2018 CNMS USER MEETING Agenda and Abstracts





Cover Image

User project highlights sent to DOE in 2017 From Left to Right

Top row:

<u>"Understanding the Nanoscale Behavior of Iron Anodes for Rechargeable Iron-Air</u> <u>Batteries</u>" Weinrich *et al., Nano Energy* **41**, 706 (2017).

<u>"Identification of Predominant Active Sites in a Platinum Group Metal(PGM)-free</u> <u>Catalyst for Polymer Electrolyte Fuels Cells</u>" Chung *et al., Science* **357**, 479 (2017).

<u>"On-Demand 3D Nanoplasmonics"</u> Winkler *et al., ACS Appl. Mater. Interfaces* **9**, 8233 (2017).

<u>"New Method to Detect Spin Current in Topological Insulators"</u> Hus *et al., Phys. Rev. Lett.* **119**, 137202 (2017).

<u>"Tuning Conducting Polymer Crystallinity with Deuteration"</u> Jakowski *et al., J. Chem. Phys. Lett.* **8**, 4333 (2017).

<u>"Nanoporous Atomically Thin Graphene Membranes for Desalting and Dialysis Applications</u>" Kidambi *et al., Adv. Mater.* **29**, 1700277 (2017).

Middle row:

<u>"Edge States and Topological Phase Transitions in Chain of Dielectric Nanoparticles"</u> Kruk *et al., Small* **13**, 1603190 (2017).

<u>"A Predictive Model to Guide Experimental Identification of Stacking in 2-D</u> <u>Materials</u>" Liang *et al., Nanoscale* **9**, 15340 (2017).

<u>"Building Wide Gap Graphene Nanoribbons"</u> Ma *et al., Nature Communications* **8**, 14815 (2017).

<u>"Theory Helps Raman Spectroscopy "see" the Pairing Mechanism in Iron-Based</u> <u>Superconductors"</u> Maiti *et al., Phys. Rev. Lett.* **117**, 257001 (2016).

<u>"Understanding Self-Propelled Droplet Jumping to Enhance Condensation Heat</u> <u>Transfer</u>" Mulroe *et al., ACS Nano* **11**, 8499 (2017), Murphy *et al., ACS Appl. Mater. Interfaces* **9**, 24308 (2017).

<u>"Soft Mechanics in a Hard Material"</u> Nicholl *et al., Phys. Rev. Lett.* **118**, 266101 (2017).

Bottom row:

<u>"Screw Dislocations Determine Nonlinear Optical Properties of WSe₂ Nanoplates"</u> Shearer *et al., J. Am. Chem. Soc.* **139**, 3496 (2017).

<u>"Carbon Nanotubes Enable Orders of Magnitude More Active Fischer-Tropsch</u> <u>Synthesis</u>" Sims *et al., Carbon* **121**, 274 (2017).

<u>"Local Ion Beam Modification of materials Enables Atomically Thin Circuits"</u> Standord *et al., Adv. Funct. Mater.* **27**, 1702829 (2017).

<u>"Neutron Results on Stretched Polymers Question the Classical Model of Polymer</u> <u>Flow"</u> Wang *et al., Phys. Rev. X* **7**, 031003 (2017).

<u>"Tuning Polymer Molecule Architecture for Targeted Self-Organization"</u> Ahn *et al., Nanoscale* **9**, 7071 (2017).

<u>"Electronic Structure at Interfaces Promotes Good Vibrations for Heat Dissipation"</u> Yan *et al., ACS Appl. Mater. Interfaces* **9**, 33299 (2016).

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*Denotes Student Poster	

NOTE:

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



CENTER FOR NANOPHASE MATERIALS SCIENCES

3:00p	Monday, August 13	Meeting Opens		
4 - 6 p	Poster Session and Student Poster Competition - SNS Atrium			
7:30a	Tuesday, August 14 Posters available for viewing			
8:30	WELCOME AND ANNOUNCEMENTS- Iran Thomas Auditorium, SNS Hans Christen, CNMS Director			
9:00	Plenary Lecture I "Direct Electrodeposition of Nanostructured High-Performance Li-ion Battery Electrodes" Paul Braun, University of Illinois, Urbana-Champaign			
9:50	Break			
	TRACK A: Room C-156 Creating the Next Generation of Materials Chairs: Ben Lawrie, Adam Moule Nina Balke, Scott Retterer		TRACK B: SNS Auditorium Observing Dynamic Processes with In-Situ and Operando Techniques Chairs: Zach Hood, Josh Agar An-Ping Li, Stephen Jesse	
10:00	INVITED: Christine Luscombe (U. Washington) Designing High Ductility Polymers for Stretchable Electronics		INVITED: Katherine Jungjohann (Sandia National Laboratory) Nanoscale Solid-Liquid Interfacial Mechanisms in Li-Ion Batteries and Corrosion	
10:40	Chanaka Kumara (Oak Ridge National Laboratory) Metallic Nanoparticles Enabled Nano and Micro-Scale Tribofilm Formation		Josh Kacher (Georgia Tech) Investigating Local Corrosion Processes in Real and Diffraction Space by in situ Liquid Cell Transmission Electron Microscopy	
11:05	Saptarshi Chakraborty (Clemson U.) Absolute Molecular Weight and Structural Analysis of Low Polydispersity Lignin through Small Angle Neutron Scattering		Ryan Bock (Amedica Corporation) Analytical Electron Microscopy Study of the Interface between Mineralized Extracellular Polymer and Osteogenic Si-Y-O-N Film Present at Annealed Silicon Nitride Surfaces	
11:30	Lunch on your own; Posters available for viewing			
1:30p	INVITED: Andrei Fedorov (Georgia Tech) Focused Electron Beam Direct-Write Processing (FEBIP) of 3D Composite Nanostructures and 2D Electronic Materials		INVITED: Robert Bartynski (Rutgers U.) Organic Molecular Self-Assembly at Metal Surfaces: From Ordered Metastable Phases to Covalently Bonded 2D Networks	
2:10	Tom Berlijn (Oak Ridge National Laboratory) On the Nature of Localization in Ti doped Si		Joshua Agar (Lehigh U.) Revealing Ferroelectric Switching Character Using Deep Recurrent Neural Networks	
2:35	Eric Young (Michigan State U.) Engineering a Protein-based Nanoma	nterial	Arashdeep Thind (Washington U.) Atomic Structure and Electrical Activity of Planar Faults in Lead-halide Perovskites	
3:00	Break			
3:30	User Group Town Hall Meeting - Iran Thomas Auditorium, SNS including announcement of Student Poster winners			
4:15	Plenary Lecture II "Controlled Synthesis of 2D Covalent Organic Frameworks" William Dichtel, Northwestern University			
5:00	Adjourn			

Agenda

Center for Nanophase Materials Sciences 2018 User Meeting

Poster Session

*denotes Student Poster

Monday, August 13, 2018 4:00 – 6:00p

Poster Locations

Main Hallway: 01-52 Posters will also be available for viewing on Tuesday, August 14

01. Semiconductor heterojunctions made by g-C₃N₄ and N-doped Sr₂Nb₂O₇ for enhanced photocatalytic H₂ production

Shiba P. Adhikari,^{1,2} Zachary D. Hood,^{3,4} and Abdou Lachgar^{1,2} ¹Department of Chemistry, Wake Forest University, Winston-Salem, North Carolina 27109 ²Center for Energy, Environment, and Sustainability (CEES), Wake Forest University, Winston-Salem, North Carolina 27109 ³School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332 ⁴Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

02. Giant magnetic response of a two-dimensional antiferromagnet

Lin Hao,¹ D. Meyers,² Hidemaro Suwa,¹ Junyi Yang,¹ Clayton Frederick,¹ Tamene R. Dasa,³ Haixuan Xu,³ Cristian D. Batista,^{1,4} M. P. M. Dean,² Jian Liu¹ ¹Department of Physics and Astronomy, University of Tennessee, Knoxville ²Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory ³Department of Materials Science, University of Tennessee, Knoxville, Tennessee ⁴Quantum Condensed Matter Division and Shull-Wollan Center, Oak Ridge National Laboratory

03. Interactions between Transition Metal Clusters and Graphene using First Principles Calculations Jonathan J. Heath & Marcelo A. Kuroda Auburn University, Auburn, AL 36849

04. Non-Transition-Metal Catalytic System based on Al-Doped Graphene for N2 Reduction to NH3

Yong-Hui Tian,¹ Shuangli Hu,¹ Xiaolan Sheng,¹ Yixiang Duang,¹ Jacek Jakowski,² Bobby G. Sumpter,² Jingsong Huang² ¹College of Life Sciences, Sichuan University, Chengdu, Sichuan 610064, PR China

²Center for Nanophase Materials Sciences and Computational Sciences & Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

05. Characterization of Carbon Nanostructures in Cu Covetics by APT, HIM, and STEM Beihai Ma,¹ Uthamalingam (Balu) Balachandran,¹ Tae H. Lee,¹ Steve E. Dorris,¹ Jianguo Wen,² Jie Wang,² Yuzi Liu,² Jonathan D. Poplawsky,³ and Adam J. Rondinone³ ¹Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439 ²Nanoscience and Technology Division, Argonne National Laboratory, Argonne, IL 60439 ³Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

06. Investigating Helium Bubble Formation in NiFe_x Alloys using Electron Energy Loss Spectroscopy Xing Wang,¹ Ke Jin,¹ Hongbin Bei,¹ William Weber,^{1,2} Yanwen Zhang,^{1,2} and Karren L. More,¹ ¹Oak Ridge National Laboratory, Oak Ridge, TN 37831 ²University of Tennessee-Knoxville, TN

***Molecular Dynamics Simulations of Liquid Metal Assembly at the Nanoscale** Ryan H. Allaire,^{1,2} Reece Emery,³ Lou Kondic,² Phillip Rack,^{1,3} Jason Fowlkes,^{1,3} David Garfinkel,^{1,3} Miguel Fuentes-Cabrera¹
¹Center for Nanophase Materials Sciences, Oak Ridge National Laboratory
²New Jersey Institute of Technology, Department of Mathematical Sciences
³The University of Tennessee, Materials Science and Engineering ***Agent-based modeling simulation of black soldier fly larvae aggregation** Ethan Brady,¹ Eagle Yuan,¹ Olga Shishkov,² Jan-Michael Carrillo,¹ David L. Hu,^{2,3} Miguel Fuentes-

Cabrera¹ ¹Center for Nanophase Materials Sciences, Oak Ridge National Laboratory ²Georgia Institute of Technology, Schools of Mechanical Engineering and Biology³

09. *Synthesis and Characterization of Functionalized Tire Carbon as Catalysts for Conversion of High Fatty Acids to Biofuel

Samuel F. Evans,^{1,2} Zachary D. Hood,^{3,4,} Shiba P. Adhikari,⁷ Legna Figueroa-Cosme,⁴ Hui Wang,⁵ Yunchao Li,^{1,2} Amit K. Naskar,^{2,6} Younan Xia,⁴ Marcus W. Wright,⁷ Miaofang Chi,³ Abdou Lachgar,⁷ M. Parans Paranthaman,^{1,2}

¹Chemical Sciences Division, Oak Ridge National Lab, Oak Ridge, TN 37831

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⁵Department of Mechanical Engineering, University of Louisville, Louisville, KY 40292

⁶Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830

⁷Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109

10. *Contact engineering of 2D PdSe₂ with interfacial metallic Pd₁₇Se₁₅ achieved by phase transformation

Akinola D. Oyedele,^{1,2} Shize Yang,³ Tianli Feng,^{3,4} Yiyi Gu,² Alex Strasser,² Alexander A Puretzky,² Dayrl Briggs,² Amanda Haglund,⁵ Christopher M Rouleau,² Matthew F. Chisholm,³ Raymond R. Unocic,² David Mandrus,^{3,5} David B. Geohegan,² Sokrates T Pantelides,^{3,4} Kai Xiao² ¹Bredesen Center for Interdisciplinary and Graduate Education, University of Tennessee, Knoxville, TN 37996 ²Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831 ³Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830 ⁴Department of Physics and Astronomy and Department of Electrical Engineering and Computer Science, Vanderbilt University

⁵Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996

11. *Carbonized 3D Structures for Integration on CMOS Readout Circuitry

Samira Shamsir,¹ Mohammad Aminul Haque,¹ Nickolay V. Lavrik,² Dale K. Hensley,² Syed K. Islam,² Nicole McFarlane¹

¹Department of Electrical Engineering and Computer Science, The University of Tennessee, Knoxville, TN 37996 ²Oak Ridge National Laboratory, Oak Ridge, TN 37831

12. *First-principles study of low-frequency Raman-active modes in Ag intercalated MoS2

Natalya Sheremetyeva,¹ Drake Niedzielski,¹ Anna Domask,² Suzanne Mohney,² and Vincent Meunier¹ ¹Department of Physics, Rensselaer Polytechnic Institute,110 8thSt, Troy, NY 12180, USA ²Materials Science and Engineering, Pennsylvania State University, Old Main, State College, PA 16801, USA

13. *Crystallization and chemical analysis of Li_{7-3x}Al_xLa₃Zr₂O₁₂ thin films deposited by a novel sol-gelderived wet chemistry method

Y. Zhu,¹ Z.D. Hood,¹ L.J. Miara,³ K. Kim,¹ J.C. Gonzalez-Rosillo,¹ J.L.M. Rupp,^{1,2} ¹Department of Materials Science and Engineering, Massachusetts Institute of Technology ²Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology ³Advanced Materials Lab, Samsung Research America, United States

14. **Optimizing polymer components in capacitors and batteries**

Jihua Chen

Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, TN 37831

15. Facile Fabrication of Large-Area Atomically Thin Membranes by Bottom-Up Synthesis of Nanoporous Monolaver Graphene

Piran R. Kidambi,^{1,2} Giang D. Nguyen,³ Sui Zhang,^{1,6} Qu Chen,⁴ Jing Kong,⁵ Jamie Warner,⁴ and An-Ping Li,³ Rohit Karnik¹

¹Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

²Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN 37235-1826

³Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

⁴Department of Materials, University of Oxford, Oxford OX1 3PH, UK

⁵Department of Electrical Engineering and Computer Science and Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA 02139

⁶Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117582, Singapore

16. *Phospholipid Bilayer Softening in the Presence of Hydrophobic Gold Nanoparticle Inclusions

Saptarshi Chakraborty,¹ Michihiro Nagao,² Christopher L. Kitchens¹ ¹Clemson University, Chemical Engineering Department, Clemson, SC ²National Institute of Standards and Technology, Gaithersburg, MD

17. *Absolute Molecular Weight and Structural Analysis of Low Polydispersity Lignin through Small **Angle Neutron Scattering**

Saptarshi Chakraborty, Christopher Kitchens Department of Chemical and Biomolecular Engineering, Clemson University

Ligand Softness Affects Catalytic Activity and Reusability of pH Responsive Colloidal Gold 18. Nanoparticle

Saptarshi Chakraborty,¹ Elizabeth Kelley,² Christopher L. Kitchens¹ ¹Department of Chemical and Biomolecular Engineering, Clemson University ²NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg

19. **PEG-based Polyampholytes as Cryoprotectants**

Aaron A. Burkey, Neda Ghousifam, Christopher L. Riley, Taylor A. Hatridge, Marissa Nichole Rylander, Nathaniel A. Lvnd

McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, TX

20. *Numerical Studies of Competing Phases of Matter in Hubbard Model and Beyond

Hanna Terletska,¹ Joseph Paki,² Emanuel Gull,² Thomas Maier³ ¹Department of Physics and Astronomy, Middle Tennessee State University ²Department of Physics, University of Michigan ³Oak Ridge National Laboratory, Oak Ridge, TN

21. Mechanically Robust Organic Photovoltaics Using Thiol-Ene Interpenetrating Networks

Jorge Mok, Zhiqi Hu, Chanxu Sun, Joshua Jackson, Rodrigo Munoz, and Rafael Verduzco Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX

*In Situ Characterization of Electric-field Induced Migration and Orientation of Species in 22. **Electroactive Polymeric Systems**

Tayler S. Hebner,^{1,2} Jason W. Dugger,¹ Brad S. Lokitz¹ ¹Center for Nanophase Materials Sciences, Oak Ridge National Laboratory ²University of Minnesota Duluth, Duluth, MN

23. *Using Broadband Dielectric Spectroscopy to probe chain dynamics in 3-Miktoarm Poly(Styrene-Isoprene₂) Star Copolymers

Thomas Kinsey,¹ Emmanuel Mapesa,¹ Weiyu Wang,² Kunlun Hong,² and Joshua Sangoro¹ ¹Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville ²Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

24. *Mechanistic Insight into the Conversion of Ethanol and Acetaldehyde to 1,3-Butadiene over Supported ZrO2/SiO2 Catalysts

Benjamin M. Moskowitz,¹ Felipe Polo-Garzon,² Si Luo,² Zili Wub,³ and Israel E. Wachs¹ ¹Department of Chemical and Biomolecular Engineering, Lehigh University, B336 Iacocca Hall, 111 Research Drive, Bethlehem, PA 18015, USA ²Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA ³Center for Nanophase Material Science, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA

- 25. *Computer-controlled high-throughput functional characterization of thin films Eric S. Muckley,¹ Rajeev Kumar,^{1,2} Bobby G. Sumpter,^{1,2} Ilia N. Ivanov¹ ¹Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831 ²Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
- 26. *Active mixing in aggregations of black soldier fly larvae Olga Shishkov,¹ Miguel A. Fuentes-Cabrera,³ David L. Hu^{1,2} ¹Georgia Institute of Technology, Schools of Mechanical Engineering and Biology² ³Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

27. *Development of an Integrated Scanning Photocurrent Microscopy System for Multifaceted Nanomaterial Characterization

Alex Strasser,^{1,2} Christopher Rouleau,² Akinola Oyedele,² Kai Xiao,² David Geohegan² ¹Department of Chemical Engineering, Texas A&M University ²Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

28. *Strongly Cross--Correlated Optical Phonons in Hexagonal Boron Nitride Defects

Matthew Feldman,^{1,2} Alex Puretzky,² David Goehegan,² Richard Haglund,¹ Ben Lawrie¹ ¹Department of Physics & Astronomy, Vanderbilt University ²Oak Ridge National Laboratory

29. *Atomic Structure and Electrical Activity of Planar Faults in Lead-halide Perovskites

Arashdeep Singh Thind,¹ Guangfu Luo,² Jordan A. Hachtel,³ Mariia Goriacheva,⁴ Sung Beom Cho,² Yangchuan Xing,⁴ Albina Y. Borisevich,⁵ Juan Carlos Idrobo,³ and Rohan Mishra^{2,1} ¹Institute of Materials Science & Engineering, Washington University in St. Louis, St. Louis MO, USA ²Department of Mechanical Engineering & Materials Science, Washington University in St. Louis, St. Louis, St. Louis, MO, USA ³Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA ⁴Department of Chemical Engineering, University of Missouri, Columbia, MO, USA ⁵Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA

30. High-Contrast Resonance Excitation and Identification in Photonic Crystal Nanobeams F.O. Afzal, S. I. Halimi, and S. M. Weiss

Vanderbilt University

31. Ultrastructure and Enzymatic Hydrolysis of Deuterated Switchgrass

Samarthya Bhagia,¹ Xianzhi Meng,¹ Barbara R. Evans,² John R. Dunlap,³ Garima Bali,⁴ Jihua Chen⁵ Kimberly Shawn Reeves,⁵ Hoi Chun Ho,⁵ Brian H. Davison,⁶ Yunqiao Pu,⁷ and Arthur J. Ragauskas^{1,6-8} ¹Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN 37996 ²Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831 ³Advanced Miergeony and Imaging Centre, University of Tennessee, Knoxville, TN 27000

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 ⁷Joint Institute of Biological Sciences, Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
 ⁸Center for Renewable Carbon, Department of Forestry, Wildlife, and Fisheries, University of Tennessee Institute of Agriculture, Knoxville, TN 37996

32. Adapting Microfluidics for Radioisotope Separations

Davern S.M.,¹ O'Neil D.W.,³ Hallikainen H.,⁴ Allman S.,² Millet L.J.,⁵ Retterer S.T.,² Doktycz M.J.,² Standaert R.F.,² Boll R.A.1, Van Cleve S.,¹ DePaoli D.W.,¹ and Mirzadeh S.¹ ¹Nuclear Security & Isotope Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831 ²Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6229 ³Oak Ridge Associated Universities, Oak Ridge TN 37830 ⁴Arizona State University, Tempe, AZ 85281 ⁵The Bredesen Center, University of Tennessee and Oak Ridge National Laboratory, TN 37831

33. Development of a Micro-Actinium-225/Bismuth-213 Biomedical Generator System

O'Neil K.M.,³ O'Neil D.W.,³ Hallikainen H.,⁴ Davern S.M.,¹ Allman S.,² Millet L.J.,⁵ Retterer S.T.,² Doktycz M.J.,² Standaert R.F.,² Boll R.A.,¹ Van Cleve S.,¹ DePaoli D.W.,¹ and Mirzadeh S.¹ ¹Nuclear Security & Isotope Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831 ²Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6229 ³Oak Ridge Associated Universities, Oak Ridge TN 37830 ⁴Arizona State University, Tempe, AZ 85281 ⁵Joint Institute of Biological Sciences, University of Tennessee and Oak Ridge National Laboratory, TN 37831 USA.

34. Microsystems for studying the effects of radiation on human cells and tissues

O'Neil K.M.,³ Buckley K., Hallikainen H.,⁴ Allman S.,² Millet L.J.,⁵ Davern S.M.¹ ¹Nuclear Security & Isotope Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831 ²Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831 ³Oak Ridge Associated Universities, Oak Ridge TN 37830 ⁴Arizona State University, Tempe, AZ 85281 ⁵The Bredesen Center, University of Tennessee and Oak Ridge National Laboratory, TN 37831

35. *Ionic and Electronic Properties of Twin Domain in MAPbI3

Yongtao Liu,¹ Liam Collins,² Anton Ievlev,² Alex Belianinov,² Stephen Jesse,² Scott T. Retterer,² Kai Xiao,² Mahshid Ahmadi,¹ Sergei V. Kalinin,² Bin Hu,¹ and Olga S. Ovchinnikova² ¹Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996 ²Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37830

36. *Oxidative coupling of methane over SrTiO3 perovskite catalysts: Influence of surface composition and catalyst bed packing modes

Lei Bai, ^{1,2}Felipe Polo Garzon,² Hanjing Tian,¹ Zili Wu² ¹Department of Chemical and Biomedical Engineering, West Virginia University, Morgantown, WV, 26506 ²Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831

37. *Self-powered fast brazing of Ti-6Al-4V using Ni/Al Reactive Multilayer Films

Denzel Bridges,¹ Christopher Rouleau,² Zachary Gosser,² Cary Smith,¹ Zhili Zhang,¹ Kunlun Hong,² Jinquan Cheng,³ Yoseph Bar-Cohen,⁴ and Anming Hu¹ ¹Department of Mechanical, Aerospace and Biomedical Engineering, University of Tennessee ²Center of Nanophase Material Sciences, Oak Ridge National Laboratory ³Composite Solutions and Digital Manufacturing LLC ⁴Jet Propulsion Laboratory (JPL), California Institute of Technology

38. *3D-Printed Carbon Electrodes for Neurotransmitter Detection

Cheng Yang,¹ Qun Cao,¹ Pumidech Puthongkham,¹ Scott T. Lee,¹ Nickolay V. Lavrik,² B. Jill Venton¹ ¹Department of Chemistry, University of Virginia, Charlottesville, VA 22901 ²Center for Nanophase Material Science, Oak Ridge National Laboratory, Oak Ridge, TN 37831

- **39.** *Mesoscale Dynamics and Transport in Double Salt Ionic Liquids Tyler Cosby and Joshua Sangoro University of Tennessee, Department of Chemical and Biomolecular Engineering, Knoxville, TN 37902
- **40. *Mechanical properties of BN nanosheets** Alexey Falin, Ying Chen, Luhua Li Deakin University, Australia

41. *Interfacial Property's Influence on Damping Ratio and Fracture Toughness of Polyurea Toughed Fibrous Composites

Li He, Xin Wang, Thomas Attard ¹University of Alabama at Birmingham, Dept. of Civil, Construction, and Environmental Engineering, Birmingham, AL 35294

42. *Implanted Defects Leading to Magnetism in Graphene Alessandro R. Mazza,¹ Anna Miettinen,² Zheng Gai,³ Tim Charlton,³ Edward H. Conrad,² Paul F. Miceli¹ ¹University of Missouri – Columbia Department of Physics and Astronomy ²Georgia Institute of Technology School of Physics ³Oak Ridge National Laboratory

43. *Volatile Organic Compound Detection using Porous-Silicon-Oxide Coated Disc-on-Pillar Arrays T. Joshua Moore and Bhavya Sharma

Department of Chemistry, The University of Tennessee, Knoxville

44. *Solution Deposition of Multi-layered Semiconducting Polymer Thin Film

Tucker L. Murrey,¹ Jean-Francis Moulin,² Kunping Guo,³ Adam Moulé⁴ ¹University of California-Davis, Department of Material Science and Engineering ²Heinz Maier-Leibnitz Zentrum, REFSANS ³Shanghai University ⁴University of California-Davis, Department of Chemical Engineering

45. *Development of Cobalt-Nickel Selenide Nanoparticles Decorated Graphene to Improve the Photo-Electrochemical Behavior of DSSC

Vignesh Murugadoss,^{1,2} Subramania Angaiah,¹ Zhanhu Guo² ¹Electrochemical Energy Research Lab, Centre for Nanoscience and Technology, Pondicherry University, Puducherry, India ²Integrated Composites Laboratory (ICL), Dept. Chemical & Biomolecular Engineering, University of Tennessee, Knoxville, TN

- **46. *Ballistic conductance through transition metal dichalcogenide heterojunctions** Adam Pfeifle, Marcelo A. Kuroda Department of Physics, Auburn University
- 47. *Influence of Hydrogen-bond Network on Charge Transport and Dynamics in Deep Eutectic Mixtures

Stephanie Spittle, Tyler Cosby, and Joshua Sangoro University of Tennessee, Department of Chemical and Biomolecular Engineering, Knoxville, TN 37902

48. Status of Solid Electrolytes for Lithium Batteries

Daniel T. Hallinan Jr. Florida A & M University – Florida State University College of Engineering

49. Properties and Applications of "White Graphene" Luhua Li Institute for Frontier Materials, Deakin University, Waurn Ponds, VIC 3216 Australia

50. Chemical Nature of Ferroelastic Twin Domains in CH₃NH₃PbI₃ Perovskite

Yongtao Liu,¹ Liam Collins,² Roger Proksch,³ Songkil Kim,² Brianna R. Watson,⁴ Benjamin Doughty,⁵ Tessa R. Calhoun,⁴ Mahshid Ahmadi,¹ Anton Ievlev,² Stephen Jesse,² Scott T. Retterer,² Alex Belianinov,² Kai Xiao,² Jingsong Huang,² Bobby G. Sumpter,² Sergei V. Kalinin,² Bin Hu,¹ Olga S. Ovchinnikova² ¹Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996

²Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37830
 ³Asylum Research an Oxford Instruments Company, Santa Barbara, CA 93117
 ⁴Department of Chemistry, University of Tennessee, Knoxville, TN 37996
 ⁵Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

51. Design of ion-transport polymers for next generation energy storage Peng-Fei Cao,¹ Michelle Lehmann,¹ Guang Yang,² Bingrui Li,² Sheng Zhao,³ Vera Bocharova,¹ Frank Delnick,² Jagjit Nanda,² Alexei P. Sokolov,^{1,2} Tomonori Saito¹ ¹Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830 ²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830 ³Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996

52. Why We Need to Look Beyond the Glass Transition to Characterize the Dynamics of Thin Supported Films

Jack Douglas

Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD

Center for Nanophase Materials Sciences

Plenary Session

2018 User Meeting

Direct Electrodeposition of Nanostructured High-Performance Li-ion Battery Electrodes

Paul V. Braun

University of Illinois, Urbana-Champaign

ABSTRACT

Lithium-ion battery electrodes are nearly universally formed via tape casting of a slurry containing a mixture of active material, binder, and conductive carbon. We suggest conformal electrodeposition of high-quality electrode materials would provide opportunities to enhance battery performance (energy density, power density, and flexibility) and broaden the scope of available electrode form factors (size, shape, porosity, and 3D integration). Here I will discuss the considerable advances we have made on the direct electrodeposition at modest temperatures of high performance tin-based Li-ion anodes and LiCoO₂, LiMn₂O₄, and Al-doped LiCoO₂-based Li-ion cathodes. The electrolytically active materials were formed either as solid films, or where significant volume changes upon cycling are present, via a templating process, as a 3D mesostructured film. The capacities are near-theoretical, and in the case of the electroplated oxides, the crystallinities and electrochemical capacities of the oxides are comparable to powders synthesized at much higher temperatures (700 \sim 1000°C). The electrodeposition method significantly broadens the scope of battery form factors and functionalities, enabling a variety of highly desirable battery properties including microbatteries, and high energy, high power, and flexible designs.

Controlled Synthesis of 2D Covalent Organic Frameworks

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ABSTRACT

Polymerizing monomers into periodic two-dimensional (2D) networks provides structurally precise, layered macromolecular sheets that exhibit desirable mechanical, optoelectronic, and molecular transport properties. 2D covalent organic frameworks (COFs) offer broad monomer scope but are generally isolated as powders comprised of aggregated nanometer-scale crystallites. Here we control 2D COF formation using a two-step procedure, in which monomers are added slowly to pre-formed nanoparticle seeds. The resulting 2D COFs are isolated as single-crystalline, micron-sized particles. Transient absorption spectroscopy of the dispersed COF nanoparticles provides two to three orders of magnitude improvement in signal quality relative to polycrystalline powder samples and suggests exciton diffusion over longer length scales than those obtained through previous approaches. These findings will enable a broad exploration of synthetic 2D polymer structures and properties.



Figure 1. Schematic of controlled 2D polymerization. A two-step seeded growth approach provides 2D COF single crystals. When HHTP and a linear bis(boronic acid) monomer are condensed in a solvent mixture containing CH₃CN, crystalline 2D COF nanoparticles are formed as stable colloidal suspensions. These nanoparticles are enlarged in a second polymerization step in which the monomers are added to the solution slowly.

Center for Nanophase Materials Sciences

Oral Presentations

Creating the Next Generation of Materials

Track A

2018 User Meeting

DESIGNING HIGH DUCTILITY POLYMERS FOR STRETCHABLE ELECTRONICS

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Organic semiconductors have been the focus of scientific research because of their interesting (opto)electronic properties and solution processability. They have been successfully employed and extensively studied in the fields of organic photovoltaics (OPVs), organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and organic thermoelectrics (OTEs). As their practical applications have extended into the health and life sciences areas (e.g., electronic skins and artificial muscles), the mechanical compliance (i.e., low stiffness and high ductility) has become increasingly important. This in turn requires one to establish an understanding of the relationship between polymer structure and their mechanical properties as well as their (opto)electronic properties. In this presentation, the synthesis of a series of indacenodithiophene-based semiconducting polymers will be discussed along with the feasibility of using these polymers in stretchable devices.



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Metallic Nanoparticles Enabled Nano and Micro-Scale Tribofilm Formation

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Recent studies showed the potential application of nanoparticles (NPs) as novel lubricant additives. Oil solubility and stability are major challenges for applying NPs to lubrication. Surface modification with oil-miscible organic functional groups could enhance the stability and solubility of NPs in oil. Dodecanethiol modified Pd and Ag NPs were synthesized and used as candidate additives in PAO 4 cSt base oil. NPs were characterized using thermogravimetric analysis, UV-visible spectroscopy and electron microscopy. The size of the synthesized Ag and Pd NPs range from 3-6 nm and 2-3.5 nm, respectively. Both Ag and Pd NP additives could be successfully dispersed in the oil up to the 2.0 wt%, aided by the surface modification with dodecanethiol. Tribological tests were conducted using a ball-on-flat reciprocating sliding configuration using an AISI 52100 steel ball against a cast-iron flat at 100 °C.

Both Pd and Ag NPs demonstrated promising friction and wear reductions in boundary lubrication tests. The addition of 0.5 wt% AgNP to the PAO4 base oil dropped the coefficient of friction (COF) by 30%, and reduced the wear volume by 94%. At the same treat rate, the Pd NPs outperformed the Ag NPs with 40% reduction in COF and 97% reduction in the wear volume. This friction and wear reductions were attributed to the formation of a wear resistance, self-healing tribofilm on the contact surface. A cross-section of the wear scars near the contact zone was lifted out by focus ion beam (FIB) and analyzed using scanning transmission electron microscopy (STEM)/Energy dispersive X-ray spectroscopy (EDS). Figure 1 illustrates the cross-sectional STEM images and EDS elemental maps of the contact zone near the cast-iron flat lubricated by PAO containing 1.0 wt% Pd NPs. The image shows a surprising 2-3 µm thick tribofilm with Pd and S rich. This Pd NPs produced tribofilm is significantly thicker than the literature reported tribofilms formed by either conventional organic anti-wear additives or other NPs. The catalytic activity of the palladium NPs together with iron oxide rich substrate may be responsible for this ultra-thick protective film formation. The major composition of the tribofilm was found to be Pd and S compounds. In contrast, the cast-iron surface lubricated by PAO+0.5 wt% Ag NPs had a 150-200 nm thick tribofilm rich in Fe, C, and O together with a small amount of Ag and S. Further, the chemical species in the tribofilm were examined by X-ray photoelectron spectroscopy (XPS). The organic-modified NPs have potential wide applications in lubricating key components in transportation vehicles and industrial machinery.



Figure 1. Cross-sectional STEM image and EDS elemental maps of a tribofilm formed on the cast-iron surface lubricated by a base oil containing 1.0 wt.% Pd NPs.

Absolute Molecular Weight and Structural Analysis of Low Polydispersity Lignin through Small Angle Neutron Scattering

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Lignin is one of the most abundant organic polymers comprising 30% of woody biomass on a dry basis only surpassed by cellulose. Majority of the lignin is burnt as a cheap fuel source but there is enormous potential to convert lignin into a valuable chemical. Lower value applications like manufacture of phenolic resins, polyurethane foams and clean burning fuels require relatively low purity lignin (1-3% ash and metal contents e.g., 1500-7500 ppm sodium) whereas higher value applications like carbon fiber synthesis require ultra-pure lignin (metal content of < 100 ppm sodium). Major challenges in exploiting lignin is in separation and purification of recovered biomass to yield a high purity lignin stream that can be used for low and high value applications. Recently, Thies and coworkers at Clemson University have developed scalable methods of isolating ultra-pure lignin (<100 ppm sodium) with narrow molecular weight fractions by exploiting a novel liquid–liquid equilibrium (LLE) phase behavior. Three fractionated–solvated lignin precursors (FSLPs) of increasing molecular weight (7200, 13800, and 28600 Da measured through gel permeation chromatography (GPC) with polyethylene glycol standards) were obtained via the continuous Aqueous Lignin Purification using Hot Acids (ALPHA) process. Carbon fibers spun by Ogale and coworkers from the high molecular weight fraction lignin demonstrated the highest mechanical properties ever obtained for carbon fibers derived from lignin.

In this work, small angle neutron scattering (SANS) was utilized to determine the absolute molecular weight of the lignin fractions through Zimm analysis and the molecular morphology of lignin was investigated for different molecular weight fractions. We observed major differences between molecular weight determined through GPC and Zimm analysis from SANS. Structurally, lignin monomers were cylindrical/ellipsoidal in shape, with effective radius of monomers remaining unchanged between different molecular weight fractions. However, an increase in effective length of the units was observed with increasing molecular weight of lignin fractions. It has been postulated that, linear or elongated lignin molecules are superior precursors for carbon fibers compared to branched or globular lignin. Our findings corroborates the mechanical strength measurements from Ogale and coworkers, where elongated lignin moieties from higher molecular weight fractions of lignin yielded the strongest carbon fibers.



Figure. (A) Scattering intensity for different lignin fraction fit to unified power law in low q regime and ellipsoid model in the intermediate to high q regime. (B) Unified power law, R_g, (C) and (D) Radius and lengths respectively, obtained from ellipsoid model fitting.

Focused Electron Beam Direct-Write Processing (FEBIP) of 3D Composite Nanostructures and 2D Electronic Materials Andrei G. Fedorov

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FEBIP is an emerging method for atom-by-atom fabrication of topologically complex nanostructures from a variety of materials. Compared to a similar technique based on an ion beam, FEBIP can achieve higher resolution, inflicts less surface damage, and involves more accessible tools [1]. However, FEBIP suffers from low deposition rate, poor material purity, and limitation on a type of precursor materials which can be delivered to a high vacuum environment of the FEBIP chamber. We are developing a family of multi-mode energized micro/nano-jet techniques for local precursor delivery to resolve the FEBID challenges and to expand the range of useful precursors from gas to liquid phase for broader FEBIP applications.

Energized micro/nano-jets of thermally or electro-kinetically energized precursors in both gas [2,3] and liquid [4] phase provide unique capabilities for localized delivery of precursor molecules to the substrate, thus establishing locally controlled deposition/etching site for FEBIP [2-4]. This expands the range of usable precursor molecules and enhances the growth rate and purity by selectively tuning of precursor and contaminant sticking and surface diffusion coefficients as well as adsorption/desorption activation energies.[5] Expanding on gas-phase jet delivery of precursors, we recently demonstrated a new approach to FEBIP using liquid phase precursors delivered using a nanoelectrospray jetting process.[4] This new technique, NESA-FEBIP, brings an important new dimension to the concept of controlled local delivery of energized/activated precursors to the substrate by (1) extending the available precursor state from gas to liquid phase and (2) using the focused electric field rather than heating to activate new energy modes of the precursor molecules. Both purely aqueous and organic solvents have been successfully delivered by nanoelectrospray jets, enabling new FEBIP capabilities of (1) dramatically increasing the growth rate of deposition/etching, (2) enabling deposition of composite materials and alloys with tailored electromechanical properties, and (3) fabrication of new, truly 3D topologies of nanostructures that are fundamentally out of reach of current gas-phase FEBID techniques. These unique new capabilities of NESA-FEBIP are matched by the complexity of the underlying physics and chemistry of ion transport and electrochemical reaction interactions, which need to be fully understood in order to take full advantage of and further develop this new mode of FEBIP from liquid phase precursors using energetic (nanoelectrospray-driven) liquid jets.

I will also discuss development and demonstration of a complete set of processing capabilities using FEBIP to fabricate electronic devices from monolayer graphene and carbon nanotubes.[6] These include high resolution, high speed etching [3], dynamic patterning and n-p-n junction formation by carbon doping of the conduction channel [7,8], formation of low resistance, Ohmic contact at the metal-graphene junctions [9], and "direct-write" reduction of graphene oxide, forming high electronic mobility conductive line patterns on the substrate. [10]

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On the Nature of Localization in Ti doped Si

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Intermediate band semiconductors hold the promise to significantly improve the efficiency of solar cells, but only if the intermediate impurity band is metallic. We apply a recently developed first principles method to investigate the origin of electron localization in Ti doped Si, a promising candidate for intermediate band solar cells. Although Anderson localization is often overlooked in the context of intermediate band solar cells, our results show that in Ti doped Si it plays a more important role in the metal insulator transition than Mott localization. Implications for the theory of intermediate band solar cells are discussed.

Y. Zhang, R. Nelson, K.-M. Tam, W. Ku, U. Yu, N. S. Vidhyadhiraja, H. Terletska, J. Moreno, M. Jarrell, T. Berlijn, arXiv:1805.05276

Engineering a Protein-based Nanomaterial

Eric J. Young, Miguel Fuentes-Cabrera, Cheryl A. Kerfeld, and Danny C. Ducat

Understanding how to build defined shapes and structures from biological materials (lipids, nucleic acids, and proteins) is an emerging approach for intelligently organizing function at the nanoscale. Proteins, perhaps, represent one of the most powerful bio-inspired engineering targets to construct defined, functional nanoarchitectures.¹ Examples of geometries built from self-assembling proteins include fibers, lattices, tubes, and compartments.¹ Nonetheless, advancing proteinbased approaches for fabricating precision nanoarchitectures still requires modules with robust design principles and a deep understanding of hierarchical assembly.

We are harnessing a naturally occurring proteindomain with the potential to self-assemble to a myriad of well-defined nanoarchitectures.¹ Generally, proteins bearing this domain will first cyclize to form stable, pseudo-hexagon shaped tiles, which can then tessellate to form distinct higher-order assemblies—Fig. 1a. Properties intrinsic to a given tile such as overall electrostatic profile and interface identity appear to drastically influence macromolecular behavior and architecture.¹ Theory predicts these small differences can create energetic preferences for some tiles to associate with angular preference leading to models in agreement with experimentally observed assemblies¹—Fig. 1b.

We look to expand these preliminary results by integrating theoretical, experimental, and deep learning approaches. Efforts will be outlined that are currently undergoing to measure behavior with advanced microscopy techniques, including visualizing *in operando* assembly with defined



cargos—Fig. 1c. As design principles for this nanomaterial are established, we envision a widediversity of precisely nanofabricated scaffolds and structures interfacing with other selfassembling systems and nanotechnologies. In addition to building intelligent nanodevices, it is our hope that the *in situ* methodologies being developed will be applied to observe other phenomena, ultimately advancing the capability to visualize dynamic processes at the nanoscale.

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Center for Nanophase Materials Sciences

Oral Presentations

Observing Dynamic Processes with In-Situ and Operando Techniques

Track B

2018 User Meeting

Nanoscale Solid-Liquid Interfacial Mechanisms in Li-Ion Batteries and Corrosion

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Two of the largest economic challenges in our society can be solved by understanding the fundamental mechanisms associated with electrochemcial reactions at solid-liquid interfaces. The first involves improving rechargeable batteries, which have become a primary consumable for portable electronics, transportation, and grid storage. Advancement of this field is reliant on solving the interfacial reactions at the electrode surfaces for Li-ion batteries. The second economic challenge is the yearly loss in over 3% of the worldwide gross domestic product to corrosion remediation, repair, and replacement. Although uniform corrosion of steel is widespread, catastrophic failures of low-carbon steel parts are related to accelerated localized corrosion events, which occur at electrochemical interfaces in the material.

In-situ transmission electron microscopy studies on Li-ion metal anodes, Sn/SnO₂ anodes, and corrosion of low-carbon steel will be detailed. Electrochemcial control at picoampere sensitivity was achieved using the Center for Integrated Nanotechnologies' Electrochemcial TEM Discovery Platform. This platform provides advantages in even liquid with thicknesses down to ~ 200 nm, multiple (10) electrodes for many test conditions within the same environment, and customization of the electrode design and materials. Discussion will include efforts on integration of Li-containing counter and reference electrodes for full cell battery testing within the TEM. Corrosion studies include pre-*in situ* and post-*in situ* structural analysis of the steel microstructure in composition, phase, and orientation to determine the site for accelerated localized corrosion. Details on this work will include experimental methodology, nanoscale site identification, localized progression, and a previously unobserved re-initiating galvanic process.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.

Investigating Local Corrosion Processes in Real and Diffraction Space by *in situ* Liquid Cell Transmission Electron Microscopy

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The development of liquid cell transmission electron microscopy (TEM) holders has extended investigations of liquid-solid and vapor-solid interactions to within an electron microscope. For example, *in situ* liquid cell TEM allows for the direct observation of active corrosion events in real time and at nanometer spatial resolution. This provides a wealth of information on localized corrosion mechanisms and kinetics, corrosion front morphology, and relationships between microstructure and corrosion initiation sites at spatial and temporal resolutions relevant to the observed phenomena.

In this research, we investigate the corrosion of sputtered Fe thin films in aqueous 20% acetic acid and water vapor-state environments using in situ liquid cell microscopy. Fe thin films were sputter deposited at room temperature to a thickness of 100 nm directly onto a silicon nitride membrane of a liquid cell microchip device. The samples were investigated in a FEI Titan operated at 300 kV using a Protochips liquid cell holder. All images were collected using a Gatan OneView camera. Videos of the corrosion behavior were collected at 100 frames per second in real space with the TEM operating in bright field mode and in diffraction space with selected area diffraction patterns collected. Pre-corrosion bright-field imaging and electron energy loss spectroscopy (EELS) characterization of the thin films showed that the initial grain size was on the order of 10-20 nm and that the films were not oxidized. During *in situ* corrosion of the thin films, corrosion fronts were seen to propagate in a start-stop fashion, with corrosion pits initiating 10's of nanometers in front of existing corrosion fronts and oxidizing the material in between. Automated image processing algorithms were developed to extract spatial information on the corrosion front propagation, including propagation rates. The corrosion rate was seen to be highly dependent on electron dose, with increasing electron dose accelerating the corrosion front propagation rates and increasing the density of corrosion initiation sites. In diffraction space, it was seen that Fe₂O₃ was formed during corrosion process, demonstrating the sensitivity of diffraction analysis to the detection of corrosion byproducts. The observed behavior will be discussed in terms of corrosion initiation processes, electron beam effects, and future opportunities in combining automated image analysis with high-speed image acquisition.

Analytical Electron Microscopy Study of the Interface between Mineralized Extracellular Polymer and Osteogenic Si-Y-O-N Film Present at Annealed Silicon Nitride Surfaces

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The process of osteogenesis at an implant surface involves osteoprogenitor cells colonizing the surface, differentiating into osteoblasts, and secreting an extracellular polymer (ECP). The ECP is then mineralized by precipitation of hydroxyapatite ($Ca_5(PO_4)_3(OH)$, HAp) from the surrounding biologic medium. The osteogenic capability of any biomaterial is governed by a number of critical surface properties such as surface chemistry, energy, potential, and topography. Prior work¹ demonstrated that silicon nitride and related materials possess desirable values for these properties. Indeed, it was observed that Si-Y-O-N phase(s) present in the form of thin (<150 nm) interrupted films at the surface of nitrogen-annealed silicon nitride bioceramics induced upregulation of osteoblastic activity².

Following a previously described² *in vitro* experiment which exposed nitrogen-annealed silicon nitride to osteosarcoma cells, analytical electron microscopy was utilized to probe the interface between the mineralized extracellular polymer and the Si-Y-O-N phase(s). A cross-section of this interface is shown in Fig. 1 as (a) a high-angle annular darkfield scanning transmission electron microscopy (HAADF-STEM)

image with (b) an energy dispersive X-ray spectroscopy (EDS) map overlay high-lighting locations of Si, Y, and Ca. The Si_3N_4 microstructure is covered by a yttrium-rich film of the intergranular phase (IGP). HAp was de-





the IGP film. A bright-field STEM image (Fig. 1(c)), obtained from the area within the red box in Fig. 1(a), shows the atomic scale interface between the partially-crystalline HAp and the Si-Y-O-N phase. The electron diffraction pattern shown in Fig. 1(d) along with EDS data revealed this phase to be monoclinic yttrium disilicate (*i.e.*, m-Y₂Si₂O₇) with ~2 atomic% N impurity and ~2 atomic% excess Si, thought to be dissolved Si₃N₄ or Si₂N₂O. Although rapid electron damage of the mineralized ECP was observed, EDS analyses suggested incorporation of Na, Mg, and Si within the HAp and a Ca/P ratio of ~1.43. The observation of Si within the mineralized ECP is seen as evidence of the release of (SiO₄)⁴⁺ tetrahedra from the Y₂Si₂O₇ into the local biological microenvironment. Identification of this phase paves the way for ongoing work to understand and optimize this novel biomaterial which has potential for use as both a coating and bone defect filler in orthopedic applications.

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Organic molecular self-assembly at metal surfaces: From ordered metastable phases to covalently bonded 2D networks

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Molecular self-assembly of organic species on metal surfaces is observed for an assortment of monolayer preparation approaches including electrochemical deposition, Langmuir-Blodgett film formation, solution sensitization and molecular sublimation. Exploiting van der Waals interactions on single crystal surfaces is a particularly interesting path towards controlled "bottom up" formation of extended, highly ordered 2D systems with potential tunability through the choice of molecular units and substrate surface. Such assemblies could give rise to novel low-dimensional organic electronic systems if one could achieve controlled covalent bonding between molecular units that preserves the order of the self-assembled array.

While there have been many studies characterizing self-assembly of organic molecules at metal surfaces, how the competition between substrate-molecule interactions and intermolecular forces impact molecular arrangement during overlayer growth is poorly understood. Moreover, the nature of surface-mediated chemical reactions that can proceed for these self-assembled systems remains elusive. To address these questions we have investigated the adsorption of zinc(II) tetraphenylporphyrins (ZnTPP) on metal surfaces (Au(111), Ag(111) or Ag(100)) in ultra-high vacuum, and their subsequent reorganization and chemical transformations upon annealing, using scanning tunnel microscopy, direct and inverse photoemission spectroscopies, ab-initio computational techniques and kinetic Monte Carlo simulations.

We show that molecule/molecule and molecule/surface interactions, as well as accumulated surface

stress, all play important roles in determining the nature of the self-assembly. In particular, highly-ordered kineticallytrapped self-assembled systems are obtained, indicating that farfrom-equilibrium processes can play an important role in building these 2D systems. Furthermore, self-assembled ZnTPP when exposed arrays are to



ZnTPP/Ag(100): (L) Metastable "2+1" SAM; (C) Thermodynamically favored square SAM; (R) 2D covalently bonded network

appropriate conditions, it is possible to generate surface-mediated chemistry that leads to site-selective dehydrogenation and intramolecular covalent bond creation. Intermolecular dehydrogenation also is observed which, if directed properly, could lead to tunable highly ordered 2D covalent structures.

Charles Ruggieri, Sylvie Rangan, Robert A. Bartynski, and E Galoppini, J. Phys. Chem. C **119**, 6101 (2015); J. Phys. Chem. C **120**, 7575 (2016).

Revealing Ferroelectric Switching Character Using Deep Recurrent Neural Networks

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The ability to alter the electrical conductivity, mechanical and optical susceptibility, and state (phase and polarization orientation) of ferroelectrics using electric field has inspired forethought into how such functionality could be leveraged for next-generation devices.¹ Most of such functionality relies on the controlled conversion between phases and/or interfaces (domain walls).² While there have been demonstration of nanoscale manipulation and control of such structures all attempts have required significant human guidance. Here, we develop a automated neural network approach (Fig. 1a), which considers the inherent temporal structure in the data, to statistically determine features of switching mechanisms, which can be correlated to the physical switching process. In particular, we develop a sparse, long-short term memory, autoencoder capable extracting ^f features from hyperspectral (a spectra at each pixel) band-excitation piezoreponse spectroscopy (BEPS). We start by demonstrating the efficacy of this approach by extracting insights about the switching mechanisms from the piezoresponse hysteresis loops obtained from tensile-strained PbZr_{0.2}Ti_{0.8}O₃ thin films (Fig. 1b); wherein Figure 1. a. Schematic drawing of an strain drives the formation of a hierarchical domain structure between autoencoder. b. Out-of-plane piezoresponse c/a/c/a and $a_1/a_2/a_1/a_2$ domain structures. We demonstrate how this image of PbZr_{0.2}Ti_{0.8}O₃ thin films with neural network approach can improve scientific inference from such hierarchical domain structures. c-h. diagram data compared to conventional machine learning approaches (e.g. showing the geometric dependence of the clustering and decomposition). Having proven the capabilities of switching mechanism and resonance response. this approach on the piezoresponse hysteresis loops, we apply this Inset shows feature map obtained from the concept to analyze the resonance loops extracted from BEPS. The autoencoder.



resonance loops have a functional form more complex than the piezoresponse hysteresis loops, which in turn, has limited such analysis. We demonstrate that using the developed approach that we can statistically quantify differences in the switching mechanism missed by analysis of just the piezoelectric hysteresis loops. Ultimately, based on the inference provided from this analysis, we detect electromechanical hardening resulting from the formation of charged domain walls during switching, providing new insights regarding the role of domain geometry in controlling ferroelectric switching mechanisms (Fig. 1c-h). This capability to automatically detect the formation of charged domains walls in operando during switching provides a route towards the controlled writing and manipulation of functional nanoscale structures and interfaces.

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Atomic Structure and Electrical Activity of Planar Faults in Lead-halide Perovskites

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Lead-halide perovskites have emerged as a promising class of highly efficient and affordable semiconductors with applications in solar cells and optoelectronic devices. One of the key features of these lead-halide perovskites is their defect-tolerance,¹ which is their ability to retain high-performance even in the presence of a large concentration of defects. Point defects in lead-halide perovskites either lead to shallow defects levels or resonant levels within the valence or conduction bands, which allow efficient carrier transport. In addition to point defects, planar-defects, such as grain boundaries, present in these perovskites can also have a significant impact on the electronic structure. However, direct observation of the atomic structure of grain boundaries in lead-halide perovskites and their effect on charge transport is missing.

In this work, we have combined aberrationcorrected scanning transmission electron microscopy (STEM) with first-principles density-functional theory (DFT) calculations to resolve the atomic and electronic structure of planar defects in fused CsPbBr₃ nanocrystals that are attractive for optoelectronic applications such as in display panels and light-emitting diodes. From STEM imaging, we observe that the fusion of these nanocrystals occurs through two prevalent planar defects: a Br-rich $\sum 5$ grain boundary and Ruddlesden-Popper (RP) planar faults. Figure 1a shows a high-angle annular dark field (HAADF) image of the $\sum 5$ grain boundary (top) and RP-planar fault (bottom). The RP-planar fault is made up of an additional layer of CsBr with the rock salt structure, whereas the $\sum 5$ grain boundary is made up of shared Pb, Cs and Br atoms.



Figure 1. (a) HAADF images and (b) DFToptimized crystal structures showing a $\Sigma 5$ grain boundary (top) and a RP-planar fault (bottom) in CsPbBr₃. The scale bars correspond to 1 nm. (d) Density of states (DOS) plot for the planar defects and pristine CsPbBr₃.

We have used DFT calculations to resolve the three-dimensional structure of both the planar faults (as shown in Fig. 1b) and their effect on the electronic properties (Fig. 1c). In conventional semiconductors, planar defects introduce mid-gap states, which can act as nonradiative recombination centers and consequently deteriorate optoelectronic performance. However, the DFT calculations reveal that neither the $\Sigma 5$ grain boundary nor the RP-planar defects in CsPbBr₃ induce mid-gap states, as shown in Fig. 1c, which lends support to the defect-tolerant nature of these perovskites. We also predict the growth conditions under which the grain boundaries lead to mid-gap states, which resolve contradictory reports on the experimentally observed activity of grain boundaries in lead-halide perovskites.^{2,3} Moreover, we predict that the $\Sigma 5$ grain boundary repels electrons but attract holes, while the RP planar fault repels both electrons and holes and lead to strong quantum confinement. Overall, our results highlight novel functionalities that can be achieved in lead-halide perovskites by the control of these planar defects.

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Center for Nanophase Materials Sciences

Poster Abstracts

2018 User Meeting

Semiconductor heterojunctions made by g-C₃N₄ and N-doped Sr₂Nb₂O₇ for enhanced photocatalytic H₂ production

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Semiconductor-based photocatalysis has received tremendous attention in the last few decades because of its potential for solving current energy and environmental issues. To maximize the use of solar radiation, the photoresponse of the catalysts should be in the visible region of the electromagnetic spectrum because visible light accounts for 45 % of the total solar radiation compared with 4% for UV light. [1]. Different strategies have been explored to extend light absorption into the visible. They include doping with metal or/and non-metal ions and surface modifications such as the formation of heterojunctions by combining with metals or other semiconductors. Semiconductor based heterojunctions have been shown to overcome the drawbacks of low photocatalytic efficiency that result from electron-hole recombination and



Figure 1: Schematic diagram of separation and transfer of photogenerated carriers in the CN/SNON-700 heterojunction under visible light irradiation.

narrow photo-response range [3, 4] Different types of visible-light-active heterojunctions made by two different semiconductors will be presented [5-7]. With the example of our recent study based on the heterojunction of $g-C_3N_4$ and nitrogen-doped $Sr_2Nb_2O_7$, the importance of design and preparation of heterojunctions to facilitate charge separation/migration for enhanced photocatalytic activity will be discussed.

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Giant magnetic response of a two-dimensional antiferromagnet

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A fundamental difference between antiferromagnets and ferromagnets is the lack of linear coupling to a uniform magnetic field due to the staggered order parameter (Fig. 1(a)). Such coupling is possible via the Dzyaloshinskii-Moriya (DM) interaction but at the expense of reduced antiferromagnetic (AFM) susceptibility due to the canting-induced spin anisotropy (Fig. 1(b)). We solve this long-standing problem with a top-down approach that utilizes spin-orbit coupling in the presence of a hidden SU(2) symmetry (Fig. 1(c)).



Figure 1 | a-c, Schematic diagrams of a pair of antiferromagnetically coupled spins. The pair is fully antiparallel and free to rotate together in all directions (a). Under a typical DM interaction (b), the pair is canted toward a preferential orientation, which is stable against magnetic field. If the DM interaction preserves the rotational symmetry (c), the pair is again highly susceptible to magnetic field via the canting.

We demonstrate giant AFM responses to sub-Tesla external fields by exploiting the extremely strong two-dimensional critical fluctuations preserved under a symmetry-invariant exchange anisotropy, which is built into a square-lattice artificially synthesized as a superlattice of $SrIrO_3$ and $SrTiO_3^{-1}$. The observed field-induced logarithmic increase of the ordering temperature enables highly efficient control of the AFM order (Fig. 2). Our results demonstrate that symmetry can be exploited in spin-orbit-coupled magnets to develop functional AFM materials for fast and secured spintronic devices².



Figure 2 | Magnetic field dependence of the AFM crossover temperature.

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Interactions between Transition Metal Clusters and Graphene using First Principles Calculations

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Graphene's properties can be fined tuned by doping, introducing adsorption agents, or through the functionalization of pores in the graphene layer. Possible adsorption agents are metal nanoparticles, which can alter the electrical, magnetic and catalytic properties of the material. In this study we characterize the adsorption of 13-atom transition metal clusters onto graphene and functionalized pores via ab initio calculations within the density functional theory. We specifically analyze the binding, magnetic and electronic properties emerging from interactions between pristine or oxygen-passivated porous graphene and clusters. We discuss trends characterizing the structure-property relationships of these heterogeneous systems and the differences/similarities between pristine and porous layers.

Non-Transition-Metal Catalytic System based on Al-Doped Graphene for N₂ Reduction to NH₃

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The prevalent catalysts for natural and artificial N_2 fixation are known to hinge upon transitionmetal (TM) elements, as can be seen from the nitrogenase enzyme of bacteria living in roots of leguminous plants and the heterogeneous Fe-based catalysts in industrial Haber-Bosch process. In this project, we demonstrate by density functional theory calculations that Al-doped graphene is a potential non-TM catalyst to convert N_2 to NH₃ in the presence of relatively mild proton/electron sources [LutH]⁺ and CoCp*₂.

In the integrated structure of the catalyst, the Al center with a strong Lewis acidity serves as a binding and catalytic site while the graphene framework with a versatile redox property serves as an electron buffer during the successive proton/electron additions to N₂ and its various downstream N_xH_v intermediates (Fig. 1). In the course of reactions, the graphene moiety shows multiple oxidation states, whereas that of Al approximately remains constant. The initial hydrogenation of N₂ can readily take place via an internal H transfer from the graphene framework to the N₂ ligand bound to the Al binding site. A similar scenario of H transfer has also been observed in Schrock's catalysis system and in the nitrogenase enzyme, where



Figure 1. Gibbs energy profile for the key $Al-N_xH_y$ intermediates formed by a sequence of proton/ electron additions. Red triangular symbols indicate the results with Li^+ additive.

hydrogenated heteroatoms were suggested to be vital for the first hydrogenation step of N_2 . In view of the recurrence of H transfer in the first step of N_2 reduction observed in biological nitrogenases and other synthetic catalysts, heteroatom-assisted hydrogenation of N_2 appears to be a ubiquitous process in homogeneous N_2 reduction systems. A Li⁺ ion is also used as an example to show that alkali metal ions as an additive can substantially facilitate the binding and activation of N_2 at the initial reaction stage and the exchange of NH₃ with N_2 at the final stage of the proposed catalytic cycle.

These findings demonstrate the feasibility of utilizing Al-doped graphene as a non-TM catalyst for N_2 reduction to NH_3 in a manner similar to that in the homogeneous catalysis based on TM complexes operated under mild conditions. They also highlight the significance of heteroatom-assisted H transfer in the design of synthetic catalysts for N_2 fixation.

Characterization of Carbon Nanostructures in Cu Covetics by APT, HIM, and STEM*

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Carbon infused metal alloys exhibit enhanced electrical and thermophysical properties. This new class of materials, known as covetics, have attracted increasing research interest because of their superior performance. In our investigation, copper covetics were prepared by electron-beam melting with electromagnetic stirring process. The enhanced electrical and thermal conductivities are results of carbon nanostructures infusion in the metal. We utilized atom probe tomography (APT), helium ion microscopy (HIM), high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) in the study of carbon nanostructures in copper covetic materials. APT revealed 3D distribution of carbon-rich clusters; the superior contrast and resolution of HIM provided unique opportunity to visualize carbon nanostructures; HRTEM and STEM elemental mapping verified the formation of carbon nanostructural nature and the interactions between carbon nanostructures and host metal matrix is critical to elucidate the origins of the superior physical and mechanical performance. Details of experimental results will be presented.

Abstract for a poster presentation at the 2018 Center for Nanophase Materials Sciences (CNMS) User Meeting, Oak Ridge, TN, August 13-15, 2018.

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Investigating Helium Bubble Formation in NiFex Alloys using Electron Energy Loss Spectroscopy

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Single phase-concentrated solid solution alloys (SP-CSAs), including high entropy alloys, have drawn a lot of attention because of the exceptional mechanical properties, high resistance to corrosion and radiation damage tolerance [1]. To design SP-CSAs with superior properties, it is important to understand how the material chemistry affects the defect evolution process in these alloys. Here we studied the effect of Fe concentration on helium bubble formation in NiFe_x SP-CSAs using electron energy loss spectroscopy (EELS). Due to its extremely low solubility in metals, helium tends to cluster with vacancies to form pressurized bubbles [2]. The accumulation of He bubbles can lead to dramatic degradation of the material's properties [3].

Three SP-CSAs (NiFe₂₀, NiFe₃₅, and NiFe₅₀) and Ni were irradiated by 200 keV He ions at 500°C. The size and density of the He bubbles were characterized using transmission electron microscopy (TEM); EELS spectrum were applied to measure the helium density inside the bubble [3]. The TEM analyses show the growth of bubbles is suppressed with increasing Fe concentration in the SP-CSAs. Bubbles having ~10 nm diameter are widely observed in NiFe₂₀, while most of the bubbles in NiFe₅₀ are smaller than 5 nm. Fig. 1(a) is a typical high-angle annular dark field (HAADF)-STEM image of a bubble and Fig. 1(b) shows the EELS collected from inside (position A) and outside (position B) of the bubble. We can clearly identify the He absorption peak at 24 eV. Fig. 1(c) summarizes the calculated He densities in the bubble in all three NiFe_x alloys, based on the measured He absorption peak energy using EELS. In general, the He density decreases as the bubble size increases. This trend agrees with the Laplace-Yong law, i.e., the gas density is proportional to $2\sigma/r$, where σ is the bubble surface tension and r is the bubble radius [3]. When focusing on bubbles within a similar size range (2nm-5nm) in different alloys, we found that the average He density increases from 76 nm⁻³ in NiFe₂₀ to 99 nm⁻³ in NiFe₃₅ and to 122 nm⁻³ in NiFe₅₀, which suggests that a higher Fe concentration could lead to a higher bubble surface tension, which may be an important factor that inhibits the bubble growth rate.



Figure 1. (a) HAADF-STEM image of a typical He bubble in NiFe₅₀; (2) EELS profiles acquired from positions A and B in (a); (c) He densities inside bubbles of different sizes in three SP-CSAs. **References:**

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Molecular Dynamics Simulations of Liquid Metal Assembly at the Nanoscale

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Understanding the destabilization of elemental and alloy thin films and correlating the temporal, chemical, microstructural, and shape evolution as they evolve towards equilibrium, can help create new type of alloying materials and structures. However, such understanding relies on developing answers to a number of complex questions, i.e.

How do competing driving forces direct the assembly of non-equilibrium/metastable liquid thin film materials at the nanoscale? How do liquid alloy thin film systems search free-energy landscapes? What are the mechanisms that guide nanoparticle formation, their structure, composition, and spatial arrangement? How can we influence the development of instabilities through external excitation or templating? How are the resultant nanoscale materials properties affected during the non-equilibrium to equilibrium transformation? Here we use a combination of experimental and simulations studies, both atomistic and continuum modeling, to answer those questions. In this poster, we focus on the segregation observed on a NiAg system and how this segregation depends on temperature and composition. Future studies will use these findings, in combination with the Rayleigh-Plateau instability, to create novel NiAg structures. This project is supported by NSF grant No. CBET 1604351 and DOE Office of Science SCGSR program. The experimental work and atomistic simulations were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.
Agent-based modeling simulation of black soldier fly larvae aggregation

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Black soldier fly larvae are insects that are raised by startups all over the world as a sustainable source of protein. The larvae are fed human food waste, and fully grown larvae are sold as chicken or fish feed. Experimental studies performed by David L. Hu and Olga Shishkov, from Georgia Tech (see their poster), reveals that larvae aggregate around food sources forming structures such as vortices in 2D and torus-like structures in 3D. Here we used agent-based modeling simulations to understand how these structures might arise. Using a model written in the language *NetLogo*, we investigated how parameters, such as density and speed of the larvae, affect the appearance of these structures.

*Ethan and Eagle both contributed equally to this work.

Synthesis and Characterization of Functionalized Tire Carbon as Catalysts for Conversion of High Fatty Acids to Biofuel

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Biofuels are anticipated to play an important role in the future as a replacement for our current dependence on petroleum-based fuels [1], however, present methods for biofuel production will not meet this growing demand on the basis of feedstock and cost. Most feedstocks come directly from highly-refined food crops due to their well-known compositions, but directly utilizing such feedstocks is costly relative to petroleum-based diesel production. The use of cheaper feedstocks, such as lower refined vegetable oils and waste cooking oils, will improve biofuel production on the basis of cost, but such feedstocks contain 5-90 % of free fatty acids undergo undesired saponification during traditional (FFAs) that based-catalyzed transesterification. To overcome this limitation, Oak Ridge National Lab, Georgia Tech, and Wake Forest University have collaboratively developed solid acid catalysts using carbon derived from waste tires (WTC) in order to convert FFAs to biofuels [2]. Waste tires are detrimental to human health and the environment, and by converting them to a value-added carbon, new applications can mitigate its environmental effects. In our work, we show that WTC can be converted into effective solid acid catalysts by using methods based on *i*) surface functionalization or *ii*) chemical impregnation. We show that surface functionalization with sulfuric acid, as well as a sequential treatment with L-cysteine, dithiothreitol, and H₂O₂, promotes the formation of catalytically active sulfonic acid (-SO₃H) groups [3,4]. Additionally, impregnation of the WTC with ferric sulfate allows for the incorporation of catalytically active acid sites [5]. The tire-derived solid acid catalysts are shown to efficiently convert FFAs and methanol to biofuels at temperatures <70 °C and at 1 atm in a simple batch reactor. Our work highlights that utilizing recyclable materials, byproducts, and/or environmentally benign procedures, the economic and environmental viability of biofuel production can be improved while promoting a circular biofuel economy.

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Contact engineering of 2D PdSe₂ with interfacial metallic Pd₁₇Se₁₅ achieved by phase transformation

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Abstract

The rise of 2D materials in the semiconductor industry is currently being challenged by the presence of Schottky-barrier at the metal-semiconductor interface, which limits device performance. Several attempts include the use of carefully-selected metals, graphene, and 1T/1T'phase as the contact electrodes, all which has suffered one setback or the other, including misalignment and stability. Achieving perfect electrical contact requires a well-aligned electronic band, and a sharp interface. Here, we present metallic-Pd₁₇Se₁₅ for 2D PdSe₂ semiconductor, a material achieved via phase engineering which is fast, stable, and scalable. Scanning transmission electron microscopy (STEM) reveals a 2D to 3D phase transformation from PdSe₂, which is supported by the disappearance of low-frequency Raman signals and the chemical composition analysis via Auger electron spectroscopy. The direct transition from PdSe₂ to Pd₁₇Se₁₅ is as a result of selenium vacancies as substantiated by density functional theory (DFT) calculations. The new phase has a sharp, distinct interface with semiconductor PdSe₂, making it an interesting contact material. The electron mobility of transistor devices with Pd₁₇Se₁₅ contact performed at least 20% better and as high as 1000%, due to lower contact resistance and ohmic junction present at the interface. Vacancy-induced phase transformation opens up the possibility of achieving seamless contacts for 2D electronic transistors.

Keywords: 2D materials, phase transformation, Se vacancy, electronics

Carbonized 3D Structures for Integration on CMOS Readout Circuitry

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The primary objective of this work is to develop an integrated single chip biosensing platform based on carbonized 3D nanostructures. Previously, research has been conducted on vertically aligned carbon nanofibers (VACNF) and carbon nanospikes (CNS) [1], [2]. These nanostructures have been used for electrochemical sensing (glucose) in conjunction with separate custom CMOS potentiostat circuits in a two chip system. However, most standard CMOS chips can only withstand up to 525 °C without any performance degradation while carbonization of VACNF and CNS normally occurs at temperatures above 700 °C. This temperature limitation severely inhibits the ability to develop a single chip, compact integrated electrochemical sensing system. The proposed method seeks to overcome this challenge by implementing carbonization of 3D printed polymeric nanostructures within a temperature range of 400-500 °C. The polymeric 3D nanostructures are grown using the new generation of Nanoscribe 3D laser lithography system, which allows feature sizes in the sub-micrometer range by means of two-photon polymerization. Initially, we have fabricated arrays of conical and cylindrical structures on Si substrate to justify the functionality as potential electrochemical electrodes. The SEM images of cylindrical and conical structures are shown in Fig. 1. The polymeric nanostructures will then be annealed by rapid thermal process. This

makes them conductive through carbonizing of the surface. Raman spectroscopy needs to be performed to study the crystal lattice structure and the surface characteristics of the nanostructures. Raman spectroscopy also provides insight about the presence of graphite like sp² atomic bonding that determines the defect sites. The defect sites consist of dangling bonds in which the electron transfer takes place during electrochemical the reaction. In future work, the newly grown carbonized structures will undergo





electrochemical testing and compared with VACNF and CNS structures. If the results are as expected, they will be grown on dummy chips and finally on integrated CMOS circuits with exposed pads.

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First-principles study of low-frequency Raman-active modes in Ag intercalated MoS2

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Two-dimensional layered materials (2DMs) have been subject of increased research interest ever since a single layer of graphen has been obtained by mechanical exfoliation in 2004 [1]. In particular, the transition metal dichalcogenides (TMDs) with the general formula MX_2 , where M is a transition metal (Mo, W) and X a chalcogen atom (S, Se, Te), have already shown a wide range of technologically relevant properties when scaled down from bulk to few-layer systems. For example, bulk MoS_2 has an indirect band gap of 1.29 eV, which becomes a direct band gap of 1.8 eV when a single layer of MoS_2 is considered [2].

Precise characterization of 2DMs is crucial for exact control of their properties that vary with the number of layers. Raman spectroscopy has become the key experimental technique in this sense, due to its nondestructive nature and the ability to identify even small structural and electronic changes.

Up until recently, the high-frequency (HF) intralayer modes have been receiving more attention than the low-frequency (LF) interlayer ones when it comes to characterization of 2DMs because of the relatively weak intensity of the Raman peaks associated with the LF modes and their close position to the strong Rayleigh line making their detection challenging. However, the LF interlayer modes that correspond to rigid motions of each layer with restoring forces governed by the weak interlayer interactions are more effective for determination of structural parameters of 2DMs such as layer number and stacking order than their HF intralayer counterparts [3]. In addition, studying LF interlayer modes provides insights into the nature of the underlying couplings between the layers. Recent advances in Raman-spectroscopy hardware have made it possible to resolve the LF modes with a standard Raman set-up opening the field of investigation of these modes in 2DMs [3].

Here, we present a combined experimental and theoretical study of LF Raman active modes of few-layer MoS2 intercalated with silver. Using Density Functional Theory (DFT) we predict a significant red shift of the modes of MoS_2 upon Ag intercalation and with increasing Ag concentration in few-layer. However, this effect subsides as the number of MoS_2 layers grows as is supported by the linear chain model for the low-frequency shear and breathing modes for systems with the number of layers corresponding to experimental sample thicknesses. The low-frequency interlayer Raman modes are more susceptible to changes of interlayer couplings [3] and are modified due to presence of silver in the van-der-Waals gap of MoS_2 .

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Crystallization and chemical analysis of Li_{7-3x}Al_xLa₃Zr₂O₁₂ thin films deposited by a novel sol-gel-derived wet chemistry method

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An increased demand for portable electronic devices and electric vehicles has attracted tremendous attention to develop next-generation electrochemical energy storage devices with higher energy and power densities, longer lifetime, and improved safety. Compared with current market-dominant conventional liquid-electrolyte lithium-ion batteries, all-solid-state batteries with ceramic Li-conducting electrolytes allow increased thermal stability, a larger electrochemical stability window, and higher volumetric energy densities. More importantly, solid electrolytes show promise to effectively prevent lithium permeation, which greatly enhances the battery safety and lifetime. While many studies have been carried out on bulk lithium-conducting solid electrolytes, thin films are the preferred choice for future applications as it can effectively reduce the bulk resistance of the electrolyte layer, and therefore, improve the energy density of the battery. Among the many Li-ion conductors, garnet-based materials, especially Li₇La₃Zr₂O₁₂ (LLZO), exhibit several exceptional properties, including its wide electrochemical stability window, high room temperature Li-ion conductivity, and good thermal stability, which makes it become one of the most promising candidates for all-solid-state batteries. Several studies have demonstrated a promising room temperature ionic conductivity of LLZO thin films using vacuum-based deposition techniques, such as pulsed laser deposition (PLD)¹ and sputtering². Only a few groups have demonstrated the possibility to synthesize LLZO thin films using scalable wet chemical methods such as sol-gel-derived spin coating³ and dip coating⁴ which are of essence for mass-manufacturing. Amongst these techniques, there is still a lack of understanding in the kinetics of the LLZO phase formation via wet chemistry routes.

In this study, LLZO thin films are prepared via a sol-gel-derived wet chemistry method. The crystallization and phase transitions of the LLZO thin films during annealing processes were studied by *in situ* Raman spectroscopy and differential scanning calorimetry (DSC). Furthermore, X-ray photoelectron spectroscopy (XPS) was used to study the surface chemistry of the films during the phase transformation processes. Our results reveal that the as-deposited films undergo several phase transformation processes and the pure garnet phases can be obtained in an attractive low temperature range. Additionally, we investigated the effect of precursor composition on the phase transformation. This work provides a better understanding of the LLZO phase formation through wet chemistry synthetic methods and offers valuable insight for the design and synthesis of electrolytes for all-solid-state lithium batteries.

Acknowledgments

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Optimizing polymer components in capacitors and batteries

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Ongoing progresses in advanced energy storage devices such as lithium ion batteries, sodium ion batteries, and supercapacitors are often focused on inorganic active lithium compounds, silicon nanostructures, and carbon materials such as nanostructures. Although those inorganic components dominated the current research of electrode and electrolyte materials because of their superior ion conductivity, cyclability, charge capacity, and capacitance, their distinctive disadvantages, however, include costly and challenging processing, grain-boundary-limited interfaces, and to-be-improved mechanical properties. In this talk, we retraces our efforts since 2007 in using polymer nanostructures to supplement or partially replace inorganic components for energy storage applications. Polymer nanostructures¹⁻⁷ such as PEO and PVDF based block copolymers and nanocomposites can provide possibilities towards mechanically robust, flexible, high performance batteries and capacitors. Other possible advantages of using polymer nanostructures includes self-healing behaviors and reduced fire hazard. We believe polymer components will play more and more important roles in future designs of next-generation advanced energy storage systems.

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Facile Fabrication of Large-Area Atomically Thin Membranes by Bottom-Up Synthesis of Nanoporous Monolayer Graphene

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Direct, bottom-up synthesis of graphene with well-defined pores over large areas can transform the fabrication of nanoporous atomically thin membranes (NATMs) and greatly enhance their potential for practical applications. However, scalable bottom-up synthesis of continuous sheets of nanoporous graphene that maintain integrity over large areas has not been demonstrated. Here, we show that a simple change in processing conditions during chemical vapor deposition (CVD) on Cu induces *in-situ* formation of nanoscale defects (\leq 2-3 nm) in the graphene lattice, enabling direct and scalable synthesis of nanoporous monolayer graphene. By solution-casting of hierarchically porous polyether sulfone (PES) supports on the as-grown nanoporous CVD graphene, we demonstrate large-area (> 5 cm²) nanoporous atomically thin membranes (NATMs) for dialysis. The synthesized NATMs show size-selective diffusive transport and effective separation of small molecules and salts from a model protein, with ~2-100× increase in permeance along with better/comparable selectivity to state-of-the-art commercially available polymeric dialysis membranes. Our membranes constitute the largest fully functional NATMs reported to date, which can be easily scaled up to large sizes permitted by CVD synthesis. Our approach highlights synergistic benefits in blending traditional membrane casting with bottom-up pore creation during graphene CVD for advancing NATMs towards practical applications.

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Absolute Molecular Weight and Structural Analysis of Low Polydispersity Lignin through Small Angle Neutron Scattering

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Lignin is one of the most abundant organic polymers comprising 30% of woody biomass on a dry basis only surpassed by cellulose. Majority of the lignin is burnt as a cheap fuel source but there is enormous potential to convert lignin into a valuable chemical. Lower value applications like manufacture of phenolic resins, polyurethane foams and clean burning fuels require relatively low purity lignin (1-3% ash and metal contents e.g., 1500-7500 ppm sodium) whereas higher value applications like carbon fiber synthesis require ultra-pure lignin (metal content of < 100 ppm sodium). Major challenges in exploiting lignin is in separation and purification of recovered biomass to yield a high purity lignin stream that can be used for low and high value applications. Recently, Thies and coworkers at Clemson University have developed scalable methods of isolating ultra-pure lignin (<100 ppm sodium) with narrow molecular weight fractions by exploiting a novel liquid–liquid equilibrium (LLE) phase behavior. Three fractionated–solvated lignin precursors (FSLPs) of increasing molecular weight (7200, 13800, and 28600 Da measured through gel permeation chromatography (GPC) with polyethylene glycol standards) were obtained via the continuous Aqueous Lignin Purification using Hot Acids (ALPHA) process. Carbon fibers spun by Ogale and coworkers from the high molecular weight fraction lignin demonstrated the highest mechanical properties ever obtained for carbon fibers derived from lignin.

In this work, small angle neutron scattering (SANS) was utilized to determine the absolute molecular weight of the lignin fractions through Zimm analysis and the molecular morphology of lignin was investigated for different molecular weight fractions. We observed major differences between molecular weight determined through GPC and Zimm analysis from SANS. Structurally, lignin monomers were cylindrical/ellipsoidal in shape, with effective radius of monomers remaining unchanged between different molecular weight fractions. However, an increase in effective length of the units was observed with increasing molecular weight of lignin fractions. It has been postulated that, linear or elongated lignin molecules are superior precursors for carbon fibers compared to branched or globular lignin. Our findings corroborates the mechanical strength measurements from Ogale and coworkers, where elongated lignin moieties from higher molecular weight fractions of lignin yielded the strongest carbon fibers.



Figure. (A) Scattering intensity for different lignin fraction fit to unified power law in low q regime and ellipsoid model in the intermediate to high q regime. (B) Unified power law, R_g, (C) and (D) Radius and lengths respectively, obtained from ellipsoid model fitting.

Phospholipid Bilayer Softening in the Presence of Hydrophobic Gold Nanoparticle Inclusions

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Liposome-nanoparticle assemblies (LNAs) are of great significance in the context of novel targeted drug delivery systems and provides a model system to study lipid bilayer dynamics in presence of functionalized nanoparticles. A major challenge in the field of stimuli-responsive LNAs is to ascertain changes in lipid bilayer structural and mechanical properties like bilayer thickness, bending modulus and area compressibility modulus, brought about by nanoparticle inclusions. Structural properties and dynamics in presence of nanoparticle inclusions are equally relevant from the nanotoxicology perspective, as bending fluctuation in lipid bilayers is directly linked to numerous biological processes and overall maintenance of membrane integrity.

In this current work, we present experimental evidences demonstrating effects of hydrophobic gold nanoparticles inclusions on the structure (bilayer thickness) and dynamics (bending modulus and area compressibility modulus) of a model liposomal mixed-phospholipid bilayer. LNA formation and structure has been investigated in great detail by a combination of cryo-transmission electron microscopy and small angle neutron scattering. Neutron spin echo spectroscopy demonstrated a remarkable bending modulus decrease of $\approx 15\%$ for LNAs relative to pure liposomes. Our findings points towards local bilayer fluidization by nanoparticle inclusions leading to an overall bilayer softening. We demonstrate the use of neutron spin echo spectroscopy as a vital tool in quantification of nanoparticle-membrane interactions. These findings adds valuable information to the field of novel liposomal drug carriers and mechanism of nanoparticle toxicity.



Figure 6. (A) Bending moduli κ of DPPC/DPPG bilayer with included AuNP. Inset shows bending moduli in fluid phase only. Dashed lines are for visual aid only. Error bars represent one standard deviation from the mean. Transition temperature of DPPC/DPPG bilayer is 41 °C. (B) Schematic demonstrating increase in area per lipid in the vicinity of an AuNP inclusion.

Ligand Softness Affects Catalytic Activity and Reusability of pH Responsive Colloidal Gold Nanoparticle

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Colloidal gold nanoparticle (AuNPs) provides the benefit of selectivity, greater surface area per catalyst mass compared to supported catalysts, catalyzes reactions under mild conditions and are very effective for chiral catalysis. Recovery of colloidal catalysts involve tedious methods like pH or temperature induced aggregation, solvent extraction, etc. For colloidal catalysts, surface functionalization with ligands is a prerequisite to prevent aggregation but surface passivation with ligands causes significant reduction in catalytic activity. Functionalization of colloidal AuNPs with stimuli responsive ligands provides enhanced recovery and reuse of catalysts.

In this work, we have introduced thiol moieties in polyacrylic acid to generate thiolated polyacrylic acid (PAA-SH) and functionalized colloidal AuNPs with PAA-SH to impart pH responsive properties in gold nanoparticles (AuNP-SPAA). Two pH triggered recovery schemes were investigated: a) pH triggered aggregation-redispersion and b) pH triggered phase transfer. We observed loss in catalytic activity with each cycle for AuNP-SPAA with low thiol content. To ameliorate this problem, we have investigated catalytic activities of AuNP-SPAA with increasing thiol contents. In AuNP-SPAA with low thiol content, loss of activity was ~98% within 5 cycles of reuse when the reuse scheme (a) was used. Catalytic activity however, was maintained when (b) recovery scheme was employed (~42% loss by 5 cycles). AuNP-SPAA with higher thiol content demonstrated loss in reaction rate, but with much greater recoverability for scheme (a) (~25% loss in 5 cycles) and (b) (17% loss in 5 cycles) recovery. Loss in catalytic activity was primarily attributed to polymer desorption leading to permanent aggregation of AuNP-SPAA during each cycle.

To demonstrate that softness of polymer (various thiol content) played a major role in catalytic activity of AuNP through surface passivation, small angle neutron scattering (SANS) was utilized to characterize the polymer conformation, shell thickness, shell scattering length density and ligand shell solvation. It was observed that polymers were arranged in a 'carpet' conformation due to multiple thiol linkages to AuNP surface. Decreasing shell thickness and shell solvation with increasing thiol content in polymer corroborated surface passivation of AuNP by polymer leading to lowering of catalytic activity.



Figure 1. (A) Scheme for pH triggered recovery of AuNP-SPAA. (B) Decrease in shell thickness and (C) decrease in shell solvation as observed from SANS. (D) Plot showing improved reusability of catalysts for higher thiol content in ligand.

PEG-based Polyampholytes as Cryoprotectants

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Improved cryoprotectants are necessary to enable complete recovery of living cells and tissue after frozen storage. A key challenge in cryopreservation is addressing both mechanical and osmotic stress on cells as ice grows and extracellular solutes become concentrated when water freezes. Herein, we synthesized a new class of polyether-based polyampholytes capable of acting as efficacious cryopreservative agents.. Excellent biocompatibility was demonstrated, and cryoprotective ability was evaluated for each material. Salt-, and membrane-binding behavior was studied through conductimetric and calorimetric techniques as well as direct imaging. Finally, we employed the high compositional tunability of these PEG-based polyampholyte materials to examine the effect of charged group structure on coacervation and cryoprotection.

Numerical Studies of Competing Phases of Matter in Hubbard Model and Beyond.

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Electron-electron interactions in strongly correlated electron systems, including high-temperature superconductors, represent an outstanding problem in condensed matter physics. Revealing the origin of emerging quantum states of matter in such 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 [3] there has been much recent progress reached. Particularly, significant progress has been achieved in numerical studies of the Hubbard model, which is one the commonly used minimal models for description of the electron-electron interactions in such systems.

There is growing recognition that the proper analysis of strongly correlated materials requires the study of more realistic (beyond Hubbard) models. The assumption of purely local on-site interactions used in Hubbard model becomes inaccurate in systems where long-range interactions cannot be neglected, and can lead to sizable screening effects, cause Wigner-Mott transitions and even lead to charge ordering. Charge ordering of electrons is now considered to be a ubiquitous feature of many low-dimensional strongly correlated systems, including high temperature superconductors, organic superconductors and manganites, and is the primary focus of our study.

Understanding the charge order and its interplay with other phases of matter requires the development and application of numerical many-body algorithms for extensions of Hubbard model. Here we discuss our progress on numerical studies of various phase transitions in the extended two-dimensional Hubbard model using our recently developed Quantum Monte Carlo non-local interaction algorithm [4] and the CNMS-based DCA+ framework. We first study the competition of charge order and metallic Fermi liquid phase in two-dimensional extended Hubbard model using the dynamical cluster approximation [3]. We find, that the model exhibits the metallic, Mott insulating and charge ordered phases under the change of control parameters (temperature, nearest neighbor electron-electron interactions, local onsite interactions and doping). The charge ordered phase is characterized by a checkerboard arrangement of electrons with non-zero staggered density. We find that the charge order phase is of band-insulating-like character with weak electron correlations. Our studies reveal noticeable non-local correlations and pronounced screening effects especially in the vicinity of the transition, indicating the necessity of non-local many-body algorithms, like ours, for proper analysis of such transition.

Our second focus 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 of the two-dimensional Hubbard model have questioned the very presence of the metal-insulator transition in two dimensions, and have shown that strong spatially extended antiferromagnetic correlations lead to insulating behavior at any finite onsite interaction. In our recent study we find that the non-local inter-site Coulomb interactions decrease correlation effects via screening, resulting in more metallic behavior. This suggests that the inclusion of an inter-site Coulomb-interaction in the analysis may stabilize the metal-insulator transition in two dimensional electron systems. Hence, the non-local electron-electron interactions can be considered as a plausible route towards the stabilization of the metal-insulator transition in two dimensional electron systems of the effect of non-local interaction on the Mott transition using the recently developed non-local Quantum Monte Carlo method [4] for several cluster sizes. Our results provide the first systematic numerical evidence of stabilization of the Mott transition by non-local electron interactions, and advance our understanding on this fundamental subject of electron localization in two dimensions.

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Mechanically Robust Organic Photovoltaics Using Thiol-Ene Interpenetrating Networks

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Conjugated polymers combine the solution processability of polymers with the electronic properties of conductors or semiconductors, enabling a variety of low-cost devices, including photovoltaics, transistors, and batteries. However, conjugated polymers have poor mechanical properties, limiting their viability for flexible devices. Molecular engineering of the semiconductive material can enhance mechanical properties but oftentimes is detrimental to electronic properties and overall device performance. Here, I will present a general approach to fabricating flexible bulk heterojunction organic photovoltaics (OPVs) through the incorporation of an elastic and mechanically robust interpenetrating network. Reactive small molecule thiol-enes are incorporated in the active layer through solution blending, casting, and post-deposition crosslinking. A thiol-ene network is formed through short, one-minute exposure to UV light or with an amine catalyst. This results in fully functional devices with significantly increased crack-to-onset strain and flexibility. The approach is compatible with a variety of donors and acceptors and results in significant enhancement of mechanical properties and device flexibility.





Optical Micrographs near critical strain

In Situ Characterization of Electric-field Induced Migration and Orientation of Species in Electroactive Polymeric Systems.

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An ionic polymer's electromechanical response to an applied electric field gives it unique properties that can be useful in systems such as transducers, batteries, or biomedical devices. While common ionic polymers such as Nafion have been extensively studied, one component of their functionality that has not been fully explored is the impact of how chemical structure, ion mobility, and morphology change the response of the material to an applied electric field. An understanding of the electromechanical response at this fundamental level would promote the rational design of ionic polymer systems for functional applications. We have used *in situ* Fourier Transform Infrared Spectroscopy (FTIR) measurements under an applied electric field to address this lack of understanding. By manipulating incidence angle and polarization, migration and orientation of species throughout a sample can be tracked. Performing this analysis under various electric fields allows the probing of electromechanical response as a function of field strength, ion identity, and film thickness. Measurements were initially done on Nafion membranes to benchmark the protocol to a well-characterized system and later on AB ionic diblock copolymer films comprising polystyrene and an imidazolium containing ionic block. These studies were compared to the electromechanical response of thin films probed using neutron reflectometry to gain insight into differences in behavior between thin film systems (~ 20 nm) and bulk membranes ($\sim 100 \,\mu$ m). Identifying the impact ion identity, film morphology, and chemical structure on the electromechanical response of a material provides a means for establishing the ability to maximize the functionality of polymeric systems when designing materials for targeted applications.

Using Broadband Dielectric Spectroscopy to probe chain dynamics in 3-Miktoarm Poly(Styrene-Isoprene₂) Star Copolymers

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Broadband dielectric spectroscopy (BDS) is used to probe the chain and segmental dynamics of three AB₂ miktoarm star copolymers based on polystyrene (PS, A block) and polyisoprene (PI, B block) with various polystyrene volume fractions ($\phi_{PS} = 0.43$, 0.30 and 0.19). The two systems displaying lower ϕ_{PS} revealed phase separated morphologies of PS spheres while the former displayed lamellar morphology as determined using small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM). Dielectric measurements were made below the dynamic glass transition temperature of the PS block to probe chain and segmental dynamics of the PI chains tethered to a glassy interface. No change in the distributions of segmental or chain relaxation rates were observed with changing molecular weights or morphology. This result is attributed to the asymmetry in the molecular architecture causing decreased constraints on chain motion allowing the effects of morphological and thermodynamic confinement to be reduced in these materials. Furthermore, the power law relation between the chain relaxation time (τ_n) and PI arm molecular weight was found to be significantly slower. These results are discussed in terms of current theories of polymer dynamics regarding cross correlation of chain motion.¹⁻⁴



Figure 1: Maximum dielectric loss chain relaxation times (τ_n) for various PI systems. 3-miktoarm star displays slowest chain relaxation times, but similar power law relation to arm molecular weight ($M_{w,arm}$).

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Mechanistic Insight into the Conversion of Ethanol and Acetaldehyde to 1,3-Butadiene over Supported ZrO₂/SiO₂ Catalysts

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Abundant and low-cost shale gas has replaced naphtha as the feedstock of choice for C₂-C₄ olefin production that has led to a shortage of 1,3-butadiene (BD), a critical intermediate for the manufacture of synthetic rubber.¹ The constrained BD supply has triggered price fluctuations and interest in on-purpose BD production.¹ Cellulosic ethanol is a sustainable feedstock quickly becoming mainstream and its conversion into BD significantly reduces lifecycle greenhouse gas emissions when compared to petroleum-derived BD.² Supported ZrO₂/SiO₂ catalysts show particular promise for the conversion of ethanol and the intermediate acetaldehyde to BD. However, the reaction over supported ZrO₂/SiO₂ catalysts remains poorly understood, with few mechanistic³ studies and no spectroscopic studies under reaction conditions. Supported ZrO₂/SiO₂ catalysts were synthesized by incipient-wetness impregnation of zirconium npropoxide, dried at room temperature and 300 °C in nitrogen and calcined at 500 °C in air. The catalysts were spectroscopically characterized with in situ UV Raman spectroscopy and operando DRIFTS. In situ Raman spectra revealed that the supported ZrO_x phase was present as a two-dimensional amorphous overlayer (≤ 1.4 Zr/nm²). During temperature programmed surface reaction, operando DRIFTS revealed that ethanol adsorbs as surface ethoxy (CH₃CH₂O^{*}). Adsorbed acetaldehyde forms a surface enolate species (CH₂=CHOH^{*}) with increasing temperature, which is concomitant with the formation of adsorbed 3-hydroxybutanal (CH₃CH(OH)CH₂CHO^{*}), crotonaldehyde (CH₃CH=CHCHO^{*}), and crotyl alcohol (CH₃CH=CHCH₂OH^{*}). Finally, 1,3-butadiene (CH₂=(CH₂)₂=CH₂) gas phase production is observed. The observed surface chemical transformations are the first direct evidence of key intermediates in the aldol condensation and Meerwein-Pondorf-Verley-Oppenauer reduction mechanisms to yield BD over supported ZrO₂/SiO₂ catalysts.

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Computer-controlled high-throughput functional characterization of thin films

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Growing demand for multifunctional thin film IoT sensors necessitates the development of specialized tools for high throughput, multi-mode characterization of thin films under a wide range of environmental conditions combined with advanced statistical and AI-coupled data analytics. A specially-designed Integrated Multifunctional Environmental System (IMES) and associated software workflow enables simultaneous testing of electrical, gravimetric, viscoelastic and optical sensing modalities of thin films using quartz crystal microbalance with dissipation mode, electrical impedance spectroscopy and spectroscopic ellipsometry to enable characterization of dielectric response of thin films to environment across a broad (mHz to THz) frequency range. Custom IMES software controls experimental testing conditions and streamlines sensor response analysis using a combination of advanced statistics, machine learning, and physical modelling protocols. 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. Future development of IMES will incorporate predictive physical modelling of thin film response into a feedback loop for automatic real-time selection and modification of experimental testing conditions.

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

Active mixing in aggregations of black soldier fly larvae

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Black soldier fly larvae are maggots that eat twice their body weight per day in decomposing organic matter, and that can be used as a nutritious feed for chickens and fish. Although one larva is tiny, these larvae live in huge aggregations that can outcompete many other scavengers eating a food source. We investigate how these larvae feed using both time lapse and high speed imaging. A large group of larvae is limited by the surface area of the food they are eating and the inability of one larva to eat continuously. We show using particle image velocimetry and individual tracking that there is a net flow of larvae around a piece of food. Agent-based modeling can also be used to investigate this flow, as in the poster by Ethan Brady, Eagle Yuan, Jan-Michael Carrillo, and Miguel Fuentes-Cabrera. Larvae in an aggregation around a piece of food crawl towards it throughout the aggregation and fall away from the food on top. This results in a region of active mixing, allowing larvae to replace each other around a piece of food and make up for some of the limitations in their eating. This same flow occurs around inedible objects, indicating that these larvae evolved to detect food through collective sensing rather than a sense of smell.

Development of an Integrated Scanning Photocurrent Microscopy System for Multifaceted Nanomaterial Characterization

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The development of a unique nanomaterial characterization tool, a scanning photocurrent microscopy system, is detailed, allowing spatially resolved photoresponsivity mapping. This mapping technique for optoelectronic properties of nanomaterials produces several meaningful results, such as carrier diffusion lengths, lifetimes, and mobilities, internal electric field distribution, band bending effects at heterojunctions, photothermal properties, and information about recombination mechanisms. In addition, the instrument can record photoresponse decay time, which provides insights into the electronic levels in the material and rate constants for charge carrier recombination, and it can also perform wavelength-dependent IV curves. The instrument employs monochromatic light from a laser to raster scan a sample to produce a spatially resolved map of photoresponsivity compared to a reference photodiode which is then used to calculate the resulting properties. The equipment has been assembled, integrated, and coded in LabVIEW into a single viable system. The tool has successfully mapped a microscale commercial photodiode as well as characterized 2D material heterojunctions of InSe/WSe2 and MoSe₂/black phosphorous. This tool's results can be used to investigate potential applications of various nanomaterials as photodetectors, solar cells, and other applications regarding their charge separation efficiency or internal gain.

Acknowledgement: This research was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility.

Strongly Cross-Correlated Optical Phonons in Hexagonal Boron Nitride Defects

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Quantum photonic technologies heralds to revolutionize the fields of computing communications. and However. quantum photonics still suffers from its primary limitation: the weak interaction of photons. To generate single photons, quantum photonics has historically relied on nonlinear optical processes suffering from low single photon purity. Hence. solid-state single photon emitters (SPEs) that are robust, bright, high in purity $g^{(2)}(0) \ll 0$, and generate indistinguishable photons are necessary advance quantum photonic to technologies.

Single photon emitters have been recently discovered in the 2D material hexagonal Boron Nitride



Figure 1 - frequency-filtered 2-photon crosscorrelations between the ZPL, LO, LOTO and 2LOTO optical-phonon sidebands.

(HBN) [1]. HBN is an insulating Van der Waals crystal with a wide indirect bandgap (~6eV), and therefore has desirable material properties (electrical, optical). SPEs in HBN have narrow linewidths, bright emission ~ 10^6 s⁻¹ [2], small Huang-Rhys factors (.2-1.2) [2], and are photostable with purities in the range of $g_{-}^{(2)}(0)$: .08-.46 up to 800K [3]. Given these attractive features, there has been a rapid growth in the study of HBN defect centers. However, the state structure and electron-phonon dynamics of these defects are still poorly understood.

We explore the electron-phonon dynamics of defects in multilayer HBN. We conduct colored Hanbury Brown-Twiss interferometry and compare our findings with a two-state model of the frequency-filtered 2-photon correlations $g_{\Gamma}^{(2)}(\omega_1, \tau_1; \omega_2, \tau_2)$. Concurrent with these measurements we perform photoluminescent spectroscopy and compare the observed spectra to a Huang-Rhys model. We report antibunching in $g_{\Gamma}^{(2)}(\omega_1, \tau_1; \omega_2, \tau_2)$ between the zero phonon line (ZPL) and the LOTO and LO one-optical-phonon sidebands as seen in Fig.1, whereas we observe $g_{\Gamma}^{(2)}(\omega_1, \tau_1; \omega_2, \tau_2) \approx 0.5$ between the ZPL and the 2-optical-phonon sideband. This is in stark contrast to the expected value of $g_{\Gamma}^{(2)}(\omega_1, \tau_1; \omega_2, \tau_2) \geq 1$ when $\omega_i/\Gamma \geq 1$ for an ideal two-level system. For a two-level system $g_{\Gamma}^{(2)}(\omega_1, \tau_1; \omega_2, \tau_2) \geq 1$ is a result of the energy-time Heisenberg uncertainty relation. These effects, which have not been observed in another defect, offer the first insights into the electron-phonon dynamics of solid-state emitters.

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Atomic Structure and Electrical Activity of Planar Faults in Lead-halide Perovskites

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Lead-halide perovskites have emerged as a promising class of highly efficient and affordable semiconductors with applications in solar cells and optoelectronic devices. One of the key features of these lead-halide perovskites is their defect-tolerance,¹ which is their ability to retain high-performance even in the presence of a large concentration of defects. Point defects in lead-halide perovskites either lead to shallow defects levels or resonant levels within the valence or conduction bands, which allow efficient carrier transport. In addition to point defects, planar-defects, such as grain boundaries, present in these perovskites can also have a significant impact on the electronic structure. However, direct observation of the atomic structure of grain boundaries in lead-halide perovskites and their effect on charge transport is missing.

In this work, we have combined aberrationcorrected scanning transmission electron microscopy (STEM) with first-principles density-functional theory (DFT) calculations to resolve the atomic and electronic structure of planar defects in fused CsPbBr₃ nanocrystals that are attractive for optoelectronic applications such as in display panels and light-emitting diodes. From STEM imaging, we observe that the fusion of these nanocrystals occurs through two prevalent planar defects: a Br-rich $\sum 5$ grain boundary and Ruddlesden-Popper (RP) planar faults. Figure 1a shows a high-angle annular dark field (HAADF) image of the $\sum 5$ grain boundary (top) and RP-planar fault (bottom). The RP-planar fault is made up of an additional layer of CsBr with the rock salt structure, whereas the $\sum 5$ grain boundary is made up of shared Pb, Cs and Br atoms.



Figure 1. (a) HAADF images and (b) DFToptimized crystal structures showing a $\Sigma 5$ grain boundary (top) and a RP-planar fault (bottom) in CsPbBr₃. The scale bars correspond to 1 nm. (d) Density of states (DOS) plot for the planar defects and pristine CsPbBr₃.

We have used DFT calculations to resolve the three-dimensional structure of both the planar faults (as shown in Fig. 1b) and their effect on the electronic properties (Fig. 1c). In conventional semiconductors, planar defects introduce mid-gap states, which can act as nonradiative recombination centers and consequently deteriorate optoelectronic performance. However, the DFT calculations reveal that neither the $\Sigma 5$ grain boundary nor the RP-planar defects in CsPbBr₃ induce mid-gap states, as shown in Fig. 1c, which lends support to the defect-tolerant nature of these perovskites. We also predict the growth conditions under which the grain boundaries lead to mid-gap states, which resolve contradictory reports on the experimentally observed activity of grain boundaries in lead-halide perovskites.^{2,3} Moreover, we predict that the $\Sigma 5$ grain boundary repels electrons but attract holes, while the RP planar fault repels both electrons and holes and lead to strong quantum confinement. Overall, our results highlight novel functionalities that can be achieved in lead-halide perovskites by the control of these planar defects.

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High-Contrast Resonance Excitation and Identification in Photonic Crystal Nanobeams

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Here we present the (i) design and realization of photonic crystal nanobeam (PCN) devices for high-contrast excitation of fundamental resonances and (ii) identification of PCN resonance modes via far-field scattering. The PCN devices were fabricated at the CNMS and measured at Vanderbilt.

I. Photonic Crystal Nanobeams for High-Contrast Resonance Excitation (arXiv:1805.09438)

Enhancement of light-matter interaction is key for achieving higher efficiency and lower threshold power in optical signal processing, photovoltaics, optical sensing and optical trapping. One metric used to characterize light-matter interaction is the ratio of the optical quality factor (Q) of a photonic structure to its mode volume (V). Photonic crystal nanobeam (PCN) cavities exhibit the highest Q/V ratio among photonic structures. However, it is generally difficult to experimentally excite their fundamental mode with the highest Q/V using a traditional in-line coupling configuration (Fig. 1(a) top). In this work, we show that by evanescently side-coupling into resonant modes with a lateral bus waveguide (Fig. 1(a) bottom), it is possible to access low order modes. Fig 1(b) demonstrates that tuning the overlap of the bus waveguide and cavity resonance modes in physical space and k-space enables a 100 times increase in the peak amplitude for the fundamental resonance peak, circled and labeled (i), compared to performance by an in-line cavity.

II. Identification of Resonance Modes via Far-Field Scattering

PCN cavities, in general, support multiple resonance modes, each with unique field profiles and optical confinement metrics. Accordingly, verification of mode order in PCN cavities is important for the characterization of Q/V performance and the application of resonant modes for enhancing light-matter interaction. As shown in Fig. 1(c), for the fundamental resonant mode in a PCN cavity, we can calculate the out-of-plane scattering in the far-field from the PCN resonance. By utilizing an IR camera, Fig. 1(d) demonstrates we can image the scattered light and identify various resonant mode orders by the unique far-field optical profiles. By minimizing undesirable scattering noise via side-coupling, this method easily provides information on mode order without having to utilize a scanning nearfield optical microscopy tool.



Fig. 1. (a) SEM images and (b) transmission spectra of in-line and side-coupled PCN cavities fabricated at CNMS. (c) FDTD simulation of electric field profile and far-field scattering profile for the fundamental resonance of a PCN cavity. (d) Experimentally measured far-field scattering profiles from an IR camera. Images correspond to peaks labeled in (b).

Abstract for Poster Presentation at 2018 ORNL CNMS User Meeting

Ultrastructure and Enzymatic Hydrolysis of Deuterated Switchgrass

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Abstract

Neutron scattering of deuterated plants can provide fundamental insight into the structure of lignocellulosics in plant cell walls and its deconstruction by pretreatment and enzymes. Such plants need to be characterized for any alterations to lignocellulosic structure caused by growth in deuterated media. Here we show that glucose yields from enzymatic hydrolysis at lower enzyme loading were 35% and 30% for untreated deuterated and protiated switchgrass, respectively. Lignin content was 4% higher in deuterated switchgrass but there were no significant lignin structural differences. Transmission electron microscopy showed differences in lignin distribution and packing of fibers in the cell walls (Fig. 1) that apparently increased surface area of cellulose in deuterated switchgrass, increasing cellulose accessibility and lowering its recalcitrance. These differences in lignification were likely caused by abiotic stress due to growth in deuterated media.



Fig. 1. TEM images of transverse sections of protiated (A, C) and deuterated switchgrass (B, D). Images C and D show magnified regions for the highlighted regions A and B in images A and B, respectively. Scale bars: A, B - 10 μ m and C, D - 1 μ m.

Adapting Microfluidics for Radioisotope Separations

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This study presents the use of microfluidic devices for the separation of radioisotopes for biomedical applications. These devices have previously been used for biochemical separations [1]. We have developed a microfluidic chromatographic system incorporating a cadmium zinc telluride (CZT) in-line gamma-ray detector and have applied this to the separation of radium-225 ($t_{1/2}=15$ d) from its daughter isotope actinium-225 ($t_{1/2}=10$ d). Ion-exchange chromatography is a crucial tool in the separation and purification of radioisotopes for biomedical applications. Often, a series of large columns using multiple resins form the basis for these multi-day campaigns. The final products have many uses from imaging and diagnostics, to palliative and therapeutic treatments. Our studies focus on the production of radioisotopes for targeted alpha-therapy which presents challenges representative of the greater field. Targeted alphatherapy (TAT) employs targeting agents, e.g. monoclonal antibodies, to deliver highly energetic alpha particles to cancer cells for their destruction, while minimizing collateral damage to adjacent normal cells. Bi-213, one of the most commonly used alpha-emitters in TAT and is available from the decay of Ac-225 in a generator system. Applying microfluidic "lab-on-a-chip" technology to these radiochemistry processes conserves valuable reagents, reduces workers' exposure to radiation, and allows production of valuable chemicals, including radiotherapeutic agents, on a scale suitable for research or for individual doses. In these proof-of-concept studies, microfluidic devices were packed the BioRad AG50 X4 cation exchange resin (40-70 μ m) with bed volumes in the range of 10 – 100 μ L. The AG50 X4 resin was loaded with uCi amounts of Ra-225 and was successfully separated its daughter Ac-225. Elution was monitored in real-time using an in-line CZT detector and samples were fractionated and counted offline with a sodium iodide gamma counter to confirm the results. The separation achieved was comparable to the results of Boll et al (2004) [2] with 95% of the Ra-225 removed in the 1.2 M HNO₃.

These positive results show potential for greater use of microfluidics in biomedical radiochemistry. The modularity of the system and compatibility with different resins allows the system to adapt quickly and easily to the various needs of a separation campaign. The reduction in materials and the improved safety could also increase access to medical radioisotopes by researchers who lack high level radiation facilities.

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Development of a Micro-Actinium-225/Bismuth-213 Biomedical Generator System

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Targeted alpha-therapy (TAT) employs targeting agents, e.g. monoclonal antibodies to deliver highly energetic alpha particles to cancer cells for their destruction, while minimizing collateral damage to adjacent normal cells. Bi-213, one of the most commonly used alpha-emitters in TAT, has a half-life of 45.6 minutes, and is available from the decay of Ac-225 ($t_{1/2}=10$ d) in a generator system. Microfluidic "lab-on-a-chip" technology allows many chemical processes to be scaled to the micro- or nano-scale. Miniaturization conserves valuable reagents, reduces workers' exposure to radiation and allows for the production of valuable chemicals, including radiotherapeutic agents on a scale suitable for research or individual doses. An Ac-225 generator using BioRad MP50 cation-exchange resin in a chromatographic column format is typically used to produce Bi-213. In this study, microfluidic devices analogous to these large, resin filled columns have been used to separate Bi-213 from Ac-225. In this proof of concept study, microfluidic devices were loaded with MP50 resin (50-70 μ m) with bed volumes in the range of 10 $-100 \,\mu\text{L}$ and were loaded with $\mu\text{C}i$ to mCi quantities of Ac-225. Similar to macro-generators, Bi-213 is eluted from micro-generators with 0.1 M KI/0.1 M HCl with an overall yield of ~75% (decay corrected to start of Bi elution), and Ac-225 breakthrough of $\sim 2x10^{-3}$ %. Further, Bi-213 from micro-generators has been shown to efficiently label a diethylenetriaminepentaacetic acid (DTPA)-conjugated monoclonal antibody. Work to optimize these devices is ongoing, and future work will examine incorporation of onchip labeling and separation of labeled antibody from free Bi-213.

Microsystems for studying the effects of radiation on human cells and tissues

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Studies of human lung injury from acute gamma radiation exposure rely on the use of animal models and static two-dimensional cell cultures, neither of which can accurately represent human physiological conditions. Animal models also poorly reflect the effects of drug treatments in humans, as seen in the many drugs studies which were successful in animal models but failed when moved to the clinical stage of development.¹ Organ-on-a-chip models allow for the creation of biologically relevant experimental co-culture systems that more accurately reflect the dynamic microenvironment of human organs.² While existing organ-on-a-chip technology is limited to 1-2 μ L internal volumes, we have developed a scaled design that allows for 16 μ L volumes of medium to flow through the device. The larger bed volume enables off-chip analysis of the collected media to monitor the production of secreted signaling molecules, and other biomarkers of damage and inflammation.

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Ionic and Electronic Properties of Twin Domain in MAPbI₃

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Abstract

The twin domains in methylammonium lead triiodide (MAPbI₃) have been inconclusively reported to be ferroelectric and/or ferroelastic, starting the discussion on the ferroic nature of these twin domains. Given the coupling of defect chemistry and the ionic states with ferroelectricity/ferroelasticity, the chemical behavior of these twin domains can no longer be ignored.

Our earlier investigations revealed these domains to be ferroelastic with ion segregation correlating to domain contrast. In this work, we systematically explore the chemical evolution of the ion migration in the MAPbI₃ twin domains. Using Band Excitation Contact Kelvin Probe Force Microscopy (BE-cKPFM), we demonstrate that there is no ferroelectric polarization switching in this material, with our data indicating an underlying electrochemical effect driven by ion diffusion. This disproves the ferroelectric origin of the previously observed butterfly hysteresis loops in Switching Spectroscopy piezoelectric force microscopy (SS-PFM). Additionally, Band Excitation Scanning Kelvin Probe Force Microscopy measurements were used to detect the electrochemical evolution of the twin domains. Detailed analyses indicate that the difference in ion migration and/or surface charging effect in the adjacent domains implies an ionic origin for different conductivity and the variation of electronic properties. To clarify the correlation between ionic diffusion, the electronic properties and chemical segregation, we used in-situ band excitation PFM (BE-PFM), nanoscale infrared spectroscopy (Nano IR), and scanning probe microscope (SEM) measurements. Combining Nano IR and SEM images, we reveal that the methylammonium segregation decreases conductivity. The relation between BE-PFM and BE-cKFPM data indicates that the presence of methylammonium leads to an increase of ionic conductivity. These results suggest that methylammonium segregation results in longterm decrease and short-term increase of conductivity. This work describes ionic and electronic conductivity in the MAPbI₃ twin domains, imperative to the performance of photovoltaic devices.

Oxidative coupling of methane over SrTiO₃ perovskite catalysts: Influence of surface composition and catalyst bed packing modes

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Abstract: Due to the increase in the production of shale gas (mostly methane), various schemes for direct catalytic methane conversion have regained attention from the research community. One of the routes for upgrading methane is the oxidative coupling of methane (OCM) to C_2 (C_2H_6 and C₂H₄) hydrocarbons. Perovskite-type oxide catalysts have shown high activity and selectivity toward C₂ hydrocarbons. This has been attributed to the segregation of oxygen ion-radicals on the surface and possibilities to create electronic defects and oxygen vacancies on their appropriate structure. However, fundamental understanding of the trends in catalytic reactivity/selectivity is yet to be fully attained. Further, the effect of surface reconstruction (which leads to different surface composition) of perovskites on OCM catalysis has not been reported yet. Doped SrTiO₃ (STO) catalysts with promising C₂-yields for OCM have been reported; therefore, STO is the perovskite structure under study in the present work. Bare STO, Sr-impregnated STO, and chemically etched STO, with surface-Sr compositions between 30 and 97 % (according to low energy ion scattering studies) were employed to catalyze the OCM reaction in a fixed bed reactor. Temperature programmed reaction (TPR) experiments were carried out from room temperature up to 850 °C at a ramping rate of 1.5 °C/min, with inlet methane-to-oxygen ratio of 5. For all samples, in the temperature range 700-850°C, the yield to C₂-products goes through a maximum before hydrocarbon oxidation rates become dominant. At 800°C, for STO catalysts with surface Srcomposition greater than 70%, the C2-yield decreased with increasing Sr-composition at the surface. Although Sr surface-doping suppresses the C₂ yield of SrTiO₃ at high temperature (750-850 °C), CH₄ conversion is enhanced at low temperature (<550 °C), i.e. light-off temperature is down-shifted from 550 °C to 450 °C when the Sr/(Sr+Ti) ratio at the catalyst surface is 0.97. Moreover, a dual-bed OCM reactor configuration was explored. The dual-bed reactor configuration, in which the reactants pass through SrO and subsequent SrTiO₃ beds, resulted in higher C₂ yield (15 %) at 850 °C than the yield obtained (10 %) for a single mixed-bed of SrO and SrTiO₃. This novel dual-bed reactor concept is proved to reduce overoxidization of methyl radicals and consequently enhance the C₂ yield. Current experimental efforts are underway to discern the optimum reaction conditions and surface composition for OCM over SrTiO₃. Kinetic analysis of OCM over STO samples is also on-going by comparing different reaction mechanism models (Eley-Rideal, Langmuir-Hinshelwood and Rideal-Redox models).

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Self-powered fast brazing of Ti-6AI-4V using Ni/AI Reactive Multilayer Films

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Self-powered brazing of Ti-6Al-4V was performed using Ni/Al reactive multilayer films (RMFs) as self-propagated heat resources. BAlSi-4 was first coated on Ti-6Al-4V by plasma welding, then alternating layers of Ni and Al were successfully deposited on BAlSi-4 up to 32.9 μ m thick with e-beam deposition. The joint microstructure was investigated and the AlNi and Ni₅Al₃ phases were identified in the RMF. The cause for the two phases was determined to be differences in the diffusivity of Ni and Al, ultrafast brazing time, and faster cooling at the interface between brazing filler metal and RMF. The maximum temperature of 683 °C has been reached in the brazed joint with a total RMF thickness of 135 μ m, which is more than sufficient to melt the BAlSi-4 brazing material (Fig. 1). A Ni-rich RMF produces dendrite structures on the RMF-BAlSi-4 interface due to reaction between the excess Ni and the brazing material, however the bonding strength

is less than 1 MPa. The maximum bonding strength obtained was 10.6 MPa with an equimolar RMF. It is possible to further improving the bondina strength by using more ductile and/or RMFs modifvina the bonding interface configuration.



Fig. 1: (a) Schematic of the configuration used in brazing experiments. (b) Temperature as a function of time simulated by LAMPS (red, blue and magenta lines) and measured using the highspeed camera (black solid line)

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3D-Printed Carbon Electrodes for Neurotransmitter Detection

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Abstract

Implantable neural microsensors have significantly advanced neuroscience research, but the geometry of most probes is limited by the fabrication methods and new methods are needed for mass manufacturing with high reproducibility. Here, a novel, implantable microsensor fabrication method is developed, using two-photon nanolithography followed by pyrolysis for fabrication of free-standing microelectrodes with a carbon electroactive surface. 3D-printed spherical and conical electrodes were characterized electrochemically and had low dopamine LODs of $11 \pm 1 \text{ nM}$ (sphere) and $10 \pm 2 \text{ nM}$ (cone), high selectivity to multiple neurochemicals, and high reproducibility. Spherical 3D-printed microelectrodes detected dopamine in a brain slice, demonstrating they are robust enough for tissue implantation. This work is the first demonstration of 3D printing of free-standing, carbon electrodes, and the method is promising for mass fabrication of customized, implantable neural sensors.

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Mesoscale Dynamics and Transport in Double Salt Ionic Liquids

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Mesoscale aggregates arising from the solvophobic separation of ionic and alkyl groups into polar and nonpolar regions have been observed for a variety of ionic liquids (ILs).¹ The existence of these distinct regions provides ILs with the ability to solvate both polar and nonpolar molecules and has important implications for applications such as energy storage, nanoparticle growth, biomass processing, and organic synthesis.¹ The influence of aggregate formation, morphology, and dynamics on physicochemical properties is not yet well understood.² In this study, broadband dielectric spectroscopy, dynamicmechanical spectroscopy, small and wide-angle x-ray scattering, and differential scanning calorimetry are employed to investigate the influence of mesoscale organization and dynamics on charge transport in mixtures 1-octyl-3-methylimidazolium tetrafluoroborate of (C₈MIm BF₄) and 1-ethyl-3methylimidazolium tetrafluoroborate ($C_2MIm BF_4$). Detailed analyses of the x-ray scattering profiles and estimations from effective medium approximation reveal a gradual disruption of the bicontinuous morphology native to neat, mesoscopically-aggregating C₈MIm BF₄ and a transition to isolated and more spherical aggregates in the mixtures. The variation in aggregate shapes results in a 100% increase in the low-temperature static dielectric permittivity due to the contribution from a slow, sub- α dielectric relaxation attributed to concentration fluctuations of the mesoscopic aggregates. These results highlight the potential for double salt ionic liquids to be utilized as a new route for elucidating the influence of mesoscale organization and dynamics on physicochemical properties of mesoscopically-structured liquids. References:



FIG. 1: The derivative representation of the real part of complex dielectric permittivity, $\varepsilon''_{der}(f) = \left(-\frac{\pi}{2}\right)\frac{\partial \varepsilon'(f)}{\partial \ln(f)}$, exhibits a slow, sub- α relaxation corresponding to the dynamics of mesoscale solvophobic aggregates (solid and dashed line). *Inset:* The dielectric strength of the slow relaxation increases with addition of C₂MIm BF₄ contributing to a 100% increase in the static dielectric permittivity.

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Mechanical properties of BN nanosheets

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Abstract

With occurrence of graphene in 2004, two-dimensional (2D) materials have received significant interest from both academic and industrial communities. The non-carbon 2D nanosheets, such as boron nitride (BN), molybdenum disulfide (MoS₂) also attracted a lot of attention due to their unique physical properties. In spite of extensive studies on the properties of 2D materials, the mechanical properties of various nanosheets and factors affecting them have not been studied experimentally. These properties have considerable importance not only from the fundamental point of view but also for future applications of nanosheets.

This work is a short review of the mechanical properties of BN nanosheets. It has been shown that Young's modulus and fracture strength of monolayer (1L) BN are close to those of graphene. However, with the increasing number of the layers, the mechanical properties of graphene started to deteriorate up to 30% while BN nanosheets were as strong as 1L BN. According to the theoretical calculations, the interlayer interaction in BN increased with increasing in-plane strain and out-of-plane compression. The interlayer interaction in graphene at the same conditions decreased which led to the interlayer slide. Also, the mechanical properties of nanosheets were highly influenced by defects and temperature.

The study of mechanical properties of BN nanosheets showed their high potential to substitute graphene nanosheets in various application almost without sacrificing the required strength and stiffness. The high-temperature stability of BN nanosheets also can be used for composite production in the areas where graphene fillers may cause rapid oxidation at elevated temperatures.

Author Biography:

The author obtained his Bachelor and Master degrees in engineering, in MSUT STANKIN, Russia. Currently, he is completing his doctoral degree at Deakin University, Australia. His Ph.D. study is mainly focused on the mechanical properties of BN nanosheets and factors affecting them.

Interfacial Property's Influence on Damping Ratio and Fracture

Toughness of Polyurea Toughed Fibrous Composites

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Abstract

Traditional high-strength fibrous composites are widely used in Engineering. However, the high-strength fibrous composites have a lower fracture toughness and damping ratio, which lead to the shorter life time of composite under repeated impact loads. Recently, we have uncovered a new interface, or boundary, between two unlikely and unique polymer functional groups, resulting in a new chemically bonded **D**ynamic Covalent Interface (DCI), which may bridge the polyurea's property to traditional high-strength fibrous composites. To study the DCI's influence on the toughness and damping property of traditional high strength fibrous composites and improve the traditional high strength fibrous composites' properties. Polyurea toughed carbon fiber reinforced polymer (CFRP) with DCI (C-DCI) is fabricated by controlling the previous curing time (t_c) of epoxy and the types of epoxy. SEM, Nano IR are used to characterize the DCI's physical and chemical properties. Dynamic Mechanical Analysis (DMA) and Compact Tension(CT) test are used to measure the damping ratio and fracture toughness of C-DCI. The DMA test and the CT are simulated using ABAQUS, where the property of the DCI is modelled by Cohesive Zone model(CZM). From the SEM the widths of the DCI are observed, and the Nano IR shows the distribution of DCI. The results of the SEM and Nano IR indicate that the more previous curing time leads to a wider DCI. The finite element models are in good agreement with the DMA and CT tests. From DMA and CT results, the DCI improves the damping ratio and fracture toughness of Polyurea toughed CFRP as a function of the width of DCI is concluded.

Keywords: Fibrous Composites, polyurea, interface, DCI, damping ratio, fracture toughness

Implanted Defects Leading to Magnetism in Graphene

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Defects from radiation damage have been shown theoretically and experimentally to induce magnetism in graphene's bipartite honeycomb lattice, yet little has been established quantitatively about these systems. Through the complimentary use of x-ray scattering, polarized neutron reflectometry, and SQUID magnetometer measurements, the relationship of structure and magnetism related to ion implantation of hydrogen/deuterium in graphene was studied. X-ray extended range reflectivity (EXRR) was used to study structural implications of low-energy ion implantation damage in-situ to monitor changes in the graphene 001 Bragg reflection revealing a strain gradient and layer expansion, in some cases exceeding $\Delta d/d=10\%$. Utilizing spin-polarized neutron reflectivity (PNR) and SQUID the relationship of defect profiles was investigated. PNR measurements are being used to determine the ion (hydrogen/deuterium) amount and its distribution in the film after implantation. SQUID provided a bulk magnetization for the samples studied. In addition to being a system with novel p-orbital magnetism that is of fundamental interest, the use of hydrogen or deuterium has the potential to provide a new avenue to nanoscale spintronic applications with exceptionally high spin mobility.

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Volatile Organic Compound Detection using Porous-Silicon-Oxide Coated Disc-on-Pillar Arrays

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The rapid detection of volatile organic compounds (VOCs) is highly desirable for many fields, including medical diagnostics,¹ industrial process monitoring,² and environmental safety.³ Typical methodology for detection of VOCs relies heavily on both gas chromatography (GC) and mass spectrometry (MS) for analysis ³⁻⁴, but other methods are becoming more prevalent, including nanomaterial-based applications.^{2, 5}. Surface-enhanced Raman spectroscopy (SERS) is an attractive alternative because it is non-destructive, offers the opportunity for real-time analysis, and requires little-to-no sample preparation. Herein we report on the development of a SERS substrate that can be used to detect vibrational signatures from off-gassed vapors of VOCs.

Gold disc-on-pillar (DOP) arrays were fabricated using previously established methods.⁶ To concentrate the VOC analytes onto the plasmonic surface, porous silicon oxide (PSO) was deposited at room temperature onto the substrate using plasma-enhanced chemical vapor deposition (PECVD, Oxford Plasmalab, Oxford, UK) at room temperature, using a mixture of 5% silane (SiH₄) and N₂O at a pressure of 600 mTorr and flow rates of 75 sccm and 600 sccm for SiH₄ and N₂O, respectively. Prior to PECVD, a 2 nm layer of alumina (Al₂O₃) was deposited to shield the PECVD from the highly conductive Au. Resulting substrates were diced into 5 mm \times 5 mm chips for SERS analysis. All fabrication processes were carried out at the Center for Nanophase Materials Sciences at Oak Ridge National Lab. SERS spectra were obtained using a home built confocal Raman system equipped with a 785 nm spectrum stabilized diode laser (Innovative Photonics Solutions, Monmouth Junction, NJ) focused through a 40× objective (Nikon, NA 0.60) at 5 mW power incident on the substrate.

Benzenethiol (BT) and pyridine are common Raman reporter molecules, and can be used to determine the enhancement provided by a SERS substrate. The fabricated substrates were suspended in the headspace above a pool of analyte to collect the off-gassed vapors for 30 s without directly contacting the analyte. SERS spectra were collected for 1 s, and the resulting spectra are shown in Figure 1. The substrate demonstrated a rapid response to collection of the off-gassed vapors, as well as rapid detection of the analytes. Further work will be focused on the detection of less strongly adsorbing molecules that are representative of VOCs that would need to be monitored in environmental and health applications.



Figure 1. Characteristic spectra obtained from off-gassing of benzenethiol (l) and pyridine (r) for 30 s.

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Solution Deposition of Multi-layered Semiconducting Polymer Thin Film

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Semiconducting polymers (SPs) have received enormous attention in recent years due to low cost, scalable solution processing, and the potential for creating light weight flexible electronic devices. The Moulé group has recently developed an in-plane pattering technique called dopant induced solubility control (DISC). For DISC patterning, molecular p-type dopants

such as F4TCNQ are sequentially introduced to the polymer using theta solvents for the polymer. The dopants undergo charge transfer with the polymer leaving a charged anion dopant and a cationic hole state on the polymer. The charged polymer is rendered completely insoluble by the charged states. Here we demonstrate that DISC processing steps can also be used to vertically pattern a multi-layer SP film. Figure 1 shows a schematic of the multiple layer deposition process. During deposition and doping of each subsequent layer the underlying layers enter a solvent swollen state, but do not dissolve because they are doped. Also, as depicted in step 6, we can de-dope the film stack by reacting F4TCNQ with a solution containing amines. Thereby recovering intrinsic film properties. In this manuscript we use neutron reflectometry to demonstrate the validity of



this multilayer deposition process and explore how solvent environments swell neutral and doped P3HT films.

Development Of Cobalt-Nickel Selenide Nanoparticles Decorated Graphene To Improve The Photo-Electrochemical Behavior Of DSSC

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ABSTRACT

A unique nanocomposite comprising Cobalt nickel selenide ($Co_{0.50}Ni_{0.50}Se$) nanoparticles onto graphene nanosheets ($Co_{0.50}Ni_{0.50}Se/GN$) has been synthesized by the simple one-step hydrothermal method to use as a counter electrode for DSSC. The structural changes and the corresponding electrocatalytic properties in terms of cathodic peak current density and charge transfer resistance at electrode/electrolyte interface for $Co_{0.5}Ni_{0.5}Se/Graphene$ nanocomposites with respect to the mass ratio of $Co_{0.5}Ni_{0.5}Se$ nanoparticles and graphene nanosheets have been investigated. $Co_{0.5}Ni_{0.5}Se/GN_{0.50}$ exhibits higher electrocatalytic activity and lower charge transfer resistance with better cyclic stability than other $Co_{0.5}Ni_{0.5}Se/GN$ composites and std. platinum as counter electrodes. Besides, the DSSC fabricated with optimized $Co_{0.5}Ni_{0.5}Se/GN_{0.50}$ as the counter electrode has delivered the PCE of 9.42%, which is much higher than that of DSSC fabricated with $Co_{0.5}Ni_{0.5}Se$ (7.59%) and std. platinum (7.68%). This improved electrochemical performance and higher PCE incited by the synergistic effect between $Co_{0.5}Ni_{0.5}Se$ nanoparticles and graphene which could make $Co_{0.5}Ni_{0.5}Se/GN_{0.50}$ nanocomposite as a promising and alternative to platinum counter electrode for DSSC.



Keywords: Cobalt-Nickel selenide, Graphene Nanosheets, Mass ratio, Electrocatalytic activity, Counter electrode, Dye-sensitized solar cell.

Ballistic conductance through transition metal dichalcogenide heterojunctions

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Metals deposited onto semiconducting (2H) transition metal dichalcogenides (TMDs) are known to form high resistance contacts. Recently, planar heterojunctions between metallic (1T or 1T') and 2H TMDs have shown to significantly reduce this large contact resistance. Here we use first principles calculations within the density functional theory to study the conductance between different transition metal dichalcogenides and their semiconducting and metallic phases. We find that heterogeneous 1T' phases (e.g. WTe₂/MoTe₂) are nearly ideal close to the Fermi level as Bloch states remain delocalized through the metal contact and TMD channel. However, the coupling between metallic and semiconducting interfaces shows a significant reduction in transmission. We rationalize the properties of these interfaces in terms of the contact/channel composition, channel length, and the band structure of contact and channel. This work may prove valuable to attaining low contact resistance suitable for optoelectronic applications.

Influence of Hydrogen-bond Network on Charge Transport and Dynamics in Deep Eutectic Mixtures

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Deep eutectic mixtures (DEMs) are low-melting liquids formed by combining two or more hydrogen-bond donating and hydrogen-bond accepting molecules. The cheap, easy synthesis of DEMs and their advantageous properties such as high ionic conductivities, low viscosities, and relatively wide thermal stability windows makes them advantageous for applications in catalysis, organic synthesis, extraction processes, drug delivery, and electrochemical energy storage.¹ Despite the perceived importance of hydrogen-bond networks on the formation of DEMs, their influence on dynamics, transport, physicochemical properties such as zero-shear viscosity and dc ionic conductivity is not well understood.² To elucidate this interplay, we investigate mixtures of glycerol and choline chloride (ChCl) by broadband dielectric spectroscopy, oscillatory shear-mechanical spectroscopy, and differential scanning calorimetry. With decreasing choline chloride concentration, a second dielectric relaxation emerges at timescales well below the structural, α -relaxation. This unexpected result is discussed within the framework of recent theories of ion transport and sub- α dynamics in supramolecular small-molecule liquids.



FIG. 1: The derivative representation of the real part of complex dielectric permittivity, $\varepsilon''_{der}(f) = \left(-\frac{\pi}{2}\right)\frac{\partial \varepsilon'(f)}{\partial \ln(f)}$, exhibits a slow, sub- α relaxation which is absent in neat glycerol.

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Status of Solid Electrolytes for Lithium Batteries

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The next generation of lithium batteries, with higher energy density, will almost certainly require solid electrolytes that are compatible with lithium metal and with high voltage (5 V) cathodes. Solid electrolytes are much safer than the organic liquid electrolytes currently in use and fall into two classes: ceramics and polymers. Ceramics tend to be brittle crystals or glasses that have reasonable room temperature ionic conductivity, relatively low activation energy for ion transport, and conduct only lithium ions. However, their rigid and brittle nature makes it quite challenging to incorporate them into a battery where interfacial contacts between electrolyte and electrodes are critically important. Polymers, on the other hand, are flexible and provide adhesion such that they can be readily incorporated into batteries. However, they have low room temperature ionic conductivity, high activation energy for ion conduction, and most conduct anions as well as lithium ions (which reduces efficiency). The solid electrolyte most likely to satisfy the demanding needs of next-generation batteries will likely be a hybrid of the two classes of solid electrolyte. The status of polymer and composite electrolytes will be reviewed with an emphasis on nanostructure, ion transport, and reaction kinetics. Recent advances in materials design will be covered as well as developments in techniques for accurately measuring ion transport and reaction kinetics in solid electrolytes. In particular, a framework for predicting the impact of nanostructure on ion transport will presented as will the importance of reaction kinetics on battery performance.

Properties and Applications of "White Graphene"

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Atomically thin hexagonal boron nitride (BN), also called "white graphene" due to its analogous structure to graphene but white appearance, is a novel two-dimensional (2D) nanomaterials. They possess some characters similar to graphene but also many unique properties unavailable to its carbon counterpart. For example, graphene is a semi-metal; while atomically thin BN has a stable wide bandgap of ~6eV insensitive to thickness reduction. In contrast to the intensive studies and wide publicity of graphene, many fundamental properties and potential applications of atomically thin BN are obscure to academics and industries.

Atomically thin BN has been one of the focuses of my research. We invented the first large-scale synthesis route of BN sheets.[1,2] The fundamental physical properties of the material have been systematically studied. It is revealed that monolayer BN nanosheets can sustain up to 850°C in air, while graphene starts to oxidize at 300°C.[3,4] We find that high-quality single-crystalline mono- and few-layer BN nanosheets are one of the mechanically strongest and thermally conductive electrically insulating materials.[5,6] We use both experiment and simulation to reveal the intrinsic dielectric screening, phonon dispersion, and Raman signature of atomically thin BN of different thicknesses.[7,8] It is also found that atomically thin BN as an adsorbent experiences conformational changes upon surface adsorption of molecules, increasing adsorption energy and efficiency.[9] Thanks to the exciting properties of atomically thin BN, the material has strong potential to solve challenges in different fields, such as corrosion protection[10], ultra-sensitive sensing,[11,12], lubrication,[2] and thermal management.[6] The unique properties and applications of BN nanosheets will be reviewed in this talk.

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Chemical Nature of Ferroelastic Twin Domains in CH₃NH₃PbI₃ Perovskite

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Abstract

Recent observations of twin domain in methylammonium lead triiodide (MAPbI₃) have raised questions on its ferroic nature. Whether these twin domains are ferroelectric and/or ferroelastic remains unclear. Previous investigations were limited to the ferroic properties, whereas, the chemistry which can correlate with either ferroelectric or ferroelastic behaviors, has largely been ignored. In this work, we unveil the ferroelastic nature and chemical variation in the MAPbI₃ twin domains using multimodal chemical imaging techniques. We show that the reported piezoelectric-like contrast originates from elastic variation rather than electromechanical effects by using multiple advanced scanning probe microscopy techniques. Combining helium ion microscopy secondary ion mass spectrometry (HIM-SIMS) with nanoscale infrared spectroscopy (Nano-IR), we demonstrate the ion segregation correlating with the twin domains. Two-photon total internal reflection fluorescence microscopy maps (TIRFM) indicate a difference in the crystallographic ordering. Furthermore, density functional theory (DFT) calculations describe an inherent coupling to the elastic strain, chemical segregation, and ferroelasticity. This work unveils a new structural-chemical interplay in MAPbI₃, providing insights into interpreting and understanding the ferroic, chemical, and optoelectronic behaviors of related HOIPs.

Design of ion-transport polymers for next generation energy storage

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Development of high performance and reliable energy storage devices that are lightweight and flexible with improved safety are imperative for next generation energy storage technologies, including lithium (Li)-ion batteries, sodium (Na)-ion battery, supercapacitors, fuel cells, flow batteries, and many others. High-performance solid state electrolytes have the potential to address various challenges in these electrical energy storage devices, especially if they can meet requirements of (i) high ionic conductivity; (ii) sufficient mechanical strength or modulus to suppress dendrites formation; (iii) high transference number; and (iv) wide electrochemical stability window. However, dry solid-polymer electrolytes lack sufficient ionic conductivity to meet cell power requirements, being typically around 10⁻⁶-10⁻⁹ S/cm. On the other hand, while gel polymer electrolytes can provide adequate ion conductivity, their weak mechanical properties diminish advantage over traditional liquid electrolytes, and limit their utilization. This presentation will discuss fundamental design principle for polymer electrolytes and our recent efforts on the development of novel gel polymer electrolytes simultaneously providing high conductivity and tailored mechanical modulus. In the first system, mechanically robust crosslinked PEO membranes were synthesized and doped with sodium triflate and tetraglyme. The relationships between ion conductivity (reached up to 10^{-4} - 10^{-3} S/cm at r.t.) and salt/gel content, glass transition temperature (T_g) and decoupling are investigated. In the second system, mechanically tailored novel single-ion conducting polymer electrolytes (SCPEs) poly[(4-styrenesulfonyl) (trifluromethanesulfonyl)imide] (poly(STF)) poly[1-[3-(methacryloyloxy)-propylsulfonyl]-1or (trifluoromethanesulfonyl)imide] (poly(MPA)) and their copolymers were successfully synthesized. The SCPEs were synthesized by covalently attaching anionic moieties to the polymer backbones that only allows specific cations, such as lithium and sodium ions, to move freely and provide ionic conductivity, i.e. the transference number is close to 1. The novel SCPE membrane includes a membrane with PDMS as polymer backbone to afford mechanical robustness and stretchability, and poly(STF) or poly(MPA) as a side chains to provide single-ion conductivity. The effect of the monomer type, the degree of polymerization of the side chain, and different cations is also studied. The obtained polymer membrane showed 100% elongation and around 10^{-10} ⁴ S/cm single-ion conductivity (no salt) at 30 °C after doped with propylene carbonate.