sup>, M. Tatarko<sup>3</sup>, E. Muckley<sup>4</sup>, M. Goswami<sup>4</sup>, T. Hianik<sup>3</sup>, Z. Keresztes<sup>1</sup>, V. Buckin<sup>2</sup>, B. Sumpter<sup>4</sup>, I. Ivanov<sup>4</sup>

<sup>1</sup>Research Centre for Natural Sciences, Functional Interfaces Research Group, Budapest, Hungry

<sup>2</sup>University College Dublin, School of Chemistry, Science Centre Belfield Dublin, Ireland

<sup>3</sup>Department of Biophysics and Chemical Physics, Faculty of Mathematics and Physics, Comenius University, Bratislava, Slovak Republic

<sup>4</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, USA

## Center for Nanophase Materials Sciences

# **Poster Abstracts**

**2019 User Meeting** 

#### **Exploring Photoinduced Dielectric Polarization in Organic-Inorganic Halide Perovskites**

Yixuan Dou, Miaosheng Wang, Jia Zhang, Hengxing Xu, Bin Hu<sup>\*</sup> Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee, 37996, USA

#### Abstract

Hybrid organic-inorganic perovskites (HOIPs) possess the possibilities of enabling photoinduced dielectric polarization. Photoinduced dielectric polarization plays an important role on suppressing the charge recombination, facilitating charge transport, and even polarizing excited states, which are critically important to the development of optoelectronic functionalities in HOIPs. However, it is difficult to realize whether photoinduced polarization contains an electrical polarization within the dipolar polarization regime in HOIPs due to lacking the mechanism of coupling dipolar and electric polarization. This issue originates from mobile ions in HOIPs, which results in the difficulty of detecting dielectric polarization. Here, we use capacitance-voltage (C-V) measurement to probe the photoinduced dipolar polarization and then confirm it by the magnetocapacitance measurement. The capacitance-voltage (C-V) detect the dipolar polarization by applying a low alternating bias of 50 mV while the mobile ions are continuously drifted by gradually scanning the bias from -0.1 V to 1.5 V. In this manner, continuously drifted ions cannot respond to the low alternating bias, enabling the detection of photoinduced electrical polarization in dipolar polarization regime. Then, to confirm the photoinduced dipolar polarization, magnetocapacitance was used to solely detect the dipolar polarization at 1 MHz in HOIPs ( $MA_xFA_{(1-x)}PbI_3$ , x in the range of 0-0.75) under photoexcitation. Magneto-capacitance measurement is a signature tool to exclude the effects of mobile ions (i.e. surface polarization) as mobile ions do not respond to magnetic fields. It was found that the photoexcitation can substantially increase the magnetocapacitance amplitude, confirming that the photoexcitation indeed induces dipolar polarization in HOIPs. In summary, our studies provide a fundamental understanding of photoinduced dipolar polarization effects on the optoelectronic functionalities of HOIPs.

#### The Effect of Surface Curvature on Coalescence-Induced Jumping of Nanodroplets on Superhydrophobic Surfaces

Xukun HE,<sup>1</sup> Lei ZHAO,<sup>1</sup> and Jiangtao CHENG\*,<sup>1</sup>

<sup>1</sup>Department of Mechanical Engineering, Virginia Tech, Blacksburg, VA 24060, United States

Keywords: coalescence-induced jumping, surface curvature, contact line dissipation

Coalescence-induced jumping of micro/nanodroplets on a surface has potential applications in self-cleaning, anti-icing, energy harvesting and condensation heat transfer enhancement, etc. However, most of the previous numerical studies focused on flat surfaces and ignored the effect of surface morphology on the jumping behaviors. In this work, we use molecular dynamics simulations to investigate the dynamics of coalescence-induced jumping of nanodroplets on nanostructured surfaces with different surface curvatures. Related scaling analyses show that contact line dissipation rather than viscous dissipation becomes dominant in nanodroplet coalescence. And we find that the surface curvature could antedate the onset of jumping due to the horizontal-motion-induced early symmetry breaking and could also reduce the contact line dissipation by decreasing contact line length and contact time. We demonstrate that increasing the curvature could significantly increase the jumping velocity and improve energy conversion efficiency about 10 times. Furthermore, by varying the wettability of surface, we find that the coalescence-induced jumping could even occur on relatively hydrophilic surfaces. This work indicates that the morphology of a surface, especially its curvature, plays a critical role in coalescence-induced jumping in nanoscale.



**Fig. 1:** a) The evolution of centroid velocity of droplet and the liquid bridge height. b) Snapshots of the coalescence-induced jumping of nanodroplets on curved surface.

### Electrochemical Reduction of Nitrogen to Ammonia under Ambient Conditions

Kui Li<sup>1</sup>, Gaoqiang Yang<sup>1</sup>, Shule Yu<sup>1</sup>, David A. Cullen<sup>2</sup>, Zili Wu<sup>2</sup>, Scott T. Retterer <sup>2</sup>, and Feng-Yuan Zhang<sup>1</sup>\*

<sup>1</sup>Nanodynamics and High-Efficiency Lab for Propulsion and Power Department of Mechanical, Aerospace & Biomedical Engineering UT Space Institute, University of Tennessee, Knoxville

> <sup>2</sup>Center for Nanophase Materials Sciences Oak Ridge National Laboratory

While ammonia (NH3) has mainly been used as a fertilizer for decades, it has recently received more attention as a potential energy storage medium and an alternative fuel for vehicles. For the six-electron process of electrochemical NH<sub>3</sub> synthesis, efficient catalysts with high Faradaic efficiency for nitrogen reduction reaction (NRR) are desired. In this study, polymetallic catalysts with cheaper transition metals are introduced and characterized for better catalytic performance under the ambient operating condition.

<sup>&</sup>lt;sup>1</sup> Corresponding author. Tel: +1-931-393-7428; Email address: fzhang@utk.edu

#### Theoretical Studies of Electroreduction of N2 in Strong Electric Field

Anna Y. Duke, Dillon G. Gagnon, Jacek Jakowski, Adam J. Rondinone,

Bobby G. Sumpter, Jingsong Huang

Center for Nanophase Materials Sciences, ORNL, Oak Ridge, TN 37831-6493

Recent experimental work at ORNL demonstrated that N-doped carbon nanospikes featuring ~1nm-wide sharp spikes could electrochemically reduce dissolved N<sub>2</sub> to NH<sub>3</sub> under ambient conditions with excellent Faradaic efficiency and production rate.<sup>1</sup> To shed light on the reaction mechanism, herein we carried out density functional theory (DFT) studies using long-range corrected functionals for the electron injection of N<sub>2</sub>, the first step of electroreduction process of N<sub>2</sub>. Using the experimentally available ionization potential (IP) and electron affinity (EA) along with Koopmans' theorem,<sup>2</sup> we obtained the sufficiently large basis set and validated the optimal values of range-separation parameters  $\omega$  for the studies of N<sub>2</sub>. We then calculated the frontier orbital energies of N<sub>2</sub> in the presence of applied longitudinal and transversal electric field in the range of [0, 0.07] atomic unit. Distortions of the frontier orbitals by applied longitudinal and transversal electric field are visualized by calculated probability densities of electrons. The calculated results indicated that it became energetically favorable to reduce N<sub>2</sub> by injecting an electron into its lowest unoccupied antibonding orbital under 0.02 atomic unit (~10 V/nm) longitudinal electric field. The studies confirm the physical effect of strong electric field on the electroreduction of N<sub>2</sub>.

- Y. Song, D. Johnson, R. Peng, D. K. Hensley, P. V. Bonnesen, L. Liang, J. Huang, F. Yang, F. Zhang, R. Qiao, A. P. Baddorf, T. J. Tschaplinski, N. L. Engle, M. C. Hatzell, Z. Wu, D. A. Cullen, H. M. Meyer III, B. G. Sumpter, A. J. Rondinone, A physical catalyst for the electrolysis of nitrogen to ammonia. *Sci. Adv.* 2018, *4*, e1700336.
- 2. T. Koopmans, On the allocation of wave functions and eigenvalues to individual electrons fo an atom. *Physica* **1934**, *1*, 104.

## Carbon polyaniline capacitive deionization electrodes: application and further insight from neutron vibrational spectroscopy

Samuel F. Evans,<sup>1,2</sup> Zachary D. Hood,<sup>3,4</sup> Yongqiang Cheng,<sup>5</sup> Marko R. Ivancevic,<sup>1</sup> Devin J. Wilson,<sup>1</sup> Shiba P. Adhikari,<sup>6</sup> Amit K. Naskar,<sup>2,6</sup> Costas Tsouris,<sup>7</sup> M. Parans Paranthaman<sup>1,2</sup>

<sup>1</sup>Chemical Sciences Division, Oak Ridge National Lab, Oak Ridge, TN 37831
<sup>2</sup>The Bredesen Center for Interdisciplinary Research and Graduate Education, Knoxville, TN 37996
<sup>3</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139
<sup>4</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
<sup>5</sup>Chemical and Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
<sup>6</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Potable water is a scare, critical resource on Earth. The west coast in the USA, in addition to other countries including India, China, and other African states already experience water scarcity. These times of water scarcity affect nearly four billion people currently and will worsen as population growth continues and living standards improve (1). Currently distillation, membrane filtration, and electrodialysis makeup the bulk of desalination processes. While effective for specific water compositions and chemical conditions, these processes are less energy and economical efficient at lower saline concentrations. A method that has been emerging to address this issue is capacitive deionization (CDI). CDI is capable of removing salt ions at lower concentrations with greater efficiency then existing methods, enabling more cost-effective options and tailored water treatments depending on water composition.

Researchers at Oak Ridge National Lab have developed an alternative carbon material for capacitive deionization from carbon derived from waste tires (2-3). There is an added benefit to removing tires from the environment as waste, since they are known to be detrimental to human health and the environment. These carbon electrodes have shown great promise in CDI applications, displaying low degradation over multiple cycling in addition to material costs. Improvements here increase the feasibility of CDI for further development. To further determine the effects of chemical treatment on the waste carbon material neutron vibrational spectroscopy has been performed (4). Insights into the chemical composition of the surface have assisted in the understanding of the waste carbon for this application in CDI, and others in catalysis, and pollutant removal from water.

- 1. M.M. Mekonnen, A.Y. Hoekstra, Four billion people facing severe water scarcity, Sci. Adv. 2 (2016).
- 2. A.K. Naskar, M.P. Paranthaman, and Z. Bi, *Pyrolytic carbon black composite and method of making the same*. 2016, Google Patents.
- S. F. Evans, M. R. Ivancevic, D. J. Wilson, Z. D. Hood, S. P. Adhikari, A. K. Naskar, C. Tsouris, M. P. Paranthaman. Carbon polyaniline capacitive deionization electrodes with stable cycle life, *Desalination* 464 (2019) 25-32.
- 4. Z. D. Hood, Y. Cheng, S. F. Evans, S. P. Adhikari, M. P. Paranthaman. Unraveling the structural properties and dynamics of sulfonated solid acid carbon catalysts with neutron vibrational spectroscopy, *Catalysis Today*, **submitted**.
#### Neutron Spectroscopic and Thermochemical Characterization of Lithium-Aluminum Layered Double Hydroxide Chloride

Samuel F. Evans,<sup>1,2</sup> Lili Wu,<sup>3</sup> Yongqiang Cheng,<sup>4</sup> Alexandra Navrotsky,<sup>3</sup> Bruce A. Moyer,<sup>1</sup> Stephen Harrison,<sup>5</sup> M. Parans Paranthaman<sup>1,2</sup>

<sup>1</sup>Chemical Sciences Division, Oak Ridge National Lab, Oak Ridge, TN 37831
 <sup>2</sup>The Bredesen Center for Interdisciplinary Research and Graduate Education, Knoxville, TN 37996
 <sup>3</sup>Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California Davis, Davis CA 95616
 <sup>4</sup>Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
 <sup>5</sup>All American Lithium, Brawley CA 92227

Global consumption of lithium has grown rapidly in recent years, due to widespread use of lithium-ion battery technology in electronics and electric vehicles (1). The U.S., while being the main consumer of lithium-ion batteries does not currently have a domestic supply of lithium. In order to further sustain the green revolution in the U.S., the development of sorbent technologies is necessary to efficiently and cheaply extract lithium. Current sorbent technologies include layered manganese and titanite oxides, which absorb lithium through a proton-lithium exchange reaction. The mechanism of these current technologies requires the use of acids to desorb lithium and re-protonate the layered sorbents for further use, adding cost to extraction processes. Lithium-aluminum layered double hydroxides (LDH) have been developed that do not require this pH adjustment for lithium removal. Instead LDH can absorb and desorb lithium at elevated temperatures allowing easy removal of lithium from the structure.

Researchers at Oak Ridge National Lab and UC Davis have been exploring the properties of Li-Al LDH and iron doped sorbent variants (2-4). Thermodynamic calculations have been instrumental in understanding the stability trends of LDH materials, which ultimately correlate to their effectiveness as lithium-ion sorbents. In addition to these insights, collaboration with spallation neutron source (SNS) scientists have helped to determine the effect of water content and synthetic precursors on LDH structural stability (3). Here, we have determined that maximizing water content leads to an overall destabilization of the LDH structure, leading to easier absorption and desorption of lithium from the sorbent. Understanding of fundamental structural and composition effects of Li-Al LDH materials open new avenues to advancing additional layered double hydroxides as well as other more effective lithium-ion sorbents.

- 1. L. Kavanagh, J. Keohane, G. Garcia Cabellos, A. Lloyd, J. Cleary, Global Lithium Sources—Industrial Use and Future in the Electric Vehicle Industry: A Review. Resources 2018, 7 (3).
- 2. L. Wu, L. Li, S.F. Evans, T.A. Eskander, B.A. Moyer, Z. Hu, P.J. Antonick, S. Harrison, M.P. Paranthaman, R. Riman, A. Navrotsky, Lithium aluminum-layered double hydroxide chlorides (LDH): Formation enthalpies and energetics for lithium ion capture, *Journal of the American Ceramic Society*, 102 (**2019**) 2398-2404.
- 3. L. Wu, S. F. Evans, Y. Cheng, A. Navrotsky, B. A. Moyer, S. Harrison, M. P. Paranthaman. Neutron spectroscopic and thermodynamic characterization of lithium-aluminum layered double hydroxide chloride: implications for lithium recovery, *Journal of Physical Chemistry C*, **Submitted**.
- M.P. Paranthaman, L. Ling, J. Luo, T. Hoke, H. Ucar, B.A. Moyer, S. Harrison, Recovery of Lithium from Geothermal Brine with Lithium-Aluminum Layered Double Hydroxide Chloride Sorbents. *Environ. Sci. Tech.* 2017, *51*, 13481-13486. DOI: 10.1021/acs.est.7b03464

#### **Characterizing Chemo-Mechanical Degradation at Solid-State Battery Interfaces**

John A. Lewis<sup>1</sup>, Jared Tippens<sup>2</sup>, Francisco Javier Quintero Cortes<sup>1</sup>, Matthew T. McDowell<sup>1,2</sup> <sup>1</sup>School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, 30332 <sup>2</sup>George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, 30332

The solid-state lithium metal battery is a promising next-generation technology due to the high energy density of the lithium metal anode and the potential for solid-state electrolytes (SSEs) to prevent failure modes seen in liquid electrolyte lithium metal batteries. However, the interfaces between many SSEs and lithium metal are (electro)chemically unstable, and we lack a detailed understanding of how interfacial transformations relate to electrochemical degradation. Using the NASICON-type Li<sub>1.4</sub>Al<sub>0.4</sub>Ge<sub>1.6</sub>(PO<sub>4</sub>)<sub>3</sub> (LAGP) as a reactive SSE, we study the reaction processes that occur at the lithium metal/SSE interface and develop a chemo-mechanical understanding of degradation in LAGP. In situ transmission electron microscopy reveals that lithium insertion into LAGP at the interface drives the transformation to form an amorphous phase with expanded volume [1]. In symmetric Li/LAGP/Li cells, the evolution of mechanical stress due to this transformation ultimately causes fracture of the SSE and complete cell failure. Ex situ characterization of LAGP after cycling shows that the morphology of the interphase layer is highly dependent on the applied current density, and the interphase morphology significantly influences mechanical stability. In situ X-ray tomography during electrochemical cycling of symmetric cells reveals the onset of fracture and growth of the crack network throughout cycling [2]. Our results show that the impedance begins to increase when fracture first initiates, indicating that the ionic conductivity of the interphase is comparable to pristine LAGP and is not responsible for the significant increase in impedance. This work highlights that the nature of the reaction at the Li/SSE interface plays a crucial role in determining chemo-mechanical degradation mechanisms, with implications for understanding degradation in a wide range of practical SSEs.

[1] Lewis, J. A.; Cortes, F. J. Q.; Boebinger, M. G.; Tippens, J.; Marchese, T. S.; Kondekar, N.; Liu, X.; Chi, M.; McDowell, M. T. ACS Energy Letters 2019, 4 (2), 591.

[2] Tippens, J.; Miers, J. C.; Afshar, A.; Lewis, J. A.; Cortes, F. J. Q.; Qiao, H.; Marchese, T. S.; Leo, C. V. D.; Saldana, C.; McDowell, M. T. ACS Energy Letters 2019, 1475.

## Ferroic and Ionic Behavior of Photovoltaic Hybrid Organic-Inorganic Perovskites

Yongtao Liu<sup>1,2</sup>, Liam Collins<sup>1</sup>, Anton V. Ievlev<sup>1</sup>, Alex Belianinov<sup>1</sup>, Stephen Jesse<sup>1</sup>, Kai Xiao<sup>1</sup>, Mahshid Ahmadi<sup>2</sup>, Bin Hu<sup>2</sup>, Sergei V. Kalinin<sup>1</sup>, Olga S. Ovchinnikova<sup>1</sup>\*

1. Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, United States

2. Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, United States

Despite the remarkable performance of hybrid organic-inorganic perovskites (HOIPs) in solar cell, light emission, and photodetector, it remains to require further advances in fundamental understandings of HOIPs photophysics. Recently, the discovery of ferroic twin domains in HOIPs has initiated contentious discussion on the ferroic nature of HOIPs. Given the interconnected nature of defect chemistry, ionic states, and ferroic properties, the effects of ferroic domains on the optoelectronic properties of HOIPs can no longer be ignored. Ferroelectric polarizationwhich has yet to be unambiguously established despite considerable effects to do so-is thought to facilitate the dissociation of photoinduced electron-hole pairs, benefitting photovoltaic action. Alternate to ferroelectricity, ferroelasticity was also proposed in these materials. Here, we systematically studied the piezoelectric response of multiple CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> thin films that exhibit twin domains and have different crystallographic planes parallel to the substrate. In doing so, we demonstrate that the piezoelectric contrast between twin domains along studied orientations is below 1 pm/V. Therefore, the ferroelectricity (if there is) along these orientations is < 1 pm/V. By applying electric biases, we find that the domain changes are governed by ion redistribution and structural deformation under electric biases. This indicates that the biases induced domain evolution in these materials is different from classical ferroelectric materials, where the ferroelectric polarization switching is the major driver. The ion redistribution and structural variation point to the potential effects of twin domains on solar cell operation. In addition, we for the first time reveal the photoluminescence (PL) variations in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> twin domains, indicating the different optoelectronic properties between domains. Density functional theory (DFT) simulation further indicates that the photogenerated electrons and holes show preferential distributions in the ferroelastic twin domains due to strain and chemical inhomogeneity between domains. In turn, this preferential charge distribution results in different lattice strain, alternating the behaviors of the ferroelastic twin domains in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. In-situ X-ray diffraction and band excitation piezoresponse force microscopy (BE-PFM) measurements present experimental evidence of the interaction between charge carriers and ferroelastic twin domains. Time-resolved time-of-flight secondary ion mass spectrometry (tr-ToF-SIMS) indicates that the photogenerated carriers also induce strong ion migration, which plays a role in screening the electric field in HOIPs. This work provides an in-depth understanding of the effects of twin domains on optoelectronic properties of HOIPs, which are helpful for further improving the optoelectronic performance of HOIPs.

#### Determining the Structure and Stability of Thermoelectric La<sub>3-x</sub>Te<sub>4</sub>-Ni Composites using High-Resolution and *In-Situ* TEM

M. P. Thomas<sup>1</sup>, A. Ullah<sup>1</sup>, D. Cheikh<sup>2</sup>, S. K. Bux<sup>2</sup>, and B. S. Guiton<sup>\*1</sup>

<sup>1</sup>Department of Chemistry, University of Kentucky, Lexington, Kentucky, USA

<sup>2</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA

#### **Abstract**

For many years, NASA has employed thermoelectric materials (TE) in radioisotope thermoelectric generators to convert heat generated from radioactive decay to electrical power in their missions.<sup>1</sup> The efficiency of a TE material is characterized by its dimensionless figure of merit, zT.  $zT = \frac{6S^2T}{\kappa}$  where  $\delta$ , S, T, and K are electrical conductivity, Seebeck coefficient, temperature, and thermal conductivity, respectively. Lanthanum telluride (La<sub>3-x</sub>Te<sub>4</sub>), is a TE material with a zT of 1.1 at 1275 K at x = 0.23.<sup>2,3</sup> It has been shown that the zT can be increased by 30% when nickel (Ni) nanoparticle (NP) inclusions are introduced to the LaTe<sub>1.46</sub> matrix.<sup>4</sup> We hypothesize that coherent interfaces between LaTe<sub>1.46</sub>/Ni permit low electrical resistivity and these interfaces are spread out sufficiently to maintain a low thermal conductivity. These interfaces are likely a key factor determining the stability and performance of the LaTe<sub>1.46</sub>-Ni composites, but their role and nature are not well understood. We postulate that the presence of a reaction layer at the interface can cause the observed enhancement in zT. Furthermore, it is important to determine the stability of LaTe<sub>1.46</sub>/Ni interface in deep-space conditions and the effect of heat and oxygen on the mechanisms and kinetics of interface degradation. In this work, we devised a method to minimize oxidation during sample preparation and sample transfer between the Focused Ion Beam Scanning Electron Microscope (FIB-SEM) and the Transmission Electron Microscope (TEM). First, the TE composite pellets were polished in a glove box, then a FIB lift-out was performed and transferred to a special Air Protection Holder (APH) inside the FIB. This APH utilizes a special mechanism to contain the sample in an isolated inert environment and can be inserted in the TEM for imaging. Using this technique, we successfully characterized the interfaces in the TE composite by high-resolution TEM. Here, we show the sample preparation methods and high-resolution structural characterization of LaTe<sub>1.46</sub>/Ni TE composites and their interfaces at high vacuum and ambient temperature conditions, using Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray Spectroscopy (EDS). We further demonstrate the LaTe<sub>1.46</sub>/Ni interface degradation over its operating temperature range (25-1000°C), in the presence and absence of oxygen, in real time, using in-situ TEM.

1. Fleurial, J.-P. Thermoelectric power generation materials: Technology and application opportunities. *JOM* **61**, 79–85 (2009).

2. Clarke, S. M. *et al.* Optimizing Thermoelectric Efficiency of La3-xTe4 with Calcium Metal Substitution. *MRS Online Proceedings Library Archive* **1490**, 83–88 (2013).

3. Ma, J. M. *et al.* Mechanochemical synthesis and high temperature thermoelectric properties of calciumdoped lanthanum telluride La3–xCaxTe4. *J. Mater. Chem. C* **3**, 10459–10466 (2015).

4. Ma, J. M. *et al.* TEMPERATURE THERMOELECTRIC COMPOSITES WITH METALLIC INCLUSIONS. 20 (2017).

#### Toward a general method for inserting metal atoms in graphene at the atomic scale

Ondrej Dyck,<sup>1</sup> Jacob Swett,<sup>2</sup> Cheng Zhang,<sup>3</sup> Philip Rack,<sup>1,3</sup> Jason D. Fowlkes,<sup>1,3</sup> Andrew R. Lupini,<sup>1</sup> Sergei V. Kalinin,<sup>1</sup> Stephen Jesse<sup>1</sup>

<sup>1</sup> Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN <sup>2</sup> Oxford University, Department of Materials, Oxford OX1 3PH, UK <sup>3</sup> Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN

A scanning transmission electron microscope (STEM) is typically regarded as a characterization instrument, allowing atomically resolved imaging and spectroscopy of a wide variety of materials. However, recently demonstrations have shown that the focused e-beam can be used for atomically localized material alteration including the insertion of Si dopants in graphene and their movement and assembly into primitive structures.<sup>1-3</sup> These demonstrations suggest a pathway for repurposing the STEM as an atomic manipulation platform.<sup>4</sup> A significant step toward this goal is developing general methods for positioning various elements in close proximity to each other in a stabilizing matrix. Here, we use graphene as the stabilizing matrix and show how various atomic species can be positioned at defect sites *in situ*. Figure 1 shows a schematic of the insertion process. The steps can be carried out in sequence or in parallel by scanning or defocusing the e-beam. Figure 2a)-c) shows an experimental demonstration of this process, inserting a Si atom into the graphene lattice. Figure 2d)-g) shows similar insertion of several other elemental species, Pt, Cr, Ti, and Fe.



**Figure 1** Schematic of dopant insertion process. a) The target 2D material is depicted in blue, suspended across a supporting substrate with a patch of source material deposited on the surface. An energetic beam is then positioned on the 2D material. b) A defect is introduced into the 2D material through energy transfer from the beam. c) The beam is positioned on the source material and acts to sputter atoms across the surface of the 2D material. d) Atoms from the source material become attached to the defect site.

**Figure 2** Experimental demonstrations of the insertion of various atomic species in graphene. a)-c) Experimental demonstration of the process schematically represented in Figure 1. d)-g) Experimental demonstration of the insertion process for a variety of atomic species and defect configurations

where the beam was delocalized by scanning over a selected area containing pristine graphene and the source material.

- 1 Dyck, O., Ziatdinov, M., Lingerfelt, D. B., Unocic, R. R., Hudak, B. M., Lupini, A. R., Jesse, S. & Kalinin, S. V. Atom-byatom fabrication with electron beams. *Nature Reviews Materials*, doi:10.1038/s41578-019-0118-z (2019).
- 2 Dyck, O., Kim, S., Jimenez-Izal, E., Alexandrova, A. N., Kalinin, S. V. & Jesse, S. Building Structures Atom by Atom via
- Electron Beam Manipulation. Small 14, 1801771, doi:doi:10.1002/smll.201801771 (2018).
  Dyck, O., Kim, S., Kalinin, S. V. & Jesse, S. Placing single atoms in graphene with a scanning transmission electron microscope. Appl. Phys. Lett. 111, 113104, doi:10.1063/1.4998599 (2017).
- 4 Kalinin, S. V., Borisevich, A. & Jesse, S. Fire up the atom forge. *Nature* 539, 485-487 (2016).

### Localized electrical transport at vertically oriented oxide interfaces

Wenrui Zhang, Christopher M Rouleau, Jong Keum, Zheng Gai, Gyula Eres Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

#### Abstract

Interfaces of correlated materials provide the ideal platform for exploring emerging functionality. When two phases with dissimilar structure come in contact, the interface on both sides undergoes relaxation to reach a minimum energy state. In typical systems, the arising lattice mismatch strain is mediated by formation of misfit dislocations or defects that can adversely affect phase coupling. In some systems, the mismatch strain can persist and force chemical interdiffusion at the interface to form a buffer region. This work employs vertically oriented oxide interfaces to probe the competing interaction from these two mechanisms, and their impact on the device performance. This unique vertical interface geometry removes the substrate-clamping limitation, and creates ultrahigh density of transport channels along the out-of-plane direction (**Figure 1**). Tuning strain coupling between the component phases controls a metal-to-insulator phase transition at the interface, which presents profound impact on the ON-OFF performance of the thin film device.



Figure 1. Schematic and plan-view of vertical aligned oxide interface.

#### Infrared Plasmonic Response and Fluorine-Induced Faceting in Colloidal F:In<sub>2</sub>O<sub>3</sub> Nanocubes

Shin Hum Cho<sup>†</sup>, Sandeep Ghosh<sup>†</sup>, Zachariah J. Berkson<sup>‡</sup>, Jordan A. Hachtel<sup>§</sup>, Jianjian Shi<sup>||</sup>, Xunhua Zhao<sup>||</sup>, Lauren C. Reimnitz<sup>†</sup>, Clayton J. Dahlman<sup>†<sup>⊥</sup></sup>, Yujing Ho<sup>†</sup>, Anni Yang<sup>†</sup>, Yuanyue Liu<sup>||</sup>, Juan-Carlos Idrobo<sup>§</sup>, Bradley F. Chmelka<sup>\*</sup><sup>‡</sup>, Delia J. Milliron<sup>\*</sup><sup>†</sup>

\* McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin
 \* Department of Chemical Engineering, University of California, Santa Barbara
 § Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge
 II Department of Mechanical Engineering, The University of Texas at Austin, Austin
 <sup>⊥</sup> Materials Department, University of California, Santa Barbara

Cube-shaped nanocrystals (NCs) of conventional metals like gold and silver generally exhibit localized surface plasmon resonance (LSPR) in the visible region with spectral modes determined by their faceted shapes. However, faceted NCs exhibiting LSPR response in the infrared (IR) region are relatively rare.

Here, we describe the colloidal synthesis of nanoscale fluorine-doped indium oxide (F:In<sub>2</sub>O<sub>3</sub>) cubes with LSPR response in the IR region, wherein fluorine was found to both direct the cubic morphology and act as an aliovalent dopant. Single crystalline 160 nm F:In<sub>2</sub>O<sub>3</sub> cubes terminated by (100) facets and concave cubes were synthesized using a colloidal heat-up method. The presence of fluorine was found to impart higher stabilization to the (100) facets through density functional theory (DFT) calculations that evaluated the energetics of F-substitution at surface oxygen sites. These calculations suggest that the cubic morphology results from surface binding of F-atoms.

In addition, fluorine acts as an anionic aliovalent dopant in the cubic bixbyite lattice of  $In_2O_3$ , introducing a high concentration of free electrons leading to LSPR. We confirmed the presence of lattice fluorine dopants in these cubes using solid-state <sup>19</sup>F and <sup>115</sup>In nuclear magnetic resonance (NMR) spectroscopy. The cubes exhibit narrow, shape-dependent multimodal LSPR extinction peaks due to corner- and edge-centered modes. The spatial origin of these different contributions to the spectral response are directly visualized by electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM).



**Figure 1.** (a) Liquid cell FTIR spectra of  $F:In_2O_3$  NCs with corresponding SEM images.  $F:In_2O_3$  cube (green), concave cube (orange), and concave cube (red). Scale bars are 100 nm. (b)  $F:In_2O_3$  cube (top), concave cube (middle), and concave cube (bottom) EELS maps for corner mode frequencies (around 3900 cm<sup>-1</sup>, left, orange) and edge mode frequencies (around 5100 cm<sup>-1</sup>, right, blue) LSPR mode. Scale bars are 200 nm.

1. S. H. Cho, et al., Syntheses of Colloidal F:In<sub>2</sub>O<sub>3</sub> Cubes: Fluorine-Induced Faceting and Infrared Plasmonic Response. Chem. Mater. 31, 7, 2661-2676 (2019).

# Mixed metal zero-mode guides (ZMWs) for tunable fluorescence enhancement

Abdullah Al Masud<sup>a</sup>, W. Elliott Martin<sup>a</sup>, Faruk H. Moonschi<sup>a</sup>, Bernadeta R. Srijanto<sup>b</sup>, C. Patrick Collier<sup>b</sup>, Christopher I. Richards<sup>a\*</sup>.

<sup>a</sup>Department of Chemistry, University of Kentucky, 505 Rose street, Lexington KY 40506 <sup>b</sup>Center for Nanophase Materials Sciences, Oakridge National Lab, Oakridge TN 37831

### Abstract

Zero-mode waveguides (ZMWs) are capable of modifying fluorescence emission through interactions with surface plasmon modes leading to either plasmon-enhanced fluorescence or quenching. Enhancement requires spectral overlap of the plasmon modes with the absorption or emission of the fluorophore. Thus, enhancement is limited to fluorophores in resonance with metals (e.g. Al, Au, Ag) used for ZMWs. The ability to tune surface plasmons beyond those exhibited by single metals to match a wider range of fluorophores across the visible spectra would significantly extend the utility of ZMWs. We fabricated ZMWs composed of aluminum and gold individually and also in mixtures of three different ratios, (Al:Au; 75:25, 50:50, 25:75). We characterized the effect of mixed metal ZMWs on single molecule emission for a range fluorophores with emission across the visible spectrum. Mixed metal ZMWs exhibited a shift in their plasmon resonance allowing us to match the emission of fluorophores off resonance with single metal ZMWs. We also compared the effect of mixed metal ZMWs on the photophysical properties of molecules in ZMWs. We quantified changes in fluorescence lifetimes and photostability that were dependent on the ratio of Au and Al. Tuning the plasmon modes of ZMWs by changing the ratio of Au and Al allowed us to match the fluorescence of molecules that emit across the visible spectrum.

# Epitaxial stabilization of Ruddlesden-Popper iridate series and iridate superlattice

Junyi Yang, Lin Hao, Han Zhang, Kyle Noordhoek and Jian Liu Department of Physics and Astronomy, University of Tennessee at Knoxville

The discovery of pseudo-spin <sup>1</sup>/<sub>2</sub> electronic system in the iridates has attract vast research effort in exploring exotic phenomenon like high-T<sub>c</sub> superconductivity. While research on bulk crystals of the Ruddlesden-Popper iridate series has produced fruitful results, the possibility of epitaxially grown single crystalline iridate thin films provides more flexibility in tunability and application prospect. Sr<sub>3</sub>Ir<sub>2</sub>O<sub>7</sub> is regarded as an important prototype with many interesting properties, including a *c*-axis collinear antiferromagnetic order that is stabilized through a dimensionalitydriven spin-flop transition in the Ruddlesden-Popper iridate series. Though it has a narrow synthesis window in thin film synthesis, we have found that by controlling the gas composition during synthesis one can overcome this limit and largely enhance the thermodynamic stability of Sr<sub>3</sub>Ir<sub>2</sub>O<sub>7</sub>. To go beyond the Ruddlesden-Popper structures, we have also established layering synthesis approach to obtain artificial quasi-2D systems of pseudo-spin 1/2 electrons and successfully tuned the electronic and magnetic state through epitaxial strain engineering. Significant modulations of structural, resistive and antiferromagnetic properties are observed through synchrotron x-ray diffraction, magnetic scattering, and transport measurements. The combined robustness of antiferromagnetism at low temperature and metal-insulator transition at high temperature shows the iridate superlattice can be a promising playground to further explore emergent phenomenon.

## Toward control of the photonic and phononic quantum state of hBN single-photon emitters

Matthew A. Feldman,<sup>1, 2</sup> Claire E. Marvinney,<sup>2</sup> Nathan Rosenmann,<sup>3</sup> Tristan Carlson,<sup>4</sup> Yu-Chuan Lin,<sup>5</sup> Yiyi Gu,<sup>3</sup> Kai Xiao,<sup>5</sup> James H. Edgar,<sup>6</sup> Ivan I. Kravchenko,<sup>5</sup> Alexander A. Puretzky<sup>5</sup> Richard F. Haglund,<sup>1</sup> and Benjamin J. Lawrie<sup>2</sup>

<sup>1</sup>Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, USA
 <sup>2</sup>Quantum Information Science Group, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
 <sup>3</sup>Department of Physics, University of Illinois, Chicago, Chicago, IL 60607, USA
 <sup>4</sup>Department of Physics and Astronomy, University of the South, Sewanee, TN 37383, USA
 <sup>5</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
 <sup>6</sup>Department of Chemical Engineering, Kansas State University, Manhattan, Kansas 66506, USA

The study of two-dimensional (2D) materials is of growing interest for a range of integrated quantum technology applications. Hexagonal boron nitride (hBN) is a 2D material of interest for quantum photonic and phononic applications because its defect-based single photon emitters (SPEs) are bright, have narrow linewidths, and are stable at room temperature [1], and because, for isotopically pure samples, the phonon interactions can have ultralow losses [2]. To date, discovering the atomistic origins of SPEs in hBN has proven challenging. Recent results have shown that spectrally resolved, two-color Hanbury Brown-Twiss (HBT) interferometry can be used to characterize electron-phonon interactions in hBN [1]. The same technique can be used to study the electronic structure of hBN defects. To create a description of the combined photonic and phononic quantum state in hBN of varying isotopic concentration, measurements of spectrally resolved correlation functions as in [1] are employed.

Here, our initial results are on naturally abundant hBN, where we explore the two-color correlation function  $g_{ik}^{(2)}(\tau)$ 

for spectrally distinct electronic transitions. While some of the features in Fig. 1a can be attributed to phonon replicas, at least three features appear to be zero-phonon lines (ZPLs). The cross-correlations between these ZPLs show markedly different statistics from one another. Figure 1d illustrates strong shelving and photon antibunching dynamics in the two-color correlation function for the ZPLs near 540 nm and 575 nm, whereas Fig. 1e illustrates no evidence of antibunching for the ZPLs near 575 nm and 460 nm. If the spectral content of Fig. 1 were a result of several non-interacting defects, then each ZPL would be uncorrelated with the others, resulting in a two-color correlation function like that shown in Fig. 1e. The cross-correlation in Fig. 1d can be explained by attributing the transitions near 575 nm and 540 nm to either different excited states of the same defect or to two strongly interacting defects. To definitively determine whether these cross-correlations are the result of two interacting defects, or two electronic levels within one defect, further experiments are being employed. These include spectrally tunable optical excitation of these states with improved spectral resolution in the colored Hanbury Brown-Twiss interferometer where resonantly pumping one transition while collecting on another becomes possible, and variable temperature operation ranging from 10mK-300K. Additional experiments exploring the variation in electronelectron and electron-phonon interactions with changing boron isotope within the sample are currently underway, where samples with  $\hat{B^{10}}$ :  $B^{11}$  concentrations of 100:0, 50:50, 20:80, are being studied with these same techniques. Examples of the samples prepared for these measurements are shown in Fig. 1f-g. These combined experiments are focused on the development of a more complete understanding of the photonic and phononic quantum state of defects in hBN.

This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains anon-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).



Fig. 1: (a) Localized defect microphotoluminescence spectra for a few-layer hBN flake irradiated with a 40  $\mu$ W, 405-nm wavelength, 1 $\mu$ m<sup>2</sup> spot size CW laser after 12.5 hrs irradiation. (b) – (e) Spectrally resolved Hanbury Brown-Twiss interferometry of defect photoluminescence at 575 nm (b), 528 nm (c), and 460 nm (inset of e) illustrates antibunching at all three wavelengths. Two-color antibunching measurements demonstrated strong anticorrelations between the transitions centered near wavelengths of 528 nm and 575 nm (d), but no anticorrelations between the transitions near 575 nm and 460 nm (e). (f) SEM image of an hBN flake with isotope ratio of 50:50 B<sup>10</sup>:B<sup>11</sup> deposited on an array of SiO<sub>2</sub> nanopillars (d = 450 nm, h = 130 nm), where the pillars can create strain localized defect emitters [3]. (g) Optical image of 50:50 B<sup>10</sup>:B<sup>11</sup> hBN flakes on a TEM grid for characterization of suspended flakes.

This research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy, by the IC Postdoctoral Fellowship, and by the National Defense Science & Engineering Graduate Fellowship (NDSEG) graduate fellowship. The nanofabrication and optical and electron spectroscopies were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

[1] Feldman, Matthew A., et al. "Phonon-induced multicolor correlations in hBN single-photon emitters." Physical Review B 99.2 (2019): 020101.

[2] Giles, Alexander J., et al. "Ultralow-loss polaritons in isotopically pure boron nitride." Nature materials 17.2 (2018): 134.

<sup>[3]</sup> Proscia, Nicholas V., et al. "Near-deterministic activation of room-temperature quantum emitters in hexagonal boron nitride." Optica 5.9 (2018): 1128-1134.

#### Abstract for the CNMS Meeting

Combined HREELS, STM, and STS study of Sr<sub>3</sub>(Ru<sub>1-x</sub>Mn<sub>x</sub>)<sub>2</sub>O<sub>7</sub>.

Yifan Yang<sup>1</sup>, Mingming Fu<sup>2</sup>, Rongyin Jin<sup>1</sup>, Ward Plummer<sup>1</sup>, Gai Zheng<sup>2</sup>

<sup>1</sup>Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA70803

<sup>2</sup> Center for Nanophase Materials Sciences Oak Ridge National Laboratory Oak Ridge, TN 37831, USA

The surface physical properties of double-layered Ruddlesden-Popper oxides  $Sr_3(Ru_{1-x}Mn_x)_2O_7$ have been studied as a function of Mn concentration x and temperature using high-resolution electron energy-loss spectroscopy (HREELS), scanning tunneling microscopy (STM), and scanning tunneling spectroscopy (STS). Previous studies have reported that Mn dopants on the Ru site stabilizes long range magnetic ordering exhibiting an *E*-type AFM insulating ground state with a Neel Temperature ( $T_N$ ) = 82 K for x = 0.16 [1, 2]. At 80 K the surface is metallic [3]. Here we report determination of the surface electronic properties and structural distortion at low temperature as a function of x. x dependent surface octahedral tilt lowers the symmetry to C2v in contrast with the bulk C4v for x<0.16, C4v surface symmetry is restored for x=0.16 and persisted at all temperature as seen in the STM FFTs. The surface for x=0.16 is metallic at all temperatures. A surface phase diagram for Sr<sub>3</sub>(Ru<sub>1-x</sub>Mn<sub>x</sub>)<sub>2</sub>O<sub>7</sub> at high doping levels is constructed.

[1] D. Mesa, et al., Phys. Rev. B 85, 180410(R) (2012).

[2] Biao, et al. Phys. Rev. B 84, 174411 (2011)

[3] Chen Chen, et al., Phys. Rev. B 94, 085420 (2016)

### Assembly of proteins in solution and at the interface

Marek Tatarko<sup>1</sup>, Eric S. Muckley<sup>2</sup>, Ivan Sukuba<sup>1</sup>, Monojoy Goswami<sup>2,3</sup>, Jan-Michael Carrillo, Bobby G. Sumpter<sup>2,3</sup>, Tibor Hianik<sup>1</sup>, <u>Ilia N. Ivanov<sup>2</sup></u>

<sup>1</sup>Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynska dolina, 842 48 Bratislava, Slovakia
 <sup>2</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6496
 <sup>3</sup>Computational Sciences and Engineering Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6494

\*Corresponding author: Ilia Ivanov: ivanovin@ornl.gov

Keywords: casein, plasmin, trypsin, protease, QCM, biosensor, machine learning

#### Abstract

We demonstrate a machine learning enabled approach to describe behavior of proteins in solutions and at the interface. In this approach we couple experiment and molecular dynamic simulation (coarse grained and all atom) to derive scalable model of protein stability and aggregation in solution at different pH and temperature. We incorporate acoustic detection to learn about protein assembly on the interface where a hydrophilic SiO<sub>2</sub>-coated quartz crystal microbalance (QCM) acts as a substrate to assemble  $\alpha$ -,  $\beta$ -, and  $\kappa$ -casein. We demonstrate that  $\alpha$ -,  $\beta$ -, and  $\kappa$ -caseins can form stable assembly on SiO<sub>2</sub> from a solution of pH-stabilized phosphate-buffered solution. The layer of protein can be cleaved from the surface, leading to observable changes in the frequency of the 1<sup>st</sup>-11<sup>th</sup> odd harmonics of QCM. The acoustic devices were shown to have excellent sensitivity to protease and can be used to differentiate interaction of different protease with a monolayer of protein, allows sub-nanomolar detection and classification of protease.

This research was conducted at the Center for Nanophase Materials Sciences, which is a US Department of Energy Office of Science User Facility. MT, IS, TH acknowledge funding from the European Union's Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement No. 690898.

#### A Physics-Inspired Representation of Local Atomic Structure for Developing Physically-Informed Machine Learning Based Interatomic Potentials

Matthew C. Barry<sup>1</sup>, Surya R. Kalidindi<sup>1, 2, 3</sup>, and Satish Kumar<sup>1</sup>

<sup>1</sup>Department of Mechanical Engineering, Georgia Institute of Technology; <sup>2</sup>Department of Materials Science and Engineering, Georgia Institute of Technology; <sup>3</sup>Department of Computational Science and Engineering, Georgia Institute of Technology

Machine learning (ML) based interatomic potentials are able to achieve chemical accuracy at a fraction of the computational cost of traditional electronic structure methods such as density functional theory. However, the success of current ML potentials has been limited to simple systems and their applications limited to simple physics, often generalizing poorly beyond the datasets from which they are developed. This suggests that current ML potentials, which use simplified representations of the local atomic structure, cannot capture the complex interactions present in atomic systems.

In this work, we present a novel, physics-preserving representation of the local atomic structure for developing ML potentials capable of achieving high accuracy with complex systems and complex physics. Unlike other ML potentials, which use simplified representations of the local atomic structure, our approach is unique in that we have developed an atomic fingerprint capable of representing the local atomic structure with high accuracy in preserving geometric information. As a result, our ML potential has less restrictions on the complexity of spatial relationships and multibody interactions that it can learn in order to best represent the physics of atomic systems. This is demonstrated by our success in developing ML potentials to study the effect of strain on thermal properties of single and multi-species systems using the phonon Boltzmann transport equation. The results show that ML potentials developed with our approach are consistent and transferable, as they are able to maintain high accuracy even as the systems are subjected to varying strains. Furthermore, it demonstrates that our ML potentials are sensitive enough to accurately predict the forces resulting from the small displacements required to calculate interatomic force constants.

# Laser-induced Carbon base Smart Flexible Sensor Array for Multi Flavors Detection

Yongchao Yu<sup>1</sup>, Lingyue Zhang<sup>1</sup>, David Hu<sup>3</sup>, Zhili Feng<sup>2</sup>, Pooran C Joshi<sup>2</sup>, Jayne Wu<sup>3</sup>, Zili Wu<sup>4</sup>, \*Anming Hu<sup>1</sup>

<sup>1</sup>Department of Mechanical, Aerospace and Biomedical Engineering, University of Tennessee, Knoxville, TN37996,

USA

<sup>2</sup> Division of Materials Science, Oak Ridge National Lab, Oak ridge, TN 37831-6061 USA
 <sup>3</sup>Department of Electrical Engineering & Computer Science, University of Tennessee, Knoxville, TN37996, USA
 <sup>4</sup>Center of Nanophase Materials Science, Oak Ridge National Lab Oak ridge, TN 37831-6061 USA

\*E-mail: <u>ahu3@utk.edu</u>. Phone: 865-974-5993

#### ABSTRACT:

We repot a flexible sensor array electronic tongue system that fabricated on a polymer substrate by the laser direct writing process for multi-flavors decoction. Electronic tongue is a sensing system that is applied to detect different elements with the same sensor array. By analyzing responses from different measurement units, it enables a cross sensitivity, namely the ability of the system responding to a range of different analytes in solution without specific functionalization of sensors. In this work, a six-unit sensing array system was fabricated by a laser direct writing process (Fig.1a). Sensing units were introduced on a fixable polyamide surface (Fig 1b). A high surface-volume ratio porous carbon structure was created by a laserinduced carbonization process, which provides stable conductive carbon electrodes with high sensitivity. Different surface treatments such as gold plating, reduced-graphene oxide (rGO) coating and polyaniline (PANI) coating, were accomplished for different measurement units. By applying principal component analysis (PCA), this sensing system shows a promising result for multi flavors detection. The detection limits for each element are about 0.1mM for NaCl and sugar solutions. And it can detect 10<sup>-4</sup> times diluted commercial table vinegar solution, which originally contains 5% of acetic acid. As Fig 1(c) shows, separation and grouping of data sets are observed after PCA process, also liner dependencies are found with changing of sample conservations. The detection limit is theoretically lower than the human threshold of 10mM for NaCl and sugar [2]. Besides, the sensing system shows a high sensitivity and selectivity for mixed elements. Additionally, by mapping the data points, the sensor system could detect flavor combinations and provide a reliable prediction of analyte concentration ratios.



Fig. 1 (a) The structure of laser direct writing system, (b) a carbon sensor array with six units fabricated on polymer surface, (c) principal component factor scores obtained for target solutions [1].

Reference:

- [1] Yu Y, Joshi P C, Wu J, et al. ACS applied materials & interfaces, 2018, 10(40): 34005-34012.
- [2] Pfaffman, C., Handbook of Physiology. American Physiological Society: 1959; Vol. 1.

Memory and Learning in biomolecular soft materials for neuromorphic computing Joseph Najem, (1) Ryan Weiss, (2) M. Sakib Hasan, (2) Graham Taylor, (3) R. Stanley Williams, (4) Garrett Rose, (2) Stephen A. Sarles, (1) <u>C. Patrick Collier</u> (5)

- (1) Mechanical, Aerospace and Biomedical Engineering, University of Tennessee Knoxville
- (2) Electrical Engineering and Computer Science, University of Tennessee Knoxville
- (3) Bredesen Center, University of Tennessee Knoxville
- (4) Department of Computer Science and Engineering
- (5) Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Up to now, neuromorphic elements have been predominantly solid-state devices which simulate the resistive and capacitive behaviors needed for neural networks and brain-inspired computing, but in non-brain-like ways. We are integrating lipid and polymer bilayer membranes with microand nanofabrication to develop fundamentally new types of neuromorphic elements that have the composition (biomolecules), structure (biomembranes), and switching mechanism (voltagesensitive ion channels) of real biological synapses, and operate at lower power than the current state-of-the-art. Our devices consist of insulating, nm-thick lipid or polymer-based bilayer membranes that assemble at the interfaces of two or more aqueous droplets in oil, and that have demonstrated both memristive and memcapacitive behaviors, including memory resistance and capacitance, synaptic functions such as paired-pulse facilitation and depression, spike rate dependent plasticity, voltage-dependent inactivation and recovery, and charging hysteresis. These behaviors are linked to electrostriction, an electromechanical phenomenon that encompasses both electrowetting and electrocompression in the membrane, which are changes in membrane area and thickness due to charging in the presence of electric fields. Electrostriction results in a voltage-dependent capacitive susceptibility that replaces the more familiar concept of static capacitance, which, up to now, has dominated electrophysiological descriptions and characterizations of biomembranes. In this picture, biomembranes are not just equivalent RC circuits dependent only on ionic currents controlled by the conductance (resistance) of ion channels. Large capacitive currents from small voltage inputs can be generated as well for the development of neuromorphic computing elements exhibiting both short-term and long-term synaptic plasticity.

#### Parametric Study of Modulated Light Transmission Through Nanoscale Hole Arrays

Alaa Adel Abdelhamid, Francis X. Hart, and Eugenii U. Donev

#### Department of Physics and Astronomy, The University of the South, Sewanee, Tennessee

Vanadium dioxide  $(VO_2)$  is a correlated-electron material that undergoes remarkable phase changes induced by temperature or light. Above a critical temperature of 67 °C, bulk VO<sub>2</sub> switches from an insulator (semiconductor) to a (bad) metal, before returning to the insulating state upon cooling. In this work, we utilize the concomitant changes in the real and imaginary parts of the  $VO_2$  dielectric function across the phase transition to control the propagation of light through nanoscale holes in bilaver films comprising a plasmonic metal and VO<sub>2</sub>. Extraordinary optical transmission (EOT), the Fano-type sequence of minima and maxima in transmission through subwavelength apertures in otherwise opaque plasmonic films, is one of the quintessential phenomena of nanoscale optics. The  $VO_2$  phase transition is one of the few means to control the EOT effect dynamically. The original experiments [1] revealed a surprising effect, 'reverse optical switching', whereby Au+VO<sub>2</sub> and Ag+VO<sub>2</sub> subwavelength holes transmitted more near-infrared light when the  $VO_2$  layer was in the metallic phase than in the semiconducting phase. Conversely, a nondecorated VO<sub>2</sub> film is more opaque to infrared light in its metallic phase, hence the term 'reverse'. We have performed several hundred finite-difference time-domain (FDTD) simulations to explore the parameter space of Au/Ag+VO<sub>2</sub> hole arrays: array periodicity, hole diameter, intra-hole medium, VO<sub>2</sub> film thickness, and angle of illumination. We have thus uncovered surprising Fano-type trends in the ratios of transmission peaks for the two VO<sub>2</sub> phases, which imply interactions between resonant and non-resonant contributions to the EOT modulation. For example, the left panel of the figure below shows the FDTD zero-order

transmission spectra for a 720-nm-period Au+VO<sub>2</sub> hole array in each VO<sub>2</sub> phase. The Fano fits confirm the phenomenological interpretation of EOT as resulting from the interference of resonant (surface-plasmon polaritons and quasi-cylindrical waves) and non-resonant transmission channels. Unexpectedly, the *ratio* (right panel, top) of the transmission peaks (right panel, bottom) as a function of array periodicity also follows a Fano-shape curve, as do the peak ratios obtained from varying the hole diameter and VO<sub>2</sub> thickness (not shown). By August 2019,



we will have begun making such nanostructures at CNMS and measuring their transmission in order to provide experimental support for the simulations. The Fano-type behavior of the transmission peak ratios suggests an interplay between interfacial or guided modes and in-plane absorption in the VO<sub>2</sub> layer. The ultimate goal is to understand the electrodynamic mechanism by which the metallic phase of the VO<sub>2</sub> film enables higher transmission than the insulating phase.

1. J. Y. Suh, E. U. Donev, R. Lopez, L. C. Feldman, and R. F. Haglund Jr., "Modulated optical transmission of subwavelength hole arrays in metal-VO<sub>2</sub> films," *Appl. Phys. Lett.* **88**, 133115 (2006).

# From suppressed void growth to significant void swelling in NiCoFeCr complex concentrated solid-solution alloy

Zhe Fan<sup>1</sup>, Tai-ni Yang<sup>2</sup>, B. Kombaiah<sup>1</sup>, Xing Wang<sup>3</sup>, P.D. Edmondson, Y.N. Osetsky<sup>1</sup>, Hongbin Bei<sup>1</sup>, Ke Jin<sup>1</sup>, Chenyang Lu<sup>2</sup>, Lumin Wang<sup>2</sup>, Karren L. More<sup>3</sup>, William J. Weber<sup>4,1</sup>, Yanwen Zhang<sup>1,4</sup>

<sup>1</sup> Materials Science and Technology Division, Oak Ridge National laboratory, Oak Ridge, TN 37831, USA

<sup>2</sup> Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI 48109, USA

<sup>3</sup> Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

<sup>4</sup> Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA

Void swelling can result in dimensional instability and undermine the safe operation of nuclear reactors. Current strategies to inhibit void swelling mainly focus on enhancing defect absorption by introducing high-density defect sinks, such as grain boundaries and phase boundaries. Complex concentrated solid-solution alloys (CSAs), including high entropy alloys, can withstand severe radiation damage due to their inherent chemical complexity without boundaries. However, the underlying

mechanisms for void suppression in CSAs are far from clear. In this research, we studied the void evolution with respect to dose and temperature in NiCoFeCr under 3 MeV Ni ion irradiations. We show that, at relatively low doses (16 and 54 dpa), voids form mainly outside of the ion-damaged region and void formation in the peak damage region is suppressed, leading to negligible swelling. However, with further increase of doses (86 up to 250 dpa), significant void growth occurs in the peak damage region, and extended dislocation lines dominate instead of short dislocation lines and loops formed at lower doses.



From 500 to 700 °C, dislocation density decreases while dislocation size increases. Although void swelling increases dramatically (0.016% to 1.18%) from 500 to 580 °C due to reduced defect recombination, void growth at the peak damage region is still suppressed. The transition from suppressed void formation to significant void growth in the peak damage region is attributed to the dislocation growth and motion, and the enrichment of Fe/Cr in the matrix at higher doses. Controlling the element diffusion and defect evolution by tuning chemical complexity can further enhance the swelling resistance of the complex CSAs.

3D Nanoprinting using an Electron Beam

Eva Mutunga<sup>a,c</sup>, R. Winkler<sup>c</sup>, J. Sattelkow<sup>c</sup>, P. D. Rack<sup>a,b,d</sup>, H. Plank<sup>c,e</sup> and J. D. Fowlkes <sup>a,b,e\*</sup>

<sup>a</sup> Bredesen Center for Interdisciplinary Research and <sup>b</sup> Materials Science and Engineering Department, The University of Tennessee, Knoxville, Tennessee 37996, United States

<sup>c</sup> Christian Doppler Laboratory for Direct–Write Nanofabrication of 3D Nano–Probes (DEFINE), Institute of Electron Microscopy, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria

<sup>*d*</sup> Nanofabrication Research Laboratory, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

<sup>e</sup> Institute for Electron Microscopy, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria

The deposition of 3D nanomaterials with accurate geometry and function constitutes a main goal of nanoscience. Currently, the best method for 3D nanoprinting is focused electron beam-induced deposition (FEBID). During FEBID, the electron beam is scanned along a surface inducing the fragmentation and deposition of absorbed precursor molecules. Until recently, the range of 3D nanostructures that could be deposited was limited by the trial-and-error nature of experiments. Our team has taken significant steps toward overcoming this roadblock. A FEBID CAD program will be presented that makes it possible to deposit complex, 3D nanoscale mesh style objects.

Precise 3D electron-based nanoprinting can be achieved by accounting for deposition artifacts during the computer-aided design (CAD) step. A CAD capability has been created at the CNMS for this purpose. If left uncorrected, artifact/errors prevent CAD replication during deposition when using a typical organometallic precursor for deposition. Empirical corrections *can* be used to avoid deposition errors/artifacts, but such solutions usually apply over a limited range of deposition conditions/parameters. Ideally, a general mathematical correction is the best solution because the identification of rate limiting factors related to deposition, such as mass-transport or reaction-rate limitations, leading to a more robust correction method which can be applied over a much larger range of deposition conditions of experiments, simulations and design will be demonstrated which enables precise 3D nanoprinting. In particular, a mathematical-based scheme will be presented that makes it possible to compensate for deposit distortions.

CNMS User Meeting abstract

#### Synthesis of Bottlebrushes from PGMA-PVDMA Block Copolymers

Bin Hu, Nikolay Borodinov, Rajeev Kumar, Scott T. Retterer, Bradley S. Lokitz

Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, One Bethel Valley Road, Oak Ridge, Tennessee 37831, United States

Bottlebrush block copolymers that self-assemble into well-defined nanostructures when confined in thin films should have potential in applications such as lithography, drug delivery and energy storage devices. Most synthetic strategies to form bottlebrushes rely on the (co)polymerization of macromonomers which can make it challenging to synthesize and study a series of bottlebrush polymers with different side chains while keeping the backbone length constant. To overcome this obstacle, we rely on the dually reactive block copolymer, poly(glycidyl methacrylate)-*b*-poly(4,4dimethyl-2-vinylazlactone), or PGMA-*b*-PVDMA, which contains epoxy and azlactone reactive groups that can be independently reacted with nucleophiles such as carboxylic acids and hydroxyl groups under specific reaction conditions. Herein, we present a synthetic strategy that allows for side chains to be grafted onto the parent block copolymer in a step-wise fashion resulting in a AB bottlebrush blockcopolymer. The side chain identity/functionality, degree of polymerization, dispersity, grafting density, and/or ratio of the A/B side chains can be systematically varied to study their effect on self-assembly and thin film morphology.

## Greyscale E-Beam Lithography Revisited: Dynamic Range and Roughness of Patterns on Silicon

Ivan Kravchenko and <u>Nickolay Lavrik</u> Center for Nanophase Materials Sciences Oak Ridge National Laboratory Oak Ridge, TN, USA <u>lavriknv@ornl.gov</u>

> Abhijeet Gujrati and Tevis Jacobs Mechanical Engineering & Materials Science University of Pittsburgh Pittsburgh, PA, USA <u>tjacobs@pitt.edu</u>

Dose-modulated e-beam lithographic (EBL) patterning, commonly referred to as greyscale EBL, is uniquely suitable for creating surface topographies of high complexity with nanoscale precision. Continued refinements in greyscale EBL are of great interest due to many emerging applications [1] as well as basic science research that benefit from 3D nanopatterning.

This study focuses on some of the remaining challenges in greyscale EBL, in particular, out-of-plane accuracy, dynamic range and surface roughness of topologies created on silicon using a combination of EBL and dry etching. This effort has been driven by our interest in asymmetric nanotextures with a topological bias [2] as well as random patterns that can mimic surfaces of typical engineered and naturally occurring materials. Our main goal is to identify processing protocols that result in 3D topologies with the highest fidelity. Our analysis of artifacts and additional surface roughness introduced by each of the processing steps involved in greyscale EBL is presented.

8-bit greyscale images were generated in a png format and then converted successively into GDSII and v30 formats using Beamer (Genisys, gmbh) software compatible with a Jeol 9300FS EBL tool. Our test images included harmonically modulated and staircase greyscales as well as random patterns. The bitmaps were up to 9 megapixels with one pixel corresponding to a 50 nm x 50 nm area on the substrate. The resulting surface topologies were characterized using optical interferometric profilometry and scanning probe microscopy (SPM) on the micro-and nano- scales, respectively. The profilometry and SPM data were analyzed both in real space and spatial frequency domain. With a PMMA 495 A4 resist spun at 2000 rpm, the optimal based doze was in the range of 350-360  $\mu$ Ccm<sup>-2</sup> with the dose modulation of -50%. Peak-to-peak roughness as small as 2.5 nm was achieved on 12  $\mu$ m x 12  $\mu$ m flat field areas when 3D patterns in the e-beam resist were transferred on silicon using a mixed SF<sub>6</sub>: Ar plasma etching.

- 1. Schleunitz, A., *et al.* Novel 3D micro- and nanofabrication method using thermally activated selective topography equilibration (TASTE) of polymers. *Nano Convergence* (2014) 1,7.
- 2. Agapov *at al.* Asymmetric Wettability of Nanostructures Directs Leidenfrost Droplets. *ACS Nano* 2014, 8, 1, 860-867.

#### Norbornene-based Bottlebrush Polymers: Controlled Synthesis, Characterization, and Solution Behavior

Tianyu Li<sup>†</sup>, Hui Li<sup>‡</sup>, Kunlun Hong \*,<sup>‡</sup>

<sup>†</sup>Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Knoxville, TN, 37996 <sup>‡</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831

Abstract: Bottlebrush polymers have attracted enormous attention due to their unique properties and potential applications, which are closely associated with their structures. To understand the connection, the precise structural and functional control are critical.<sup>1</sup> In this study, a series of welldefined norbornene-based bottlebrush polymers with different lengths in main-chains and polymethacrylate (PMMA) side-chains was synthesized by ATRP and ROMP. First, a macroinitiator was prepared by modification of *exo*-5-norbornene-2-methanol with 2bromoisobutyryl bromide,<sup>2</sup> followed by polymerizing MMA as side chains with different molecular weights through ATRP.<sup>3</sup> The final bottlebrush polymers were obtained by ROMP of the  $\alpha$ -norbornenyl macromonomers, and characterized by <sup>1</sup>H, <sup>13</sup>C NMR and GPC methods.<sup>1,3</sup> These bottlebrush polymers can show interesting solution behavior, which was monitored by light scattering and small angle X-ray scattering.

Reference(s):

Verduzco, R.; Li, X.; Pesek, S. L.; Stein, G. E., Structure, function, self-assembly, and applications of bottlebrush copolymers. *Chemical Society Reviews* 2015, *44* (8), 2405-2420.
 Cheng, C.; Khoshdel, E.; Wooley, K. L., ATRP from a Norbornenyl-Functionalized Initiator: Balancing of Complementary Reactivity for the Preparation of α-Norbornenyl Macromonomers/ω-Haloalkyl Macroinitiators. *Macromolecules* 2005, *38* (23), 9455-9465.
 Xu, Y.; Wang, W.; Wang, Y.; Zhu, J.; Uhrig, D.; Lu, X.; Keum, J. K.; Mays, J. W.; Hong, K., Fluorinated bottlebrush polymers based on poly(trifluoroethyl methacrylate): synthesis and characterization. *Polymer Chemistry* 2016, *7* (3), 680-688.

#### An Ab Initio Description of Electronic Response to Electron Beam Irradiation

D. B. Lingerfelt, J. Jakowski, P. Ganesh, and B. G. Sumpter

Center for Nanophase Materials Sciences, Oak Ridge National Laboratory.

The use of scanning transmission electron microscopes to manipulate substitutional defects in graphene has recently been demonstrated and modeled using ground state (Born-Oppenheimer) molecular dynamics, but the role of electronic excitations induced through inelastic electron scattering in promoting these transformations has remained relatively unexplored. Using our recently developed time dependent density function theory (TD-DFT) approach for modeling

excitations induced by external charges, [1] we have investigated the effects of electronic excitations that can be enacted through electron beam exposure on the structural dynamics of Silicon and Phosphorous doped graphene quantum dots of differing edge morphologies. [2] The potential energy surfaces (PESs, Figure 1c) for pyramidal inversion of these nonplanar doped species in ground and excited electronic states were evaluated using TD-DFT. Excited states in which the potential energy barrier for inversion is decreased are identified in the low energy region of the electronic spectrum. Transitions to these states are





optically allowed, suggesting that photoexcitation can modulate the reactivity of defects in graphene under electron beam irradiation. Electronic excitation rates between these inversion-favoring excited states and the ground state due to the presence of an external point-charge, (Figure 1a, 1b) as well as real-time simulations of the material's response to a point charge impulse enacted immediately above the defect, indicate that focusing an electron beam near the defect can promote the population of these states. This result suggests that beam electrons incident on a defect can simultaneously excite the material to an inversion-favoring state through inelastic (beam electrons) scattering and transfer momentum to the defect to initiate the inversion through the elastic (beam electrons—material nuclei) scattering, highlighting the importance of considering electronically non-adiabatic reaction pathways for materials under electron beam irradiation.

[1] Lingerfelt, David B., Panchapakesan Ganesh, Jacek Jakowski, and Bobby Sumpter. First Principles Determination of Electronic Excitations Induced by Charged Particles. **2019**, *ChemRxiv*: 7726139

[2] Lingerfelt, David B., Panchapakesan Ganesh, Jacek Jakowski, and Bobby Sumpter. Electronically Nonadiabatic Structural Transformations Promoted by Electron Beams. **2019**, *Adv. Funct. Mater*, 1901901

#### Systematic Computational Fluid Dynamics Study of the Gas Transport in a Closed Desorption Cell to Combine Atomic Force Microscopy and Atmospheric Pressure Mass Spectrometry in a Multimodal Imaging Platform

Matthias Lorenz,<sup>1,2</sup> Ryan Wagner,<sup>3</sup> Roger Proksch,<sup>3</sup> Olga S. Ovchinnikova<sup>2</sup>

<sup>1</sup>University of Tennessee, Knoxville, TN; <sup>2</sup>Oak Ridge National Laboratory, Oak Ridge, TN; <sup>3</sup>Oxford Instruments, Santa Barbara, CA

#### Introduction

We recently introduced the multimodal combination of atomic force microscopy (AFM) and mass spectrometry (MS) based on a photoinduced cantilever heating technology developed by Oxford Instruments for the localized thermal desorption. We developed a closed desorption cell design on a Cypher microscope to interface with a Thermo Fisher Scientific LTQ Orbitrap Velos mass spectrometer using inline atmospheric pressure chemical ionization (APCI). We previously demonstrated <500 nm spatial resolution for spot-sampling of small molecules in full scan MS mode. With the objective to further improve the achievable spatial resolution of the combined platform, we performed systematic computational fluid dynamics (CFD) studies of the gas transport in the closed desorption cell.

#### Methods

An Oxford Instruments Cypher AFM was coupled with a Thermo Fisher Scientific LTQ Orbitrap Velos MS using a closed desorption cell based on the Cypher ES design. A 50 mm long, 0.7 mm i.d. stainless steel capillary was used in the desorption cell and positioned at ~0.5 mm from the AFM cantilever to aspirate desorbed material. A modified MS ion transfer tube (Prosolia) attached to a Swagelok stainless steel union cross fitting that served as custom-built inline APCI stage, featuring a corona needle in one side arm. An adjustable flow of dry nitrogen was fed into the opposite arm. COMSOL Multiphysics 5.2 equipped with the CFD Module was used to perform CFD simulations.

#### **Preliminary Data**

CFD simulations were used to study the gas transport in the closed desorption cell and the impact of directed gas flows on the transport of thermally desorbed material. We identified the gas transport in the closed desorption cell as critical to facilitate the efficient uptake of thermally desorbed material and to prevent its re-deposition. While large range trajectories of directed gas flows through the cell can easily be manipulated by the re-positioning of gas inlets, simulations revealed a very limited impact on the transport conditions close to the desorption site. The AFM cantilever and the chip are effectively shielding the desorption site and reducing gas velocities in the vicinity of the AFM tip. Systematic modifications of the flow cell geometry in CFD simulations enabled us to understand how to improve the control of transport conditions and to develop alternative designs – enabling improved uptake at the desorption site, but also improved overall transport with, e.g., reduced wall contact and long temporal stability. We present systematic CFD data for various desorption cell geometries and discuss the potential to efficiently transport thermally desorbed material based on gas velocities in the vicinity of the desorption site.

#### Investigation of Carbon Nanostructures in Cu Covetics by APT, HIM, and TOF-SIMS

Beihai Ma<sup>1</sup>, Uthamalingam Balachandran<sup>1</sup>, Tae H. Lee<sup>1</sup>, Steve E. Dorris<sup>1</sup>, Jianguo Wen<sup>2</sup>, Yuzi Liu<sup>2</sup>, Jonathan D. Poplawsky<sup>3</sup>, Anton Ievlev<sup>3</sup>, Artem Trofimov<sup>3</sup>, and Alex A. Belianinov<sup>3</sup>

 <sup>1</sup>Applied Materials Division, Argonne National Laboratory, Argonne, IL 60439
 <sup>2</sup>Nanoscience and Technology Division, Argonne National Laboratory, Argonne, IL 60439
 <sup>3</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Nanocarbon-infused metal alloys, known as "covetics," are emerging as strategically important materials due to their superior electrical and thermophysical performance. In our investigation, copper covetics were prepared in a vacuum by electron-beam melting with an electromagnetic stirring process. To study the enhanced electrical and thermal conductivities of these materials as a result of carbon nanostructure infusion in the metals, we utilized atom probe tomography (APT), helium ion microscopy (HIM), transmission electron microscopy (TEM), and time-of-flight secondary ion mass spectrometry (ToF-SIMS). APT revealed the 3D distribution of carbon-rich clusters. The superior contrast and resolution of HIM combined with elemental analysis capability of ToF-SIMS allowed characterization of the carbon nanostructures. In addition, elemental mapping with high-resolution TEM and scanning TEM verified the formation of carbon nanoparticles and networks in the copper metal hosts. Our experimental findings provide improved understanding about the chemical and structural nature of carbon nanostructures and their interactions within the host metal matrix. These results can help to elucidate the origins of the superior physical and mechanical performance in covetics. Details will be presented.

This work was supported by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under Contract DE-AC02-06CH11357. TEM/STEM was performed at the Center for Nanoscale Materials, an Office of Science user facility, supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. APT, HIM, and ToF-SIMS were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

#### Tunable quadruple-well ferroelectricity in a van-der-Waals layered material

Sabine Neumayer,<sup>1</sup> John A. Brehm,<sup>2,3</sup> Lei Tao,<sup>3</sup> Andrew O'Hara,<sup>3</sup> Marius Chyasnavichus,<sup>1</sup> Michael A. Susner,<sup>5</sup> Michael A. McGuire,<sup>2</sup> Sergei V. Kalinin,<sup>1</sup> Stephen Jesse,<sup>1</sup> Panchapakesan Ganesh,<sup>1</sup> Sokrates T. Pantelides,<sup>2,3,4</sup> Petro Maksymovych,<sup>1</sup> and Nina Balke<sup>1</sup>

<sup>1</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA <sup>2</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

<sup>3</sup>Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA <sup>4</sup>Department of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, Tennessee, 37235, USA

<sup>5</sup>Aerospace Systems Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433 USA

The interest in van-der-Waals (vdW) layered  $CuInP_2S_6$  arises from its intriguing functional properties, comprising giant negative electrostriction [1] leading to piezoelectric coefficients comparable to perovskite oxides, ferroelectric switching, and high ionic conductivity enabling reversible extraction of Cu [2]. Moreover, the layered structure allows for exfoliation into ultrathin flakes and the vdW interfaces are suitable to create functional heterostructures with 2D materials such as graphene or  $MoS_2$  [3].

Here, we use density-functional-theory (DFT) calculations and piezoresponse force microscopy to reveal the existence of four uniaxial stable polarization states in  $CuInP_2S_6$ . The polarization depends on the position of the Cu ions, which can either be situated within the layers leading to positive or negative low polarization (LP) states, or high polarization (HP) states when displaced into the vdW gap (see Figure 1). The co-existence of these four phases and the ability to transition between them via temperature, pressure and electric fields provides exciting opportunities for data storage and electronic devices.



Figure 1: CuInP<sub>2</sub>S<sub>6</sub> lattice of the four polarization states

[1] Neumayer et al, PRM 3, 024401 (2019)
 [2] Balke et al, ACS AMI 10(32), 27188 (2018)

[3] Si, ACS Nano 12(7), 6700 (2018)

Research was supported by the Division of Materials Science and Engineering, Basic Energy Sciences, DOE. Experiments were conducted at the CNMS, which is a DOE Office of Science User Facility.

#### Unveiling Nanoscale Information in Zeolites Via Atom Probe Tomography

Jonathan D. Poplawsky<sup>1</sup>, Joel E. Schmidt<sup>2</sup>, Simon R. Bare<sup>3</sup>, and B.M. Weckhuysen<sup>2</sup>

<sup>1</sup>CNMS, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

<sup>2</sup>Debye Institute for Nanomaterials Science, Utrecht University, Utrecht 3584, Netherlands

<sup>3</sup>SSRL, SLAC National Accelerator National Laboratory, Menlo Park, CA 94025, USA

Zeolite catalysts are used in several different industrial applications, some of which include oil refining and catalytic conversion of toxic emissions. Using atom probe tomography (APT), 3D elemental distributions of all elements can be determined at the nanoscale, including light framework elements, within zeolite catalysts. There are limited techniques capable of such a precise measurement in zeolite materials due to difficulties differentiating between the active and inactive framework elements, such as Si, Al, O, and P that make up the microporous structure, as these elements are light and have a similar Znumber. APT is not restricted in this way because it relies on time-of-flight mass spectrometry to differentiate elements. Mapping the 3D elemental distributions is important for understanding failure mechanisms as well as mechanisms that improve catalytic activity and longevity.

APT has been applied to two zeolite catalytic systems, including ZSM-5 for a methanol-tohydrocarbons reaction and Cu-exchanged chabazite (Cu-SSZ-13) and Cu-ZSM-5 for NO<sub>x</sub> reduction in diesel exhaust. The ZSM-5 subjected to a <sup>13</sup>C methanol-to-hydrocarbons reaction was studied by APT to understand chemical deactivating mechanisms at nano-sized length scales. The <sup>13</sup>C distribution (residual coke) was found to be heterogeneous from length scales of several nms to 10s of nms in size with the nano-clusters being a similar size as known coke species. The most striking result was the <sup>13</sup>C cluster proximity to AI Brønsted acid sites, revealing that formation of coke species at AI sites blocks hydrocarbon passage. APT was also performed on Cu-exchanged zeolite catalysts used in the diesel fuel automotive industry for selective NO<sub>x</sub> reduction with amonia. Cu-SSZ-13 was recently discovered and commercialized because it outperforms and has superior stability compared to other catalysts, most notably Cu-ZSM-5. 3D elemental distributions of all elements were able to be determined using APT within Cu-SSZ-13 and Cu-ZSM-5 before and after an industry-standard 135,000 mile exhaust exposure simulation, which were subsequently correlated with their catalytic activity. A heterogeneous Cu distribution was found in each fresh catalyst, but a remarkable difference was witnessed after the 135,000 mile simulation. Although both catalysts showed aggregation of Al and Cu species, the Cu-ZSM-5 material exhibited a much more severe Al/Cu co-clustering behavior, identified as copper aluminate (CuAl<sub>2</sub>O<sub>4</sub>), which was responsible for the deactivation of Cu-ZSM-5 after the 135,000 mile exhaust simulation. The results from both studies have identified nano-scale degradation mechanisms in zeolite catalysts. The information gathered from these studies can be used for the design of better, more robust future catalysts. APT was conducted at the CNMS, which is a DOE Office of Science user facility.

# Understanding effects of alloy chemical complexity on helium bubble formation by accurate segregation measurements using atom probe tomography

Xing Wang<sup>1</sup>, Hongbin Bei<sup>1</sup>, Yanwen Zhang<sup>1, 2</sup>, Jonathan Poplawsky<sup>1</sup>, and Karren L. More<sup>1</sup> <sup>1</sup> Oak Ridge National Laboratory, TN, USA. <sup>2</sup> University of Tennessee-Knoxville, TN, USA.

Because of its low solubility, helium (He) tends to cluster with vacancies to form detrimental bubbles in irradiated materials [1]. Previous studies showed that tuning the alloy chemical complexity in concentrated solid-solution alloys (CSAs) can be an effective approach to tailor defect energy landscapes and suppress He bubble growth [1,2]. In CSAs, multiple elements are randomly arranged in simple lattice structures, generating extreme chemical complexity at the unit-cell level. A comprehensive understanding of how such chemical complexity affects defect generation and migration during irradiation is required. Here, atom probe tomography (APT) is used to accurately measure radiation-induced segregation near He bubbles, providing insight into defect energetics in CSAs.

Four CSAs (NiFe, NiCo, NiCoCr, and NiCoFe) and Ni were irradiated by 200 keV He ions at 500°C to a fluence of  $5 \times 10^{16}$  He/cm<sup>2</sup>. Transmission electron microscopy (TEM) analyses showed that the alloy resistance to He bubble growth followed as NiCoFe > NiFe > NiCoCr > NiCo, with Ni showing the lowest resistance. In general, the alloy becomes more resistant to He bubble growth as its chemical complexity increases. One interesting exception is NiCoCr, which exhibits a lower resistance to bubble growth than the binary NiFe and ternary NiCoFe. To understand this unexpected trend, the elemental segregation behavior near bubbles of similar sizes (~9 nm diameter) were measured using APT (Fig. 1a) and compared between different CSAs. As shown in Fig. 1b and 1c, Cr- and Fe- depletion and Ni- and Co-enrichment near the bubbles are typically observed, indicating vacancies diffuse primarily via Cr and Fe lattice sites, while interstitials diffuse via Ni and Co sites. More importantly, the magnitude of the Cr-depletion around the bubble in NiCoCr is larger than that of Fe in NiCoFe. The Cr-content near bubbles in NiCoCr is as low as 5 at.%, while the Fe content near bubbles in NiCoFe is ~10 at.%. A larger depletion of an element indicates a higher vacancy mobility for that element. Thus, the segregation measurements show that in Nibased CSAs, vacancies diffuse much faster via Cr than via Fe, leading to faster vacancy clustering and a higher bubble growth rate in NiCoCr than NiCoFe or NiFe. This conclusion is also supported by defect migration barriers calculated using density functional theory [3].



**Figure 1.** (a) An example of APT reconstruction of NiFe sample containing He bubbles (in white) and Fedepleted zones around bubbles. (b) One-dimensional elemental concentration profiles across He bubble in NiCoCr and (c) NiCoFe. Position of He bubble is marked by two dashed vertical lines in each profile.

#### **References:**

[1] Z Fan, et al., Acta. Mater. **164** (2019), p. 283. [2] X Wang, et al., Materialia **5** (2019), p. 100183.

[3] S Zhao, et al., Phys. Rev. Mater. 2 (2018), p. 013602.

#### **3D-Printed Carbon Electrodes for Neurotransmitter Detection**

Qun Cao<sup>1</sup>, Nickolay V. Lavrik<sup>2</sup>, and B. Jill Venton<sup>1</sup>

<sup>1</sup>Dept. of Chemistry, University of Virginia, Charlottesville, VA 22901

<sup>2</sup>Center for Nanophase Material Science, Oak Ridge National Lab, Oak Ridge, TN 37831

Carbon microelectrodes enabled rapid and selective detection of neurotransmitters. While different fabrication strategies of carbon microelectrodes were explored, the geometry of most probes was limited by the fabrication methods. New methods are needed for manufacturing geometry customized electrodes with high reproducibility. Here, we introduce a novel, implantable and free-standing microsensor fabrication method using two-photon nanolithography followed by pyrolysis. This 3Dprinting method allows the fabrication of free-standing microelectrodes with customizable geometries and sizes. As proof or principle, the geometries of sphere and cone, and some tiny structures as small as 1 µm were successfully fabricated. Then we characterized the electrochemical properties of the sensors. Cyclic voltammograms of Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> and dopamine demonstrated highly electrochemically active surface of the pyrolyzed carbon microelectrodes. The carbonized microelectrodes showed promising dopamine LOD of  $11 \pm 1$  nM (sphere) and  $10 \pm 2$  nM (cone). For a variety of neurochemicals, FSCV curves of 3D-printed microelectrodes were comparable to carbon fiber microelectrodes. The Spherical 3D printed microelectrodes were used to monitor stimulated dopamine release in vivo, proving the potential of using this microsensor as an implantable neural probe. This work is the first demonstration of 3D printing of free-standing carbon electrodes, and the method exhibits great promise to batch-fabricate sensors with customizable geometries and sizes.



Figure 1. Process flow for the fabrication of 3D-printed carbon electrodes.

#### **References:**

Yang, C.\*, Cao, Q.\*, Puthongkham, P., Lee, S. T., Ganesana, M., Lavrik, N. V., & Venton, B. J. (2018).
3D - printed carbon electrodes for neurotransmitter detection. *Angewandte Chemie International Edition*, *57*(43), 14255-14259.

Cao, Q.\*, Puthongkham, P.\*, & Venton, B. J. (2019). Review: new insights into optimizing chemical and 3D surface structures of carbon electrodes for neurotransmitter detection. *Analytical Methods*, *11*(3), 247-261.

#### Formation, Migration and Oxidation of Silver Oxide Phase in Au-Ag Core-Shell

#### Nanoparticles at High Temperature

#### Peifu Cheng,<sup>1</sup> Dmitri Zakharov,<sup>2</sup> Naiya Soetan,<sup>1</sup> Rizia Bardhan,<sup>1</sup> Adri van Duin<sup>3</sup> and Piran R. Kidambi<sup>1\*</sup>

<sup>1</sup>Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee 37235, USA. E-mail: piran.kidambi@vanderbilt.edu <sup>2</sup>Center for Functional Nanomaterials Brookhaven National Laboratory, Upton, New York 11973, USA. <sup>3</sup>Department of Mechanical Engineering, The Pennsylvania State University, University Park,

Abstract:

Pennsylvania 16802, USA.

Silver oxide has been a popular functional material applied in many fields such as catalysis, photocatalysis, silver-oxide battery, gas sensing and antibacterial application due to its specific physical and chemical structure. However, it is generally recognized that Ag<sub>2</sub>O cannot exist at above 200 °C, which restricts its application at high temperature. In this work, we observed the formation of Ag<sub>2</sub>O phase in Au@Ag nanoparticles in  $10^{-4}$  Torr O<sub>2</sub> at 450 °C using Environmental Transmission Electron Microscope. Furthermore, we found unusual droplet-like migration of crystalline Ag<sub>2</sub>O nanodots at the same condition. Moreover, thermodynamically less favorable phases, including AgO, Ag<sub>3</sub>O<sub>4</sub> and Ag<sub>2</sub>O<sub>3</sub>, were also demonstrated to exist in O<sub>2</sub> at 450 °C. This work may open a door for the potential application of silver oxide at high temperature.



# High Q factor meridian whispering gallery modes sensing in a water droplet on nano-structured surfaces

Weifeng CHENG<sup>1</sup>, Jiangtao CHENG<sup>1,\*</sup>, Meng ZHANG<sup>2</sup>, Jiansheng LIU<sup>2</sup>, and Zheng ZHENG<sup>2</sup>

<sup>1</sup>Department of Mechanical Engineering, Virginia Tech, 635 Prices Fork Road, Blacksburg, VA 24061,USA

<sup>2</sup>School of Electronic and Information Engineering, Beihang University, 37 Xueyuan Road, Beijing 100191, China.

\*Corresponding Author. Tel: (1) 540-231-4164; Email: chengjt@vt.edu

Keywords: optofluidics, interface wetting, whispering gallery modes

#### Abstract

Optical whispering gallery modes (WGMs) in a water droplet cavity can be employed for high sensitivity biosensing in a more natural way. Yet, most of the droplet-based WGMs are very tricky to implement and require for complex and precise coupling mechanism, which brings many experimental difficulties. In this work, we show that WGMs could be stimulated along the meridian periphery of a liquid microdroplet on a properly designed nanostructured surface through coupling with a planar waveguide embedded in the surface, which significantly reduces the complexity of the overall system. Via electrowetting on dielectric (EWOD), we can tune the water droplet sagging and morphology on a nanostructured surface, leading to a spherical shape with high contact angle. The textured superhydrophobic surface and its impact on the microdroplet morphology are modeled by Surface Evolver (SE), which is validated by comparing with the experimental results. The influence of the microdroplet morphology on the optical characteristics of WGMs is further numerically studied using the Finite-Difference Time-Domain method (FDTD) and it is found that meridian WGMs with a high intrinsic quality factor Q exceeding 10<sup>6</sup> can exist. This systematic study could pave the way for developing novel optofluidic resonators and platforms for high-resolution sensing of trace analytes and for the fundamental studies of biological reaction processes.

#### Ion transport through and permeability of extended DNA nanotube channels anchored by their ends in synthetic membranes

Naresh Niranjan Dhanasekar, Yi Li, Rebecca Schulman Johns Hopkins University, Department of Chemical and Molecular Engineering, Baltimore, Maryland 21218, USA

Transport through nanoscale channels is a fundamental mechanism of exchange in living systems. The ability to direct such transport using membrane-based synthetic devices could make it possible to systematically study or control these transport processes. Such man-made devices been shown to incorporate into lipid bilayers and forms channels with currents ranging from 100 to 1000's of picoamperes. In the past few years, DNA nanotechnology have recently made it possible to emulate the structural and functional aspects of naturally occurring membrane channels using easy-to-design DNA nanostructures. In contrast to biological channels, DNA-membrane based nanopores can be finetuned to precise molecular dimensions and chemically functionalized via DNA bioconjugates.

One of the primary goal in synthetic biology is could long channels (microns in size) transport ions from one location to another such that a significant portion of the channel extends past the membrane? To understand this question we need to understand not only the extent to which ions can travel along the length of the channel but also the amount of materials that is being lost through walls. To understand this question, we seek to measure net transport through the central (channel) vs transport across the walls (undesired) across the structure. To design such long-range channel we also need a method to create "giant" membrane channels, the design principles, the high yield, stability in the membranes is always challenging.

Here we utilize both the folded DNA origami (seed) and the DNA tiles (10 strands, REdSEd) which nucleate from the seeds to form tubes forms channels with conductance similar to biological counterparts. In the present study, we were able to show DNA seed nanostructures of sever nanometers in length forms well defined pores of unitary conductance of 1.2 nS in synthetic bilayers. In addition, micro range DNA nanotubes nucleating from the DNA origami seeds also forms stable channels in our lipid bilayers with a conductance similar to the seeds. Interestingly, we were able to cap the DNA origami seeds which reduces the channel conductance one-fold lesser than the actual conductance of the long seeds. The caps could also bind to microns range tube like structures giving rise to different channel conductances such as 200, 600 and 1200 nS. Thus, the caps acts as a origami shutter to the DNA seed and the tube in preventing the flow of ions through the channel. We believe that our simple design will open up the contest in understanding the mechanism of transport across synthetic tubes which pays extensive application including sensing electric circuits and nanofluidic research and transport.



Graphical representation of the DNA origami seed and tube insertion in synthetic bilayers. The caps acts as a shutter in preventing the flow of ions across the channel

#### Bottom-Up Synthesis of Ultrathin PdSe2 Crystals with High Electron Mobility

Yiyi Gu,<sup>1,2,6</sup> Hui Cai,<sup>2</sup> Jichen Dong,<sup>4</sup> Yiling Yu,<sup>2</sup> Anna N. Hoffman,<sup>3</sup> Chenze Liu,<sup>3</sup> Akinola Oyedele,<sup>2</sup> Yu-Chuan Lin,<sup>2</sup> Alexander A. Puretzky,<sup>2</sup> Gerd Duscher,<sup>3</sup> Philip D. Rack,<sup>2,3</sup> Christopher M. Rouleau,<sup>2</sup> Xiangmin Meng,<sup>1</sup> Feng Ding,<sup>4,5</sup> David B. Geohegan,<sup>2</sup> Kai Xiao<sup>2</sup>\*

<sup>1</sup>Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

<sup>2</sup> Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States.

<sup>3</sup> Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, United States.

<sup>4</sup> Center for Multidimensional Carbon Materials, Institute for Basic Science (IBS), Ulsan 44919, Republic of Korea.

<sup>5</sup> Department of Materials Science and Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea.

<sup>6</sup> Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

#### Abstract:

PdSe<sub>2</sub> is a high-mobility 2D material that has an unusual pentagonal structure, leading to buckled and puckered layers. Its strong interlayer coupling results in highly interesting and asymmetric optoelectronic properties and makes it difficult to exfoliate. However, to date it has not been directly synthesized on substrates. In this work, we report the bottom-up, vapor transport growth of few-layer PdSe<sub>2</sub> crystals with growth temperature dependent morphology. A theoretical model based on density functional theory (DFT) calculations simulate the growth process of PdSe<sub>2</sub> crystals. The high quality of the PdSe<sub>2</sub> crystals was confirmed by low-frequency Raman spectroscopy, scanning transmission electron microscopy (STEM), and device performances. Second-



harmonic generation (SHG) mapping analysis of the  $PdSe_2$  flakes was used to characterize their strong optical anisotropy. Field-effect transistors made from the few-layer  $PdSe_2$  crystals revealed tunable ambipolar charge carrier conduction with a high electron mobility of ~294 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> after annealing, which is comparable to that of exfoliated PdSe<sub>2</sub>, indicating the promise of this anisotropic 2D material for electronics.

Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division. Characterizations were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

#### Photonic Crystal Design with Mix and Match Unit Cells for Mode Manipulation

S. I. Halimi, Z. Fu, F. O. Afzal, J. A. Allen, S. Hu, and S. M. Weiss, Vanderbilt University

Photonic crystals (PhC) cavities have been demonstrated in a wide variety of on-chip applications, including optical modulators, lasers, and optical biosensors. While PhCs can have compact design and have high temporal confinement with quality factors (Q) >  $10^5$  in simulations and >  $10^3$  in experiments, manipulation of the mode distribution in the unit cells remains difficult. Recent work has shown it is possible to leverage subwavelength design for subwavelength mode concentration in PhC cavities. However, these designs rely on very small critical feature sizes that are not currently scalable to fabricate with high fidelity at a foundry. Here, we report our novel design methodology that can mix and match fabrication-tolerant unit cells with a subwavelength-critical unit cell to achieve much broader control of the mode distribution across the unit cells of the PhC. In the conventional design approach, all unit cells in the PhC have a highly uniform shape. However, we found that through careful design and a simulated parameter sweep of critical unit cell dimensions, unit cells with differing geometries can be mixed within the same PhC. While this work introduces the mix and match methodology by using two unit cell building blocks, we believe it is possible to include additional unit cell types without significant additional losses.

The design process for the "mix and match" method consists of two primary steps: a "mix" step and a "match" step. In the mix step, we first determine the shape of default unit cells, which typically have large, eas to fabricate features, and we then identify the geometries of the functional unit cells, which are chosen for certain purposes, such as subwavelength mode concentration, opto-mechanics, and polarization control. The "match" step requires matching of the band structures of both types of unit cells in *k*-space through multi-dimensional parameter sweeps.

To confirm our concept, we designed PhCs with a bowtie-shaped functional unit cell as the center cavity unit cell and anti-slot unit cells as the default nanobeam unit cells, as shown in Fig. 1A. An air mode PhC localizes light within the low index air hole region of the unit cells, and subwavelength features further concentrate light, providing two levels of confinement. Three-dimensional finite-difference time-domain (FDTD) simulations were conducted, varying the bowtie unit cell dimensions. For the mix-and-match PhC nanobeam considered, a simulated Q of  $3.6 \times 10^4$  was calculated. Mix-and-match PhCs were fabricated at the CNMS on a silicon-on-insulator wafer using standard electron beam lithography and reactive ion etching protocols (Fig. 1B), and the transmission spectrum was measured experimentally (Fig. 1C).



**Figure 1.** (A) Simulated mode profile of a mix and match PhC with a single bowtie unit cell in the center of a PhC composed of anti-slot unit cells. (B) SEM image of fabricated mix and match PhC. (C) Transmission measurement of mix and match PhC with a loaded  $Q \sim 3 \times 10^3$ .
#### **Carbonized Polymer Structures for Electrochemical Sensing**

Mohammad Aminul Haque<sup>\*</sup>, Nickolay V. Lavrik<sup>†</sup>, Dale K. Hensley<sup>†</sup>, Nicole McFarlane<sup>\*</sup>

\*Department of Electrical Engineering and Computer Science,

The University of Tennessee, Knoxville, TN 37996, USA, mhaque4@vols.utk.edu

<sup>†</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Carbon nanostructures have gained attention in biosensing due to their small size, compatibility with electrochemical detection and high sensitivity. Integration of carbon electrodes with CMOS technology will enable implantability and cost efficiency. Previous work has shown the efficacy of carbon nanostructures as biosensing elements [1]. Carbonization of polymeric precursors normally occurs above 700 °C. However, CMOS chips can withstand up to 525 °C without performance degradation [2]. This project attempts to solve this issue by demonstrating carbonization of polymeric 3D structures for biosensing without exceeding 550 °C. Experimental results show the potential of these carbonized electrodes to be used in building low-cost and monolithic CMOS electrochemical sensors.

The polymer structures were formed using a Photonic Professional GT (Nanoscribe GmbH) 2photon polymerization (2PP) tool. A drop of a diacrylate based photopolymer (IP-S, Nanoscribe GmbH) was first placed on the metalized (100 nm thick titanium) silica substrate and then exposed to a scanning laser beam. However, strong adsorption of the laser beam energy was observed in titanium at 790 nm and generating heat and/or shock waves. To address this, we overcoated titanium with a 50 nm thick gold to increase the substrate reflectivity in the NIR and minimize absorption of the laser beam. The substrates with double layer metallization were successfully used to form polymeric 3D structures. Un-crosslinked IP-S was washed away by SU-8 developer and isopropanol. Plasma sputter etching of gold films was carried out for 75 s in an Oxford Plasma Tech tool to remove gold and expose titanium which can be readily oxidized exposing only the carbonized structures for electrochemical sensing. The first annealing step was an oxidative anneal in pure oxygen at 450  $^{\circ}$ C for 10 minutes to oxidize titanium surface outside the polymeric structures and also to expedite the subsequent carbonization carried out in argon at 500 °C for 15 minutes. Raman spectroscopy has been performed on the annealed nanostructures to verify carbonization using an InVia Raman microscope (Renishaw, Inc.). Electrochemical testing of the carbonized electrodes has been done using a standard 3-electrode electrochemical test setup. Chronoamperomety and impedance measurements were carried out to study electrochemical responses caused by presence of carbonized structures in the presence of  $K_3[Fe(CN)_6]$  which is used as a model electrochemically active agent added to the background electrolyte. Results show that the electrochemical reaction associated with the measured current occurs predominantly on the surface of the carbonized structures while the surrounding area is significantly less electrochemically active due to the presence of an electrically insulating  $TiO_2$  layer.



Figure: (a) Sequential steps for fabricating carbonized polymeric array on a metalized silica wafer. (b) Standard three electrode electrochemical cell to characterize electrochemical activity of carbonized polymer structures. (c) Chronoamperometric response of a sample with carbonized nanostructure and a sample with no carbonized structure in 10 mM  $K_3$ [Fe(CN)<sub>6</sub>] and 3.5 M KCl.

#### **References:**

- A. G. Zestos, C. Yang, C. B. Jacobs, D. Hensley, and B. J. Venton, Carbon nanospikes grown on metal wires as microelectrode sensors for dopamine, Analyst, vol. 140, no. 21, pp. 72837292, 2015..
- [2] S. Sedky, Experimental determination of the maximum post-process annealing temperature for standard CMOS wafers, IEEE Trans. Electron Devices, vol. 48, no. 2, pp. 377385, 2001.

#### First principles analysis of magnetoresistance in tunneling junctions based on 2D materials

J.J. Heath and M.A. Kuroda

Department of Physics, Auburn University

Recently, novel magnetic tunnel junctions (MTJs) have been reported using magnetic insulator Crl<sub>3</sub> as a tunneling barrier between graphene electrodes [Klein et al., Science 360, 1218 (2018)]. Here we use first principles calculations to analyze the complex band structures of CrX<sub>3</sub> (X = I, Br, Cl, F) in several metamagnetic configurations. We find that layer-layer interactions and quantum confinement effects in few layer CrX<sub>3</sub> are significant as they alter the electronic band alignments and consequently change the tunneling current through the junctions. In particular, we produce a comprehensive characterization of ballistic quantum transport through graphene/few layer Crl<sub>3</sub> heterojunctions. We obtain tunneling magnetoresistance values in remarkable agreement with experiments for bilayer and trilayer Crl<sub>3</sub> junctions. We discuss mechanisms to enhance magnetoresistance in these heterostructures that may prove useful in the advancement of spintronics in 2D material systems. This work has been partially supported by the NSF DMR-1848344 grant.

# Effective conversion of two-dimensional transition metal dichalcogenides for atomic alloys and vertical heterojunctions by pulsed laser deposition

Yu-Chuan Lin,<sup>a</sup> Yiling Yu<sup>a</sup> Chenze Liu,<sup>b</sup> Alexander Puretzky,<sup>a</sup> Mina Yoon,<sup>a</sup> Christopher Rouleau,<sup>a</sup> Gyula Eres,<sup>a</sup> Gerd Duscher,<sup>b</sup> Kai Xiao,<sup>a</sup> and David Geohegan<sup>a</sup>

a. Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

b. Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, United States

The non-equilibrium nature of laser-based synthesis and processing provides a promising alternative for the synthesis of van der Waals alloys and heterostructures of 2D transition metal dichalcogenides (TMD). Using chalcogen plasma plumes generated by pulsed excimer laser ablation of solid S, Se, or Te targets in vacuum and low-pressure background gases, the chalcogen composition of existing 2D crystal monolayers or multilayers can be digitally modulated to form new alloys or vertical heterostructures in order to controllably alter and explore their optoelectronic properties. In this talk, starting with existing monolayer and bilayer WS<sub>2</sub> or WSe<sub>2</sub> grown on various substrates (and suspended) we demonstrate the versatility of this approach to adjust the composition and property-tune mixed  $WSe_xWS_{2-x}$  monolayers, and partially convert bilayers to form vertical heterojunctions. In both cases, depending on the global strain inherent in the initial TMD crystal (resulting from the initial growth at elevated temperatures), the plasma-induced exchange of S-Se atoms in the TMD layer creates an additional biaxial strain that can subsequently induce unfavorable cracks or wrinkles in the 2D alloys. However, by choosing a suitable thermal expansion coefficient for the substrate for the initial growth of the 2D crystals, we show that the additional biaxial strain-induced deformation induced by chalcogen replacement can be mediated to allow the 2D crystals to avoid wrinkles and cracks, while retaining their lattice structure. Using this pulsed laser deposition conversion approach, we demonstrate that a homogenous bilayer TMD (e.g., a WS<sub>2</sub> bilayer) grown by chemical vapor deposition (CVD) can be converted into vertical heterojunctions, such as bilayer WSe<sub>2</sub>/WS<sub>2</sub>. The conversion of different bilayer stacking configurations is explored. Photoluminescence and Raman spectroscopy, and scanning transmission electron microscopy confirm that the original bottom layer is nearly intact, even when the top layer is fully converted into another chalcogen composition. Second harmonic generation measurements reveal that the degree of conversion of the top layer depends on the crystallographic stacking between the top and bottom layers. For example, while the 2H-stacking configuration of bilayer  $WS_2$  is found to be the most stable under Se plume irradiation, other stacking configurations are found to have lower thresholds for chalcogen replacement, enabling full conversion of the top WS<sub>2</sub> layer to WSe<sub>2</sub> at 350 °C to form a vertical heterostructure. This approach provides a simple and efficient way to fabricate both 2D alloys and vertical heterostructures.

Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division. Characterization and computational science at CNMS were supported by the Scientific User Facilities Division, BES.

#### Using Nanomaterials and Advanced Imaging to Discern Plant Peptide Signaling and Trafficking Mechanisms

Jessica Morgan<sup>1</sup>, Dian Liu<sup>2</sup>, Joanna Jelenska<sup>3</sup>, Bozhi Tian<sup>1,4</sup>, & Jean Greenberg<sup>1,3</sup>

<sup>1</sup>Biophysical Sciences, <sup>2</sup>Biocheistry and Molecular Biophysics, <sup>3</sup>Molecular Genetics and Cell Biology, and <sup>4</sup>Chemistry University of Chicago, Chicago IL

Plants use intracellular signaling and cell-cell communication to coordinate their growth, development, and to maintain homeostasis. Small secreted peptides, like phytosulfokine (PSK), regulate cellular differentiation, growth, and response to stress. These peptides act via cell surface receptors to trigger short and long range signaling effects. PSK is a sulfated pentapeptide active at nanomolar concentrations through its receptors PSKR1 and PSKR2. Conserved among higher plants, PSK signaling regulates cell growth, cell longevity, differentiation, and stress/infection responses. A key goal in the field is to interrogate signaling mechanisms and outputs in whole plants under physiologically relevant conditions. However there are major experimental limitations to achieving this goal. In particular, sensitive signaling probes are often membrane impermeable and difficult to introduce into intact plant cells. Furthermore, genetically encoded probes require either the time-consuming production of stable transgenic lines or the use of conditions that can be non-physiological. I propose to create nanofiber arrays for the in planta delivery of small molecules. Nanofibers are pointed structures that do not elicit wound responses and can stay embedded in plasma membranes that seal around them. I will use nanofibers together with molecular genetic manipulations in Arabidopsis to study PSK trafficking and signaling.

# High-throughput multifunctional materials characterization with real-time analytics and feedback

Eric S. Muckley<sup>1</sup>, Monojoy Gosami<sup>1,2</sup>, Bobby G. Sumpter<sup>1,2</sup>, Ilia N. Ivanov<sup>1</sup>

<sup>1</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831 <sup>2</sup>Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Rapid design and synthesis of novel materials necessitates the development of specialized tools for high-throughput, multimodal characterization of thin films under a wide range of environmental conditions with dedicated software for analytics and modeling. An integrated multifunctional environmental system (IMES) and associated software workflow at CNMS enables simultaneous testing of electrical, gravimetric, viscoelastic and optical response of thin films to dynamic environments. The system utilizes quartz crystal microbalances with dissipation mode, electrical impedance spectroscopy, and spectroscopic ellipsometry to enable characterization of dielectric response of thin films across a broad (mHz to THz) frequency range. Custom software controls experimental testing conditions and streamlines analysis of material response using a combination of advanced statistics, machine learning, and physical modeling protocols for real-time feedback and automated control of experimental parameters. IMES has been used for characterization of environmental response of a broad range of thin film materials including metal oxides, nanomaterials (carbon nanotubes, graphene, MXenes), conjugated polymers and ionic liquids.

This work was performed at CNMS, a U.S. Department of Energy Office of Science User Facility.

#### Nanobrazing of Nickel Superalloys and Advanced Characterization of Nanobrazing behavior

D. Bridges, B. Nielsen, C. Rouleau, J. Poplawsky, K. More, R. Xu, A. Hu

Department of Mechanical, Aerospace, and Biomedical Engineering, University of Tennessee, Knoxville Center for Nanoscale Material Sciences, Oak Ridge National Laboratory Rolls Royce Corporation

Due to the demand to remove melting point depressants (MPDs) from high temperature brazing materials, nanomaterials are being investigated as a viable alternative. The Gibbs-Thomson effect for NMs provides the necessary melting point depression without the use of problematic MPDs. Additionally, NMs have enhanced diffusion due to the lower diffusion activation energy.

Ni nanoparticles and nanowires were successfully used as a melting point depressant-free filler metal to vacuum braze Inconel 718. Ni nanoparticles of 22, 29, and 42 nm in diameters were synthesized by controlling the reducing agent injection rates and the brazing was carried out at up to 1100 °C with heating rates of 2 - 15 °C/min. Ni nanowires were 213 nm in diameter. Based on the Gibbs-Thomson equation and surface melting models, bonding using Ni nanomaterials occurs due to competing solid-state sintering and surface melting processes. It was found that larger particle size, faster heating rate, and



Fig. 1: (upper left) Brazing heating profile and lap joint configuration (inlet). (bottom left) Ni nanoparticles prior to brazing. (upper right) Strength of Ni nanoparticles and BNi-2 brazing materials (bottom right) Ni nanoparticle pellet after brazing

higher maximum temperature resulted in higher bonding strength due to less grain boundary contamination, smaller crystallite size, and more robust metallurgical bonding, respectively. Using a faster heating rate limits the amount of solid-state nanoparticle-nanoparticle sintering that occurs at lower temperatures. Using EBSD it was found that at higher heating rates the average grain size at the Ni-Inconel interface was greatly decreased, resulting in localized Hall-Petch strengthening where the stress is most concentrated. The maximum bonding strength achieved using Ni nanoparticles is 243 MPa and the maximum strength using Ni nanowires is 293 MPa. Ni nanowires have better wettability and densification behavior compared to Ni nanoparticles.

Using a combination of EDS and APT, we calculated the diffusion coefficients of nanobrazed Inconel 718. It was found that the effective diffusion coefficient for the nanojoints (1.5- $6 \times 10^{-7} \text{ cm}^2/\text{s}$ ) was two orders higher than what was predicted using the bulk effective diffusion coefficient (3.04 x  $10^{-9} \text{ cm}^2/\text{s}$ ) and the Hart equation. Particularly at the nanoscale, grain boundary diffusion and surface diffusion is dominant. High resolution TEM allows us to observe the localized joining behavior of Ni nanowires and provides insight to role of nanoscale surface wetting and diffusion in nanobrazing processes.

### High-Throughput Approach to the Characterization of Two-Dimensional Heterostructures

Adam Pfeifle\*, Panchapakesan Ganesh<sup>+</sup>, and Marcelo A. Kuroda\*

\*Department of Physics, Auburn University, <sup>†</sup>Oak Ridge National Laboratory

Following the isolation of individual graphene layers, several other two-dimensional (2D) materials have been discovered, including boron-nitride (BN), phosphorene, and transition metal dichalcogenides (TMDs) [1]. These 2D materials lack dangling bonds allowing for their seamless stacking to create multilayered heterostructures preserving their sharp interfaces [2]. The physical properties of these multilayer structures, including out-of-plane tunneling rates, may be tailored via composition and stacking order. As thousands of 2D materials have been isolated or predicted to be stable [3], the number of heterostructures that can be formed grows very rapidly. Here we develop methodology to characterize carrier transport in heterostructures formed with 2D materials. Our approach efficiently combines high-throughput first principles calculations and ballistic quantum transport. Our workflow generates vertical heterostructures with low-strain epitaxial mismatches between layers. Their geometries and electronic properties are obtained via first principles calculations within the density functional theory. Ballistic transport methodology based on the Landauer formalism employs representations of the electronic structure formed by projections of pseudo-atomic orbitals for efficient computations [4]. In particular, we analyze the modulation of the tunneling current as a function of strain perpendicular to the basal plane [5,6] for a variety of heterostructures based on graphene electrodes, and boron-nitride or transition metal dichalcogenides as tunneling barriers. Results are rationalized in terms of composition, stacking order and orientations. For the same number of layers, BN junctions exhibit larger tunneling currents than TMDs as its smaller thickness counterweights its larger band gap. We find, however, that the interlayer tunneling current of TMDs are more susceptible to mechanical strain than BN ones. We also compare results for the case of bulk electrodes and discuss virtues and limitations of approximations employed in this description. The results of this work may prove useful to the study of novel physical phenomena such as charge and spin transport in tunneling heterostructures based on 2D materials. This work has been partially supported by the NSF DMR-1848344.

- [1] Novoselov et al., PNAS 102, 10451 (2005)
- [2] Geim and Grigorieva, Nature 499, 419 (2013)
- [3] Mounet et al., Nature Nanotechnology 13, 246 (2018)
- [4] M. Buongiorno-Nardelli et al, Comp. Mat. Sci. 136, 76 (2017)
- [5] Nayak et al., Nature Communications 5, 3731 (2014)
- [6] Fu et al., Appl. Phys. Lett. 103, 183105 (2013)

# Polymeric phosphonium zwitterions: A systematic investigation of the structure-property relationships of novel phosphonium ionomers

Philip J. Scott<sup>a</sup>, Bradley S. Lokitz<sup>b</sup>, and Timothy E. Long<sup>a</sup>

<sup>a</sup> Department of Chemistry, Macromolecules Innovation Institute (MII), Virginia Tech <sup>b</sup>Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory

Ion-containing polymers provide unique material properties, such as ion conductivity and actuation, and complex morphologies and driven by ion association. Applications for these properties include transport membranes, electromechanical devices, and artificial muscles.<sup>1,2</sup> Zwitterionic polymers enable higher charge densities, increased dipole moments, and exhibit

unique self-assembly, antifouling, and solution properties. Phosphonium-containing polymers have shown promising ionic properties, particularly compared to ammonium analogs<sup>3,4</sup>, however there currently lacks any investigation into phosphonium zwitterionic polymers.<sup>5</sup> This is primarily due to synthetic difficulties with polymerization of sensitive trialkylphosphines.

4-(diphenylphosphino)styrene (DPPS) is a commercially available monomer which readily polymerizes via multiple pathways (anionic, RAFT, free radical polymerization) to yield stable triarylphosphine-containing homopolymers and copolymers.<sup>6,7</sup> These polyphosphines prove significantly more stable than their trialkylphosphine analogs which enables a suitable intermediate for



further modification. Subsequent alkylation of these phosphine moieties yields phosphonium ions and zwitterions pendant to the polymer backbone. Comonomer and alkylating agent selection enable a wide range of tunability in polymer and ion structure. Through this novel synthetic pathway, this work enables an ideal platform for a systematic study of the structure-property relationships for polymers containing phosphine, phosphonium ion, and novel phosphonium-sulfonate zwitterionic functionalities.

#### References

- 1. Green, M. D., Wang, D., Hemp, S. T., Choi, J.-H., Winey, K. I., Heflin, J. R., Long, T. E. *Polymer (Guildf).*, 2012, **53**, 3677–3686.
- 2. Gao, R., Wang, D., Heflin, J. R., Long, T. E. J. Mater. Chem., 2012, 22, 13473–13476.
- 3. Hemp, S. T., Zhang, M., Allen, M. H., Cheng, S., Moore, R. B., Long, T. E. *Macromol. Chem. Phys.*, 2013, **214**, 2099–2107.
- 4. Chen, M., White, B. T., Kasprzak, C. R., Long, T. E. Eur. Polym. J., 2018, 108, 28–37.
- 5. Laschewsky, A. Polymers (Basel)., 2014, 6, 1544.
- 6. Jangu, C., Schultz, A. R., Wall, C. E., Esker, A. R., Long, T. E. *Macromol. Rapid Commun.*, 2016, n/a-n/a.
- 7. Schultz, A. R., Chen, M., Fahs, G. B., Moore, R. B., Long, T. E. *Polym. Int.*, 2017, **66**, 52–58.

#### Carbon nanomaterial enabled ultra conductive Cu composites

Tolga Aytug, Lydia Skolrood, Kai Li, Ilia Ivanov, Mina Yoon, Michael McGuire, Andrew Lupini, Tsarafidy Raminosoa, Chengyun Hua, Annie Stevens, and Burak Ozpineci

Oak Ridge National Laboratory, Oak Ridge, TN

Growing demand for electrical energy and increasing need for high power grid systems necessitates development of new conductors for enhanced electrical and thermal conductivity. The power losses associated with the electrical resistance of Cu adversely impact the efficiency and performance of all electric devices. Ballistic electrical transport in carbon nanotubes (CNTs) is expected to improve the conductivity of the Cu matrix with additional CNT-enabled benefits that can enable low-weight, flexibility, and better thermal management. By using scalable, costeffective, and commercially viable processing methods, we demonstrate a novel technological platform to produce high-performance conductors that incorporates CNTs into the Cu matrix ultra-conductive metal composites (UCC), which promise significant technological and economic impact in all energy sectors, ranging from electrical vehicles to power grid. Our technology platform is concentrated on Cu tapes and involves processes from production of stable CNT dispersions, techniques to deposit shear induced aligned CNT coatings along the direction of the current flow, post thermal treatment procedures, and homogeneous deposition of metal overlayers onto CNT coated tapes. Here, we demonstrate that the prototype Cu-CNT composites exhibit improved electrical conductivity (by 5-7%) as well as higher current carrying capacity than the reference pure Cu. In addition, thermal conducting properties and the impact of using UCCs on the power density of electric motors will be discussed.

# Printed flexible silver sensors with electrodeposited TiO<sub>2</sub> nanowires for room temperature CO<sub>2</sub> gas sensing

Lingyue Zhang<sup>1</sup>, Yongchao Yu<sup>1</sup>, Curtis Hill<sup>2</sup>, Zili Wu<sup>3</sup>, \*Anming Hu<sup>1</sup>

<sup>1</sup>Department of Mechanical, Aerospace and Biomedical Engineering, University of Tennessee, Knoxville, TN37996,

USA

<sup>2</sup>National Aeronautics and Space Administration, 300 E St SW, Washington, DC 20546, USA <sup>3</sup>Center of Nanophase Materials Science, Oak Ridge National Lab Oak ridge, TN 37831-6061 USA

\*E-mail: ahu3@utk.edu. Phone: 865-974-5993

#### ABSTRACT:

The concentration of CO<sub>2</sub> gas is important to the health of astronauts and pilots; it is also related with global climatic change on large scale. The detection of CO<sub>2</sub> gas concentration is necessary and important. Hence, CO<sub>2</sub> sensors needs to be developed. In this work, we report a flexible silver electrode sensor coating with TiO<sub>2</sub> nanowires works under room temperature. A silver electrode sensor was first printed on polyimide using a VOLTERA printer (Fig.1a, b). TiO<sub>2</sub> nanowire was deposited to silver electrodes by an electro-deposition method. The silver electrode sensor works at room temperature without additional heating. As Fig 1(c) shows, the lowest carbon dioxide concentration detection limit for the sensor is 78 ppm, which is much lower than the CO<sub>2</sub> concentration in regular environment. In addition, the response time is around 60s. This indicates the significant progress compared to conventional metal oxides CO<sub>2</sub> sensors where a high working temperature (around 250-450°C) is usually required **[1-4]**.



Fig. 1 (a) The VOLTERA printer machine (b) a silver electrode sensor fabricated on polymer surface, (c) Variation of the resistance for lower limit test (d) sensor response time test result

Reference:

[1] Y.M. Hunge, A.A. Yadav, S.B. Kulkarni, V.L. Mathe, Actuators B: Chemical 274 (2018): 1-9.

[2] Sumangala, T. P., Isabelle, P., Lionel, P., Yohann, T., Corine, B., & Venkataramani, N., et al. (2018). *Ceramics International*, S0272884218318108-.

[3] Shimizu, Youichi & Yamashita, Nami. (2000). Sensors and Actuators B Chemical. 64. 10.1016/S0925-4005(99)00491-8.

[4] Struzik, M., Garbayo, I., Pfenninger, R., & Rupp, J. L. (2018). Advanced Materials, 30(44), 1804098.

## Spatially extended gap states induced up-conversion photoluminescence Xixiang Zhu University of Tennessee

Quasi-2D Ruddlesden-Poper perovskites have demonstrated interesting optical properties in down-conversion regime. In our work, we found the infrared-to-visible up-conversion photoluminescence (PL) peaked at 521 nm occurring in quasi-2D perovskite [(PEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>Br<sub>16</sub> with n = 5] films by using infrared CW 980 nm laser beam to excite the gap states at room temperature. With increasing the CW laser intensity, the up-conversion PL intensity is almost quadratically increased with the power dependence factor of 1.7. This presents an evidence to show that the upconversion PL is essentially a two-photon process occurring through the gap states. Furthermore, the two-photon up-conversion PL shows a strong dependence of n value in the 2D perovskites. As lowering the n value, the up-conversion PL signal is dramatically decreased, becoming negligible when the n value is lower than 3. Simultaneously, the gap states are non-detectable in optical absorption when n < 3. This verifies that the gap states are indeed responsible for generating the two-photon upconversion PL. Moreover, it was found that the two-photon up-conversion PL shows an appreciable dependence of magnetic field through spin mixing mechanism. This provides direct evidence that the gap states are essentially spatially extended states to enhance two-photon up-conversion PL in 2D perovskites.

#### Converting lignin into value-added polymer materials

Mengmeng Cui<sup>†</sup>, Logan T. Kearney<sup>†</sup>, Ngoc A. Nguyen<sup>†</sup>, Peter V. Bonnesen<sup>‡</sup>, Kunlun Hong<sup>‡</sup>, David Uhrig<sup>‡</sup>, Jong K. Keum<sup>§</sup>, and Amit K. Naskar<sup>†</sup>

#### <sup>†</sup>Carbon and Composite Group, Materials Science and Technology Division, <sup>‡</sup>Center for Nanophase Materials Science, §Neutron Science Directorate, Oak Ridge National Laboratory

Biomass offers the most practicable solution to the rapidly rising global population, as well as climate change, by replacing the petroleum chemicals during the manufacture of polymer materials. However, converting lignin, the second-most-abundant terrestrial polymer, into well-defined compounds is often challenged by structural complexation and inorganic contamination induced by the pulping process. Understanding the lignin chemical structure and optimizing the designed material property requires the ability of characterization under molecular scale, architecture scale and further phase-separation scale.

Our research focuses on developing individual lignin component, but also on further applications in enduse materials. First, instead of breaking down lignin into small molecules, we extracted a uniform and rigid oligomer from lignin waste stream. To fully understand the effect of extraction, we developed a new method to characterize lignin compositions by combining several nuclear magnetic resonance (NMR) techniques. A multifunctional polyphenol oligomer containing carboxylic acid, alcohol and phenol groups which is highly reactive and brings stiffness into material matrix, was identified after extraction. The distinct feature of extracted lignin (ACN-lignin) lies in its uniformity and high glass transition temperature ( $T_g$ ). Second, tough and self-healing elastomers are economically prepared from this oligomer by a reaction with epoxyterminated polyethylene glycol, without needing any solvent. Specifically, the polyaromatic backbone's rigidity enhances the elastomer's toughness, and the multiple polar substituents form a network of hydrogen bonding that heals the elastomer.

Third, wrapping a three-dimensional (3D) object with a two-dimensional (2D) sheet is not uncommon, but when the sheet is bestowed with strong interfacial activities, interesting phenomena will occur. Amphiphilic lignin macromolecules form a scalable thin surfactant sheet with a thickness of ~10 nm at an oil/water interface through an interfacial jamming process that marks three distinct stages of interfacial behavior. The surfactant sheet wraps, traps, and stabilizes both oil and water droplets in non-equilibrium morphologies, and promptly reassembles into adapted morphologies upon environmental stimulus. Beyond preserving exotic morphologies, the surfactant sheet can also actively participate in the morphology evolution by driving interfacial instability around the wrapped content, leading to novel morphologies as well as many potential applications.

Mengmeng Cui et.al., "Recycling of a waste-stream lignin into a tough, self-healing elastomer", ACS Macro Letters, 7(11), 1328-1332, 2018.

Mengmeng Cui et.al., "A cast net thrown onto interface: wrapping 3D objects with a large-scale amphiphilic sheet", submitted for publication.

# Interplay of the polydisperse set of crowders in compacting Escherichia coli nucleoid

# Da Yang<sup>1</sup>, Jaana Männik<sup>2</sup>, Scott T. Retterer<sup>3</sup>, Jaan Männik<sup>1</sup>

 <sup>1</sup> Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996, USA
<sup>2</sup> Department of Biochemistry, and Cellular and Molecular Biology, The University of Tennessee, Knoxville, Tennessee 37996, USA
<sup>3</sup> Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

DNA binding proteins, supercoiling, macromolecular crowders, and transient DNA attachments to the cell membrane have all been implicated in organizing bacterial chromosomal DNA. However, it is unclear what role these factors play in forming a distinct organelle-like entity in the cell, the nucleoid.

Here, we report on two sets of microfluidic experiments where we quantitatively study the role of molecular crowders in determining the size of the *Escherichia coli* nucleoid in live cells. In the first set of measurements, we vary the concentration of cytosolic crowders by changing the osmolality of the growth media. In the second set of measurements, we squeeze individual cells in a device, which we refer to as the micro-anvil, for the same effect. The two types of measurements show that for small increases in the crowder concentration, the nucleoid behaves as a linear anisotropic spring, which has high compressibility along the long axes of the cell. However, as the crowder concentration increases above 30% from the physiological level, the compressibility of the nucleoid decreases significantly, akin to a compression spring. These mechanical properties of the nucleoid hold true for two significantly different growth rates, where a different ratio of proteins to ribosome-based cytosolic crowders is expected to be present.

The above experimental findings match well with the results from our coarse-grained Brownian dynamics simulations. Altogether, our results support the idea that both cytosolic proteins and stable RNA species are the main factors compacting the bacterial DNA to a nucleoid.

#### The Influence of Side-chain Length on Backbone Rigidity for Conjugated Polymers

Zhiqiang Cao $^{\rm a},$  Song Zhang $^{\rm a},$  Luke Galuska $^{\rm a},$  Tianyu Li $^{\rm b},$  Kunlun Hong $^{\rm b},$  and Xiaodan Gu $^{\rm a}$ 

<sup>a</sup> School of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg

<sup>b</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge

Although huge progress has been made to optimize the optical and electronic properties of conjugated polymers (CPs), fully elucidating the origin of the increase in optical and electronic properties of CPs is still much-needed. Notably, the backbone rigidity of these CPs—which determines the delocalized electron

cloud from its pi-conjugation—is critical for the materials' property. However, it remains a challenge to experimentally characterize conjugated backbone rigidity and relate these to the fundamental optical and electronic properties (electronic coupling, charge transport, etc.). To fill this underexplored area, we utilized chemical deuteration and neutron scattering techniques to quantify the chain rigidity then elucidate the role of the chain rigidity plays for CPs.

The length of the conjugated polymer side chain plays an important role in the ultimate performance of conjugated polymeric devices, considering that longer side chains can contribute significant steric effects on the dihedral potentials, allowing kinks to happen in the backbone, thus reduce the persistence length. In order to study the effect length of the alkyl sidechain on the backbone rigidity for Poly(3-alkylthiophenes) (P3ATs), we synthesized deuterated polythiophene with various length of side-chains to understand the influence the sidechain length on the polymer backbone conformation as shown in **Figure 1**. Selective deuteration of



**Figure 1:** Two key techniques used to probe the backbone rigidity: (a) synthesis of P3ATs with deuterated side-chains, and (b) use of contrast matching technique to conceal the sidechain in deuterated solvents as illustrated by the same red color between solvents and sidechains in the cartoon.

polymeric side chains and contrast matching with solvents provides a unique way to hide the scattering signal from the long alkyl side-chains and probe only the scattering from the backbone. As shown in **Figure 1**, upon deuteration, the local scattering length density for the side chains increases, which can be matched by a deuterated solvent mixture. The neutron scattering will be performed on empty banjo quartz cell, mixture solvents in sample cell, the CPs dissolved in solvent in sample cells. The scattering will be performed at several sample to detector distance to cover a large enough scattering vector for easier data fitting. A typical Q range we would like to achieve is around 0.002 A<sup>-1</sup> to 0.3A<sup>-1</sup>. Through modelling the scattering data using various models (Worm-like chain model or Debye chain model<sup>1,2</sup>), the "naked" backbone rigidity can be extracted by comparing radius of gyration (R<sub>g</sub>) and the molecular weight. The resultant persistence length (L<sub>p</sub>) for CPs with various sidechains will be rationalized with respect to various sidechains.

- (1) McCulloch, B. et. al. Polymer Chain Shape of Poly(3-Alkylthiophenes) in Solution Using Small-Angle Neutron Scattering. *Macromolecules* **2013**, *46* (5), 1899–1907.
- (2) Chen, W.-R. et. al. Incorporating Intermicellar Interactions in the Fitting of SANS Data from Cationic Wormlike Micelles. *Langmuir* **2006**, *22* (15), 6539–6548.

### Multimodal detection-enabled analysis of complex protein -enzyme mixtures

<u>A.Vass<sup>1</sup>, G. Papoutsidakis<sup>2</sup>,</u> I. Sukuba<sup>3</sup>, M. Tatarko<sup>3</sup>, E. Muckley<sup>4</sup>, M. Goswami<sup>4</sup>, T. Hianik<sup>3</sup>, Z. Keresztes<sup>1</sup>, V. Buckin<sup>2</sup>, B. Sumpter<sup>4</sup>, I. Ivanov<sup>4</sup>

<sup>1</sup>Research Centre for Natural Sciences, Functional Interfaces Research Group, Budapest, Hungry <sup>2</sup>University College Dublin, School of Chemistry, Science Centre Belfield Dublin, Ireland <sup>3</sup>Department of Biophysics and Chemical Physics, Faculty of Mathematics and Physics, Comenius University, Bratislava, Slovak Republic

<sup>4</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, USA

## Abstract

A unique mixture composed of 13 percent of solids, with fat- and water-soluble vitamins (including riboflavin B2), proteins, carbohydrates and minerals (magnesium, calcium, potassium, phosphorous) is natural, and nutritionally balanced food, which is milk. Its quality became an important issue due to diversification of the sources of raw product and subsequent advert changes in the quality of milk and milk-derived products. There are just a handful of high cost and time-consuming analytical techniques to analyze milk quality which include viscoelastic properties as well as enzymatic content which are unsuitable for continuous monitoring of milk quality ("from the farm to the table").

The goal of our project is to develop a low-cost platform for the assessment of milk quality using multimodal detection, which is based on quartz crystal microbalance, which we use in dissipation mode to access broad range of overtones along with the fundamental.

We will share our recent research on characterization of viscoelastic properties of milk and detection of low concertation of enzymes. We will also discuss recent development of sensor workflow to include Molecular Dynamic simulations of environment-controlled protein dynamics.

## Acknowledgement

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. AV, GP, IS, MT, TH, ZK, VB acknowledge funding e funding from the European Union's Horizon 2020 research and innovation program under the Marie Sklodowska-Curie grant agreement No. 690898