# 2016 CNMS USER MEETING
# Agenda and Abstracts

OAK RIDGE National Laboratory | CENTER FOR NANOPHASE MATERIALS SCIENCES

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***Exploring Electronic and Ionic Processes in Functional Materials***

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## Cover Image

**From Left to Right**

**Top row**:
STM image of Co nano islands and Ta nano-rods self-assembled on a Cu(111) substrate.

A model mechanical system for studies of nanoscale friction and flows in liquids and gases implemented using direct laser write based on 2-photon polymerization.

The detection of phase transitions in nanoscale volumes by use of an AFM cantilever, through monitoring of elastic changes in the sample by the resonant frequency shifts of the cantilever.

HAADF-STEM image of [100] oriented $Ba_8Ni_yGa_zGe_{46-y-z}$.

**Bottom row**:
Self-assembly of bacterial microcompartment proteins on a planar surface happens via nucleation-growth mechanism.

Thermally-responsive and surfactant-guided assembly of conjugated polymers in aqueous solution for controlled molecular ordering and functional expression.

$WS_2$ crystals grown by chemical vapor deposition amidst lithographically-patterned Si nanopillars.

Truncated icosahedron (bucky ball) structure grown using electron beam induced deposition (EBID) from the organometallic precursor *(trimethyl)methylcyclopentadienyl(Platinum)(IV).*

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

OAK RIDGE National Laboratory
CENTER FOR NANOPHASE MATERIALS SCIENCES

# Agenda

**2016 CNMS User Meeting**
Oak Ridge National Laboratory
Oak Ridge, Tennessee

| | | | |
|---|---|---|---|
| 3:00p | Wednesday, August 10 | **Registration Opens** | |
| 4-6p | **Poster Session and Student Poster Competition** – SNS Atrium | | |
| 7:30a | Thursday, August 11 | **Registration -** Posters available for viewing | |
| 8:00 | **WELCOME AND ANNOUNCEMENTS**- *Iran Thomas Auditorium, SNS*<br>**Hans Christen,** CNMS Director | | |
| 8:20 | **PLENARY LECTURE I**<br>"Opportunities and Challenges in Printed Electronics"<br>**C. Daniel Frisbie,** *University of Minnesota* | | |
| 9:05 | **Poster Session with Coffee** | | |
| | **Track A**<br>*SNS Auditorium* | **Track B**<br>*Room C-156* | **Track C**<br>*Room C-152* |
| | **Directed Assembly of Materials and Interfaces**<br>***Chairs:*** *Enrique Gomez, Scott Retterer* | **Observing and Controlling Matter at the Nanoscale**<br>***Chairs:*** *Eric Formo, Stephen Jesse* | **Exploring Electronic and Ionic Processes in Functional Materials**<br>***Chairs:*** *Evgheni Strelcov, An-Ping Li* |
| 9 :50 | **Bharat Jalan, U. Minnesota** | **Matthew McDowell, Georgia Tech** | **Ilya Sochnikov, U. Connecticut** |
| 10:25 | Brett Lewis, U. Tennessee | Maxim Ziatdinov, ORNL | Dipanshu Bansal, ORNL |
| 10:45 | Enrique Gomez, PSU | Liangbo Liang, ORNL | Valentino Cooper, ORNL |
| 11:05 | **James Rondinelli, Northwestern U.** | **Eric Stach, BNL** | **Xiaoguang Zhang, U. Florida** |
| 11:40 | Lunch on your own; Posters available for viewing | | |
| 1:00 | **Bryan Boudouris, Purdue U.** | **Yong Chen, Purdue U.** | **William McGehee, NIST** |
| 1:35 | Rachael Ford, Caltech | Benjamin Lawrie, ORNL | P. R. Pudasaini, U. Tennessee |
| 1:55 | Roger Narayan, NCSU | Travis Humble, ORNL | Yang Zhang, U. Illinois |
| 2:15 | Break | | |
| 2:40 | **Joshua Sangoro, U. Tennessee** | **Jaan Mannik, U. Tennessee** | **Marina Leite, U. Maryland** |
| 3:15 | Sophia Suarez, Brooklyn College | Jingjie Zhang, U. Virginia | Viktoriia Babicheva, Georgia State U. |
| 3:35 | Break | | |
| 4:00 | **User Group Town Hall Meeting –** Iran Thomas Auditorium, SNS<br>*including announcement of Student Poster winners* | | |
| 4:30 | **PLENARY LECTURE II**<br>**"**Revising the Narrative of Ceramic and Ceramic–Polymer Composite Processing to a Fast, Sustainable Manufacturing Approach"<br>**Clive Randall,** *The Pennsylvania State University* | | |
| 5:15 | Adjourn / Closing Comments | | |

**Plenary Lecture I**

**C. Daniel Frisbie**, University of Minnesota
*Opportunities and Challenges in Printed Electronics*

**Track A:** Directed Assembly of Materials and Interfaces

**Bharat Jalan**, University of Minnesota
*MBE Growth, Structure, Defects and Transport in High-Mobility Epitaxial La-doped $BaSnO_3$ Films*

Brett Lewis, University of Tennessee
*Direct-Write Nanofabrication Via Laser-Assisted Electron Beam Induced Deposition: Growth Kinetics, Enhanced Purity and Electrical Resistivity*

Enrique Gomez, The Pennsylvania State University
*Controlling the microstructure through conjugated block copolymers for solar cells and transistors*

**James Rondinelli**, Northwestern University
*Design of New Multiferroics at the Interfaces of Conducting Complex Oxides*

**Bryan Boudouris**, Purdue University
*Controlling the Self-Assembly and Nanoscale Structure of Block Polymers for the Design and Fabrication of Nanofiltration Membranes and Membrane Adsorbers*

Rachael Ford, California Institute of Technology
**USANS as a Tool for Kinetic Analysis: Polymeric Particle Growth and the Dendrimer Effect in Mixed Matrix Membranes*

Roger Narayan, North Carolina State University
*Two Photon Polymerization for Medical Applications*

**Joshua Sangoro**, University of Tennessee

Sophia Suarez, Brooklyn College
*$^{1}H$ and $^{13}C$ NMR Spin-lattice relaxation time study of newly engineered Poly Triethylene Glycol Methyl Ether Methacrylate (PTGME)-co-Poly (2-vinyl-4,4-dimethylazlactone) (PVDMA) $CO_2$ capturing co-polymer*

**Track B:** Observing and Controlling Matter at the Nanoscale

**Matthew McDowell**, Georgia Institute of Technology
*Multi-modal in situ characterization of dynamic processes in battery materials*

Maxim Ziatdinov, ORNL
*Data Mining the Graphene: Analysis of Correlation between Structure and Electronic Degrees of Freedom*

Liangbo Liang, ORNL
*Integration of experimental and theoretical Raman scattering for characterization of 2D materials*

**Eric Stach**, Brookhaven National Laboratory
*Characterizing Working Catalysts with Correlated Electron and Photon Probes*

**Yong Chen**, Purdue University

Benjamin Lawrie, ORNL
*Nanoscale Mapping of Plasmon-Emitter Coupling Energetics beyond the Jaynes-Cummings Model*

Travis Humble, Oak Ridge National Laboratory
*Computational Design of Silicon Donor Qubits*

**Jaan Männik**, University of Tennessee
*Lab-on-a-chip devices for studies of self-organizing processes in a bacterial cell*

Jingjie Zhang, University of Virginia
**Atomic-scale mapping of thermopower by ab-initio simulations and scanning tunneling microscopy*

**Track C:** Exploring Electronic and Ionic Processes in Functional Materials

**Ilya Sochnikov**, University of Connecticut
*Scanning SQUID microscopy for studies of superconducting and magnetic materials*

Dipanshu Bansal, ORNL
*Spin-phonon coupling in triangular lattice antiferromagnet multiferroic $CuCrO_2$*

Valentino Cooper, ORNL
*Strain response of weak ferromagnetism in $BiFeO_3$: High-throughput simulations with NEXUS*

**Xiaoguang Zhang**, University of Florida
*Multi-phonon processes in solids from first-principles*

**William McGehee**, National Institute of Standards and Technology
*Applications of the Lithium Focused Ion Beam: Nanoscale Electrochemistry and Microdisk Mode Imaging*

Pushpa Raj Pudasaini, University of Tennessee
*Tuning the electrical transport properties of mono and few-layer $WSe_2$ via focused helium-ion beam processing: Enabling nanoscale direct write homo-junctions*

Yang Zhang, University of Illinois at Urbana-Champaign
*Dynamic Odd-Even Effect in Multiphasic Ionic Materials*

**Marina Leite**, University of Maryland
*Imaging lithiation in all-solid-state batteries at the nanoscale*

Viktoriia Babicheva, Georgia State University
*Near-field edge fringes in nanolayer polarizability mapping*

**Plenary Lecture II**

**Clive Randall**, The Pennsylvania State University
*Revising the Narrative of Ceramic and Ceramic – Polymer Composite Processing to a Fast, Sustainable Manufacturing Approach*

# Center for Nanophase Materials Sciences
# 2016 User Meeting
# Poster Session

**denotes Student Poster*

**Wednesday, August 10, 2016**
**4:00 – 6:00p**

**Poster Locations**
Main Hallway: 01-63

*Posters will also be available for viewing on Thursday, August 11*

**01. Decoupling of Chain and Junction Dynamics in Associative Polymer Melt**

Yangyang Wang,[1] Tyler Cosby,[2] Joshua R. Sangoro[2]
[1]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN, 37996

**02. High-Throughput Screening of Microbial Interactions on a Novel Transparent Microwell Array Platform**

M. C. Halsted,[1] N. Jiang,[1] J. L. Wilmoth,[2] A. C. Timm,[2] P. A. Briggs,[2] D. P. Briggs,[3] K. C. Lester,[3] F. E. Löffler,[4] S. T. Retterer[1-3]
[1]Bredesen Center, University of Tennessee, Knoxville, Tennessee, 37996
[2]Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[3]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[4]Department of Civil and Environmental Engineering, University of Tennessee, Knoxville, Tennessee, 37996

**03. *USANS as a Tool for Kinetic Analysis: Polymeric Particle Growth and the Dendrimer Effect in Mixed Matrix Membranes**

Rachel R. Ford,[1] Joey D. Kim,[1] Kunlun Hong,[2] Mamadou S. Diallo,[3,4] Julia A. Kornfield[1]
[1]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN
[3]Energy, Environment, Water, and Sustainability, KAIST, Daejeon, Korea
[4]Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA

**04. *Accessing Siloxane Functionalized Vinyl-added Polynorbornenes and their Development as Advanced Gas Separation Membranes**

Kevin R. Gmernicki,[1] Eunice Hong,[1] Christopher R. Maroon,[1] Shannon Mahurin,[2] Alexei Sokolov,[1,2] Tomonori Saito,[2] Brian K. Long[1]
[1]Department of Chemistry, University of Tennessee, Knoxville, TN, 37996
[2]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

**05. *Investigation of Thin-Film MEAs for High-Efficiency Energy Storage**

Zhenye Kang,[1] Jingke Mo,[1] Gaoqiang Yang,[1] Scott T. Retterer,[2] David A. Cullen,[2] Feng-Yuan Zhang[1]
[1]Department of Mechanical, Aerospace & Biomedical Engineering, UT Space Institute, University of Tennessee
[2]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge

**06. Electromechanical Response of Lamellar Forming Neutral-Charged**

Yao Fu,[1] Mingtao Chen,[2] Timothy E. Long,[2] Jason Dugger,[1] Jim Browning,[3] Bobby Sumpter,[1] Brad Lokitz,[1] Rajeev Kumar[1]
[1]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN
[2]Department of Chemistry, Virginia Tech, Blacksburg, VA
[3]Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge

**07. *Diblock Copolymer Thin Films Fabrication of Pollen Particles**

M. Matherne,[1] N. Lavrik,[2] D. Hu[1]
[1]School of Mechanical Engineering, Georgia Institute of Technology, GA
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN

**08. *Anti-frosting Surfaces using Ice as Humidity Sinks**

Saurabh Nath,[1] Bernadeta R. Srijanto,[2] Scott T. Retterer,[2] C. Patrick Collier,[2] Jonathan Boreyko[1]
[1]Department of Biomedical Engineering and Mechanics, Virginia Tech, Blacksburg, Virginia 24061
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

**09. *Fabrication of Synthetic Moth Antennae**

T. Spencer,[1] N. Lavrik,[2] K. Kalaitzdou,[1] D. Hu[1]
[1]School of Mechanical Engineering, Georgia Institute of Technology, GA
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN

**10. *In Situ Mitigation of Subsurface and Peripheral Focused Ion Beam Damage via Simultaneous Pulsed Laser Heating**

Michael G. Stanford,[1] Brett B. Lewis,[1] Vighter Iberi1,[2] Jason D. Fowlkes,[1,2] Shida Tan,[3] Rick Livengood,[3] Philip D. Rack[1,2]
[1]Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN, 37996
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[3]Intel Corporation, Santa Clara, MS: SC9-68, 2200 Mission College Blvd., California 95054

**11. *Comparison of Carbon Nanotube Fiber Microelectrodes for Neurotransmitter Detection: Correlation of Electrochemical and Surface Properties**

Cheng Yang,[1] Elefterios Trikantzopoulos,[1] Christopher B. Jacobs,[2] B. Jill Venton[1*]
[1]Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

**12. Chemical Doping Enables Intermolecular Long-Range Covalent π–π Bonding**

Yong-Hui Tian,[1] Jingsong Huang,[2] Xiaolan Sheng,[1] Bobby G. Sumpter,[2] Miklos Kertesz[3]
[1]College of Life Sciences, Research Center for Analytical Instrumentation, Sichuan University, Chengdu, Sichuan 610064, P.R. China
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[3]Department of Chemistry, Georgetown University, Washington, D.C. 20057

**13. Property Descriptors for Electron- and Hole-Conducting Conjugated Polymers for Organic Spin Valves Applications**

Jingsong Huang,[1,2] Jacek Jakowski,[1,2] Jong Kahk Keum,[1,3] Kunlun Hong,[1] Bobby G. Sumpter[1,2]
[1]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Computer Science & Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[3]Chemical & Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

**14. Experimental and Theoretical Studies of La Filled $CoSb_3$ Skutterudites**

Chongze Hu,[1,2] Xiaoyu Zeng,[3] Jian He,[3] Jingsong Huang,[4] Bobby G. Sumpter,[4] Menghan Zhou,[3] Yufei Liu,[3] Huijuan Zhao,[1] Terry M. Tritt[3]
[1]Department of Mechanical Engineering, Clemson University, South Carolina 29634
[2]Department of Mechanical Engineering, University of Minnesota-Twin Cities, Minneapolis, Minnesota 55455
[3]Department of Physics & Astronomy, Clemson University, South Carolina 29634
[4]Center for Nanophase and Materials Sciences and Computer Science & Mathematics Division, ORNL, Oak Ridge, TN 37831

**15. Role of 2-D Materials in Photocatalytic Hydrogen Production from Water Splitting: Transition Metal Carbides (MXenes) and Transition Metal Dichalcogenides (TMDs)**

Rui Peng, Hui Wang, Zili Wu[*]
Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

**16. *Imidazole-containing Block Copolymers: Towards Understanding the effect of Morphology on Electromechanical Response**

Mingtao Chen,[1] Bradley S. Lokitz,[2] Rajeev Kumar,[2] Timothy E. Long[1]
[1]Department of Chemistry, Virginia Tech, Blacksburg, VA
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN

**17. *Slow Relaxations in Ionic Liquids: A Signature of Hydrophobic Aggregation**

Tyler Cosby,[1] Katsuhiko Tsunashima,[2] Joshua Sangoro[1]
[1]Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN, 37902
[2]National Institute of Technology, Wakayama College, Department of Materials Science, Wakayama, Japan

**18. *Origin of Fast Proton Transport in Stoichiometric Acceptor Doped Perovskites**

Jilai Ding,[1] Janakiraman Balachandran,[4] Xiahan Sang,[4] Wei Guo,[1] Jonathan A. Anchell, Gabriel Veith,[2] Craig Bridges,[2] Yongqiang Cheng,[5] Jonathan Poplawsky,[4] Nazanin Bassiri-Gharb,[1] Raymond Unocic,[4] Panchapakesan Ganesh[4]
[1]Georgia Institute of Technology Atlanta, GA 30332
[2]Materials Science and Technology Division, Oak Ridge National Laboratory , Oak Ridge, TN 37831
[3]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[4]Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[5]Chemical & Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

**19. *Ion Dynamics in Ammonium-based Polymerized Ionic Liquid Diblock Copolymers**

Matthew Harris,[1] Maximilian Heres,[1] Veronika Strehmel,[2] Joshua Sangoro[1]
[1]Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN, 37996
[2]Department of Chemistry, Hochschule Niederrhein, University of Applied Sciences, Krefeld, Germany 47805

**20. *Ion Dynamics in Ultra-Thin Films of Polymerized Ionic Liquids**

Maximilian Heres, Tyler Cosby, Joshua Sangoro
Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN, 37996

**21. *A New, Air-Stable $Na_3SbS_4$ Solid Electrolyte for All-Solid-State Sodium Batteries**

Hui Wang, Yan Chen, Zachary D. Hood, Gayatri Sahu, Amaresh Samuthira Pandian, Jong Kahk Keum, Ke An, Chengdu Liang

**22. *Conduction below 100˚C in nominal $Li6ZnNb_4O_{14}$**

Yunchao Li,[1,2] Mariappan Parans Paranthaman, [1,2] Lance W. Gill,[1] Edward W. Hagaman,[1] Yangyang Wang,[1] Alexi P. Sokolov,[1] Sheng Dai,[1] Zach Hood,[3] Cheng Ma,[3] Miaofang Chi,[3] Gabriel M. Veith,[4] Arumugam Manthiram,[5] John B. Goodenough[5]
[1]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Bredesen Center, University of Tennessee, Knoxville, Tennessee, 37996
[3]Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[4]Materials Science and Technology Division, Oak Ridge National Laboratory , Oak Ridge, TN 37831
[5]Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712

**23. *Computational Investigation of Half-Heusler/MgO Magnetic Tunnel Junctions**

Jianhua Ma,[1] Yunkun Xie,[1] Kamaram Munira,[2] Avik W. Ghosh,[1] William H. Butler[2,3]
[1]Department of Electrical and Computer Engineering, University of Virginia, Charlottesville,VA-22904, USA
[2]Center for Materials for Information Technology, University of Alabama, Tuscaloosa, Alabama 35401, USA
[3]Department of Physics and Astronomy, University of Alabama, Tuscaloosa, Alabama 35401, USA

**24. *Effect of Electronic Structure on Phonon Transport at the Interface of Monolayer MoS2 and Metal Substrates**

Zhequan Yan,[1] Wenqing Shen,[1] Mina Yoon,[2] Satish Kumar[1]
[1]G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, GA
[2]Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN

**25. Quantum Trajectory/Electronic Structure Study of the Nuclear Quantum effects in the Graphene and Polymer/Fullerene Models**

Sophya Garashchuk,[1] Jacek Jakowski[2]
[1]Department of Chemistry, University of South Carolina, Columbia, SC
[2]Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN

**26. *Ab initio* study of cross-interface electron-phonon couplings in FeSe thin films on $SrTiO_3$ and $BaTiO_3$**

Yan Wang,[1] Tom Berlijn,[2] Andreas Linscheid,[3] Steve Johnston[1]
[1]Department of Physics and Astronomy, University of Tennessee, Knoxville, TN
[2]Oak Ridge National Laboratory, Oak Ridge, TN
[3]Department of Physics, University of Florida, Gainesville, FL

**27. Synthesis of Indene-$d_8$, $IC_{60}BA$-$d_{16}$ and $IC_{70}BA$-$d_{16}$ for CNMS User Project 2015-053**

Peter V. Bonnesen and Bobby G. Sumpter
Macromolecular Nanomaterials Group, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge TN 37831

**28. Direct Write of 3-Dimensional Structures with Helium Ion Microscopy**

Matthew J. Burch,[1] Michael Stanford,[2] Brett Lewis,[2] Anton Ievlev,[1] Raymond R. Unocic,[1] Jason Fowlkes,[1] Philip Rack,[1,2] Alex Belianinov,[1] Olga Ovchinnikova[1]
[1]Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN
[2]Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN

**29. Termination control of magnetic coupling at a complex oxide interface**

S. Das,[1,2] A. D. Rata,[1] I. V. Maznichenko,[1] S. Agrestini,[3] E. Pippel,[4] K. Chen,[5] S. M. Valvidares,[6] H. Babu Vasili,[6] J. Herrero-Martin,[6] E. Pellegrin,[6] K. Nenkov,[2] A. Herklotz,[7] A. Ernst,[4] I. Mertig,[1,4] Z. Hu,[3] K. Dörr[1,2,*]
[1]Institute of Physics, Martin Luther University Halle-Wittenberg, 06099 Halle, Germany
[2]IFW Dresden, Institute for Metallic Materials, Postfach 270116, 01171 Dresden, Germany
[3]Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Strasse 40, 01187 Dresden, Germany
[4]Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany
[5]Institute of Physics II, University of Cologne, Zülpicher Strasse 77, 50937 Cologne, Germany
[6]ALBA Synchrotron Light Source, E-08290 Cerdanyola del Vallès, Barcelona, Spain
[7]Materials Science and Technology Division, Oak Ridge National Laboratory , Oak Ridge, TN

**30. Determining the Electromechanical Response Mechanism of Nanostructured Ionic Block Copolymers**

J. W. Dugger,[1] M. Chen,[2] T. E. Long,[2] U. Fu,[1] R. Kumar,[1] B. S. Lokitz,[1] J. F, Browning[3]
[1]Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge
[2]Department of Chemistry, Virginia Tech
[3]Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge

**31. How a Nanostructure's Shape Affects its Lifetime in the Environment**

Eric Formo
University of Georgia

**32. Multifunctional Probing of Electronic, Magnetic, Transport, and Thermoelectric Properties in Two-Dimensional Materials: Roles of Heterogeneities**

Saban Hus, Jewook Park, Chuanxu Ma, Corentin Durand, Kendal Clark, An-Ping Li
Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge

**33. Multidimensional Probes of Complex Functional Ferroelectric Domain Structures**

J.C. Agar, R. Xu, S. Pandya, and L.W. Martin
Department of Materials Science and Engineering, University of California, Berkeley

**34. Examination of Carbon Nanostructures in Covetic Materials by Helium Ion Microscopy**

Beihai Ma,[1] Uthamalingam Balachandran,[1] Adam J. Rondinone[2]
[1]Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439
[2]Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

**35. Impact of Structural and Physico-chemical Differences on Catalytic Activity of Two Commercially-Sourced Platinum Nanocatalysts**

Rui Serra-Maia, Kevin Tranhuu, Andrew Subowo, Marion Bellier, F. Marc Michel
Department of Geosciences, Virginia Tech, Blacksburg, 24060, USA

**36. Local coexistence of $VO_2$ phases revealed by deep data analysis**

Evgheni Strelcov,[1,2] Anton Ievlev,[1] Alex Belianinov,[1] Alexander Tselev,[1] Andrei Kolmakov,[1] Sergei V. Kalinin[1]
[1]Institute for Functional Imaging of Materials and Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899
[3]Maryland Nanocenter, University of Maryland, College Park, MD 20742

**37. *Strengthening $Al_{0.3}CoCrFeNi$ High Entropy Alloys by B2 Precipitate**

Haoyan Diao,[1] Chuan Zhang,[2] Wei Guo,[3] Jonathan D. Poplawsky,[3] Dong Ma,[3] Fan Zhang,[2] Karin. A. Dahmen,[4] Peter K. Liaw[1]
[1]Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN, 37996
[2]CompuTherm, LLC, 437 S. Yellowstone Dr., Suite 217, Madison, WI 53719, USA
[3]Oak Ridge National Laboratory, Oak Ridge, TN 37831
[4]University of Illinois at Urbana–Champaign, Department of Physics, Urbana, IL 61801

**38. Combining Electron Microscopy and Photonics to Study Complex Plasmonic Resonances**

Jordan A. Hachtel,[1,2] Roderick B Davidson II,[1,3] Andrew R. Lupini,[2] Benjamin J. Lawrie,[3] Richard F. Haglund Jr.,[1] Sokrates T. Pantelides[1,2]
[1]Department of Physics and Astronomy, Vanderbilt University, Nashville, TN, USA
[2]Material Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA
3Quantum Information Science Group, Oak Ridge National Laboratory, Oak Ridge, TN, USA

**39. *Effect of Morphology on Dynamics of Poly(styrene2-b-1,4-isoprene2) Miktoarm Block Copolymers**

Thomas Kinsey,[1] Maximilian Heres,[1] Tyler Cosby,[1] Weiyu Wang,[2] Jimmy Mays,[2] Joshua Sangoro[1]
[1]Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville
[2]Department of Chemistry, University of Tennessee, Knoxville

**40. *In-situ Transmission Electron Microscopy Study of High-Entropy Alloys: Microstructure Transformations**

Chih-Hsiang Kuo,[1] Louis J. Santodonato,[1,2] Raymond R. Unocic,[2] Peter K. Liaw[1]
[1]Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN, 37996
[2]Oak Ridge National Laboratory, Oak Ridge, TN 37831

**41. *Investigation of Microstructure Evolution in NbTaTiV and NbTaTiVZr Refractory High-entropy Alloys**

C. Lee,[1] P. Chen,[1] R. Feng,[1] M. C. Gao,[2] F. Zhang,[3] C. Zhang,[3] J. Poplawsky,[4] W. Guo,[4] P. K. Liaw[1]
[1]Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN, USA
[2]AECOM at National Energy Technology Laboratory, 1450 Queen Ave SW, Albany, OR, USA
[3]CompuTherm, LLC, 437 S. Yellowstone Dr., Suite 217, Madison, WI, USA
[4]Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA

**42. *Machine Learning on Molecular Level**

Artem Maksov,[1-3] Maxim Ziatdinov,[2,3] Shintaro Fujii,[4] Manabu Kiguchi,[4] Shuhei Higashibayashi,[5] Hidehiro Sakurai,[6] Sergei Kalinin,[2,3] Bobby Sumpter[2]
[1]Bredesen Center, University of Tennessee, Knoxville, Tennessee, 37996
[2]Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA
[3]Institute for Functional Imaging of Materials, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[4]Tokyo Institute of Technology, Japan
[5]Institute for Molecular Science, Japan
[6]Osaka University, Japan

**43. *Van der Waals heterojunctions built via an all dry-transfer method**

Akinola Oyedele,[1,2] Masoud Mahjouri-Samani,[2] Xufan Li,[2] Kai Wang,[2] Ilia Ivanov,[2] Chris Rouleau,[2] Pushpa Raj Pudasaini,[2,3] Ming-Wei Lin,[2] David B. Geohegan,[2] Kai Xiao[2,1]

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**44. *Carbon ordering in the nanocrystalline ferrite matrix of bainitic steels**

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**45. *Carbon Nanospikes Grown on Metal Wires for Biosensing Applications**

Aysha S. Shanta,[1] Khandaker A. Mamun,[1] Dale Hensley,[2] Nick Lavrik, [2] Syed K. Islam,[1] Nicole McFarlane[1]

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**46. *Ultra-thin layer chromatography with integrated silver colloid-based SERS detection**

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**47. *Microstructural Characterization of Novel Creep-resistant Ferritic Superalloys**

Shao-Yu Wang, Peter K. Liaw

University of Tennessee, Knoxville, TN, USA

**48. *Development of Pressure-Actuated Microvalves for Studies Subcellular Organization in *Escherichia coli***

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**49. *Atomic-Scale Mapping of Thermopower by ab-initio Simulations and Scanning Tunneling Microscopy**

Jingjie Zhang,[1,2] Liangbo Liang,[2] Jewook Park,[2] An-Ping Li,[2] Avik W. Ghosh[1]

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**50. Point Defects and Ionic Transport in Solid Oxides - Insights from High-throughput Ab-Initio Modeling**

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**51. One-Pot Melamine Derived Nitrogen Doped Magnetic Carbon Nanoadsorbents with Enhanced Cr(VI) Removal**

Yonghai Cao, Jiangnan Huang, Zhanhu Guo

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**52. The Microstructure and Isotope Effects on Spin Response in Organic Spintronic Devices**

Nuradhika Herath,[1] Jong Keum,[2,3] Honghai Zhang,[3] Kunlun Hong,[3] Jacek Jakowski,[3] Jingsong Huang,[3] Jim Browning,[2] Steven Bennett,[1] Chris Rouleau,[3] Ilia Ivanov,[3] Valeria Lauter [1]

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**53. Topographical and Chemical Imaging Using a Combined Atomic Force Microscopy/Infrared Spectroscopy/Mass Spectrometry Platform**

Vilmos Kertesz,[1] Tamin Tai,[1] Orsolya Karácsony,[1] Vera Bocharova,[2] Kevin Kjoller,[3] Ming-Wei Lin,[4] Bernadeta R. Srijanto,[4] Dale Hensley,[4] Kai Xiao,[4] Gary J. Van Berkel[1]

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**54. Integrated Nanoporous Interfaces within Microfluidics for Imaging Bacterial Growth and Metabolism**

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**55. Exploring the Microstructure-Determined Corrosion behaviors of $Al_xCoCrFeNi$ High-Entropy Alloys through the Electron-Work Function**

Yunzhu Shi,[1,2] Liam Collins,[3] Rui Feng,[2] Nina Balke,[3] Bin Yang,[1] Peter K. Liaw[2]

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**56. 3D Analysis of PEM Fuel Cell Electrocatalyst Degradation by STEM Tomography: Pt Nanoparticle Dispersion & Coarsening on Alternate Carbon Supports**

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**57. Computational Study of Electrostatically Tunable Band Offsets in $MoS_2$ Multilayers**

Martin Wang, Marcelo A. Kuroda

Department of Physics, Auburn University

**58. *Epoxy Nanocomposites with Reduced Flamability Derived from Magnesium Hydroxide-Melamine Polyphosphate Hybrids**

Alexandra M. Galaska

University of Tennessee, Knoxville, TN

**59. *Developing Microfluidics Platforms for Single Bacterial Cell Imaging**

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[4]Department of Biochemistry and Cellular and Molecular Biology, University of Tennessee, Knoxville, Tennessee 37996

**60. *Bio-Inspired Optimization of Flow Network Accommodation around Obstacles**

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**61. *A Radial Thermoelectric Generator Based on n- and p-type Conducting Polymers**

Akanksha K. Menon, Shannon K. Yee

G.W.W. School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, USA

**62. Dynamical Response Functions with the Density Matrix Renormalization Group Method**

Alberto Nocera

Computer Science & Mathematics Division and Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

## 63. Ultratrace Plasmonic Sensing below the Shot Noise Limit

Raphael Pooser, Benjamin Lawrie
Quantum Information Science Group, Oak Ridge National Laboratory, Oak Ridge, TN

# Plenary Session

## 2016 User Meeting

# Opportunities and Challenges in Printed Electronics

C. Daniel Frisbie
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Currently there is great interest in developing manufacturing methods for integrating electronic circuitry into flexible and stretchable substrates for a spectrum of applications including roll-up displays, wearable biosensors, smart labels, and electronic skins ('e-skins') for robotics, for example. One fabrication strategy that has captured imaginations involves the use of digital or analog printing techniques to pattern electronically functional inks onto paper, plastic, rubber, or metal foils. However, "printed electronics" has a number of significant challenges, including spatial resolution, pattern registration, and printed circuit performance. In this talk, I will describe a multi-pronged approach to address these challenges that may bring roll-to-roll printed electronics closer to reality. To begin, I will show that innovations in materials allow the fabrication of printable, low voltage thin film transistors (TFTs), the key building blocks of flexible circuits, and that these can be incorporated into simple printed circuit demonstrations involving two dozen TFTs and an equivalent number of printed resistors and capacitors. The second half of the talk will describe a novel liquid-based fabrication approach that we term SCALE, or Self-Aligned Capillarity-Assisted Lithography for Electronics. The SCALE process employs a combination of digital printing and in-substrate capillary flow to produce self-aligned devices with feature sizes that are currently as small as 1 μm. The talk will finish with a discussion of the new opportunities in flexible microelectronics afforded by liquid-based processing.

# Revising the Narrative of Ceramic and Ceramic – Polymer Composite Processing to a Fast, Sustainable Manufacturing Approach

**Clive A. Randall**
*The Pennsylvania State University*

For over 30,000 years, the general practice of sintering ceramics has involved a high temperature thermal treatment to drive the transport processes to densify the particles and minimize the surface energy of the material. Typical sintering temperatures consider 0.6 to 0.8 of the melting temperature ($T_m$) for many oxides; this means we sinter around 800 $^oC$ to 1200 $^oC$ for 2 to 10 hours. Here we introduce a broad body of systems that utilize a transient aqueous based liquid phase (1 to 10 wt%) that sinters under a uniaxial pressure, while being heated from room temperature to 250 $^OC$, over a time period of 10 to 60 minutes. During this process, there are all the aspects of liquid phase sintering, namely particle rearrangement, dissolution precipitation, and grain growth. We believe transport processes are enhanced through mechanisms such as diffussiophoresis, which in turn is driven by concentration gradients. This phenomenon has very fast transport velocities, and therefore does not require high temperatures ~ 10 micrometers/sec. The driving for precipitation is also enabled by the transient evaporation of the water and a sustained supersaturation under local hydrothermal conditions. These mechanisms work together to create a pathway to sinter ceramics under extremely low temperatures and fast times; many of the systems that we will show are sintered at 120 $^oC$, 15 minutes, under 300 MPa uniaxial pressure. We have termed this fabrication method the Cold Sintering Process (CSP). We fully realize that there are many subtle differences in the CSP of each system, but as this is the start of a new approach, we will share our qualitative understanding, as determined from microstructural observations. We have also benchmarked and compared properties where possible, and it will be seen that the properties are in comparison to conventionally processed materials; we will in particular contrast conduction and dielectric properties.

Given the massive drop in sintering temperature of the ceramic, this offers many new opportunities in material design, especially in composites. We will show three different types of polymer ceramic composites with high percentages of ceramic, 100% to 60%, with the thermoplastic polymers for dielectric applications, ionic electrolytes, and semiconducting composites. We will also show preliminary data with CSP with multilayer ceramics and printable electronics.

# Oral Presentations

## *Directed Assembly of Materials and Interfaces*

## *Track A*

## 2016 User Meeting

# MBE Growth, Structure, Defects and Transport in High-Mobility Epitaxial La-doped $BaSnO_3$ Films

Bharat Jalan

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Metals possessing high oxidation potential (e.g. Sr, Ba) are readily oxidized, whereas those with lower potential (e.g. Sn, Ir, W) require stronger reaction conditions. For ternary oxides such as perovskite oxides ($ABO_3$), a difference in oxidation potentials of metal A and B can make synthesis more demanding as compared to their binary oxide counterparts. For instance, if metal B has a lower oxidation potential than that of metal A, a more severe oxidation condition may be required to achieve full oxidation of B in the presence of A. Modern MBE approaches overcome these challenges to a certain extent by using high oxygen pressure, reactive gases such as ozone or by employing oxygen containing metal-organic precursors. The first two approaches often accompany undesirable consequences in MBE such as metal flux instability due to the surface oxidation, or filament oxidation, or even damage to the vacuum pumps due to high oxygen pressure. The latter approach although works for titanates and vanadates, it is not always possible to find an oxygen-containing metal precursor that is compatible with the MBE system, i.e. those with the high vapor pressure, and thermal stability [1].

In this talk, I will review the grand challenges of the synthesis of complex oxides and will present our group's effort to address these challenges using a new radical-based MBE approach. Using Stannate ($BaSnO_3$) as a model material system, I will present a detailed growth study of epitaxial, phase-pure, stoichiometric $BaSnO_3$ films using hexamethylditin, $(CH_3)_6Sn_2$ (HMDT) as a tin precursor, elemental solid source for Sr and Ba, and a rf plasma source for oxygen. We will demonstrate that the reactivity of tin radicals is so strong that it produces phase-pure $BaSnO_3$ films not only with oxygen plasma but also with molecular oxygen suggesting a rather unique MBE approach to grow metal oxides of low-oxidation potential element. Combined with a battery of structural characterization techniques, we will present a comprehensive electrical characterization of La-doped $BaSnO_3$ and will discuss how transport can be influenced by the presence of structural defects such as dislocations, and non-stoichiometry, and dopant concentration. We will also discuss different scattering mechanisms in La-doped $BaSnO_3$, which limits the room temperature electron mobility. Finally, we will present pathways to enhance electron mobilities towards high room temperature mobility oxide heterostructures using defect-managed thin films and interfaces.

Work supported by the NSF, and partially through AFOSR YIP Program.

[1] A. Prakash, J. Dewey, H. Yun, J.S. Jeong, K.A. Mkhoyan, and B. Jalan, "Hybrid molecular beam epitaxy for the growth of stoichiometric $BaSnO_3$", J. Vac. Sci. Technol. A **33**, 060608 (2015)

# Direct-Write Nanofabrication Via Laser-Assisted Electron Beam Induced Deposition: Growth Kinetics, Enhanced Purity and Electrical Resistivity

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Electron beam induced deposition (EBID) is a technique uniquely suited for diverse application in nanofabrication due to its ability to direct-write complex 3D structures with a resolution on the order of 10s of nanometers. EBID creates structures through the electron induced dissociation and condensation of precursor molecules adsorbed onto a substrate in a focused scanning electron microscope. One of the major drawbacks of EBID is that, while the shape is very precisely controlled, the purity is often not. For the expanded versatility of EBID this purity issue must be resolved. To this end, we investigate the growth, purity, and electrical resistivity of 3D platinum nanowires synthesized with different conditions including an *in situ* purification technique using a pulsed laser heating system and reactive co-reactant gases. Notably, we demonstrate a 100-fold improvement in the conductivity of suspended nanowires grown with an *in situ* purification process, while retaining a high degree of shape fidelity.

**Controlling the microstructure through conjugated block copolymers for solar cells and transistors**

Enrique Gomez, Brandon Smith, Melissa Aplan, Youngmin Lee
Chemical Engineering, The Pennsylvania State University

Microphase separated block copolymers provide an opportunity to control the mesoscale structure in the active layer of organic electronic devices. Donor-acceptor block copolymers have been shown to self-assemble into lamellar morphologies in the active layer, leading to power conversion efficiencies in photovoltaic devices as high as 3% with remarkable open-circuit voltages above 1.2 V. These materials can also serve as testbeds to address fundamental questions regarding charge photogeneration. For example, we have explored the role of crystal texturing in microphase-separated active layers on the performance of solar cells. We have also utilized conjugated block copolymers as model donor-acceptor complexes, allowing us to explore the role of energetics and dielectric constant on the formation of intramolecular charge transfer states using steady state and ultrafast spectroscopy. Furthermore, coupling a strongly crystallizable block to a weakly crystalline block perturbs crystallization within films; in particular, order within the weakly crystalline phase is enhanced. As a consequence, electron mobilities higher than either of the homopolymers are extracted using bottom gate, bottom contact transistors with aluminum source and drain contacts and block copolymer active layers. Thus, our results suggest that block copolymer architectures can be used to enhance charge mobilities in polymer semiconductors.

## Design of New Multiferroics at the Interfaces of Conducting Complex Oxides

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The metallic features in materials, which provide low-resistance channels for electrical conduction, lead to effective screening of local electric dipole moments. Itinerant electrons disfavor both dipole formation and cooperative ordering. Consequently, most metals with a finite density of states and partial band occupation exhibit centric (inversion symmetric) crystal structures. Despite this contraindication, noncentrosymmetric metals (NCSM) lacking inversion were proposed more than fifty years ago with some examples discovered serendipitously later. In the first part of the talk, I describe a design framework to alleviate such property disparities and accelerate NCSM discovery [1,2]: The primary ingredient relies on the removal of inversion symmetry through displacements of atoms whose electronic degrees of freedom are decoupled from the states at the Fermi level. Next, I discuss a superlattice composed of the polar metal $LiOsO_3$ with half-filled Os $t_{2g}$ orbitals and weak electron-electron interactions that are essential to sustaining the metallic state in bulk. I then propose how to turn this non-magnetic polar metal into a multiferroic through the design of a superlattice [3], which increases the degree of correlation, leading to Mott localization of the Os orbitals. I conclude by summarizing how the NCSM materials class enables a new strategy for finding room-temperature multiferroics: Start with a polar metal and drive a correlation-induced electronic transition.

This work was performed in collaboration with D. Puggioni, M. Capone, and G. Giovannetti and supported by the Army Research Office under award no. W911NF-15-1-0017.

[1] D. Puggioni and J.M. Rondinelli, *Nat. Commun.* **5**, 3432 (2013).
[2] T. H. Kim, D. Puggioni, et al., *Nature* **533**, 68-72 (2016).
[3] D. Puggioni et al., *Phys. Rev. Lett.* **115**, 087202 (2015).

# Controlling the Self-Assembly and Nanoscale Structure of Block Polymers for the Design and Fabrication of Nanofiltration Membranes and Membrane Adsorbers

*Bryan W. Boudouris, Assistant Professor of Chemical Engineering, Purdue University*

**Abstract**

Tailor-made polymers provide a platform by which to generate nanostructured, multifunctional materials with designer chemical functionalities. Furthermore, the solution-processable nature of functional polymers allows for device fabrication procedures that are compatible with high-throughput (*e.g.*, roll-to-roll coating) manufacturing processes. As such, these macromolecules offer the promise of providing made-to-order, low-cost materials solutions to some of the most pressing polymer and soft materials challenges of the day. Here, we discuss the synthesis, nanoscale self-assembly, and stimuli-responsive nature of block polymer-based thin films for nanofiltration membrane and membrane adsorber applications.

Specifically, A-B-C triblock polymers, composed of polyisoprene-*b*-polystyrene-*b*-poly(*N*,*N*-dimethyl acrylamide) (PI-PS-PDMA), are generated using the reversible addition-fragmentation chain transfer (RAFT) controlled radical polymerization technique. By tuning the molecular weight, molecular weight distribution, block polymer chemical composition, and casting techniques employed, we are able to generate mechanically-robust nanoporous thin films that are well-suited for nanofiltration and reverse osmosis applications. In fact, high-flux separations (*i.e.*, at permeabilities equal to or greater than current commercial membranes) of particles down to ~1 nm in diameter are presented. Additionally, we show that, through the appropriate selection of the C-block of the triblock polymer, the chemistry of the nanopore walls can be tuned to any number of functional groups. In an example demonstration, we show that the chemistry of the pore wall can be easily converted from PDMA to poly(acrylic acid) (PAA). This PAA moiety is capable of providing selective binding of copper ions relative to nickel ions. Using this strategic design, we are able to demonstrate that membranes cast from these materials are able to separate ionic species of similar size but with different binding affinities to the third block of the triblock polymer. Importantly, the binding capacities of these membrane adsorbers are on the same order of magnitude as commercial packed bed systems. Therefore, these tailored macromolecules provide an excellent handle by which to generate size-selective and chemically-selective separations devices. Moreover, we demonstrate that these adsorption events are reversible. As such, the membrane adsorbers can be regenerated through flushing with a simple acidic solution such that repeated capture and cycling can occur in these systems.

Finally, because of the high density of PAA chains that are present due to the A-B-C triblock polymer self-assembly and due to the confined nature of the nanoporous thin film, we are able to demonstrate an unusually long-lived hysteresis in the nanostructural and transport properties of the membrane as a function of the solution pH that passes through the membrane. We show that this hysteresis occurs due to hydrogen bonding events associated with the highly-confined PAA chains and highlight the potential for this rarely-observed phenomenon in future applications. In this way, we are able to systematically tie together the synthesis, operation, and application of these unique nanoporous thin films based on block polymer precursors.

# USANS as a Tool for Kinetic Analysis: Polymeric Particle Growth and the Dendrimer Effect in Mixed Matrix Membranes

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Herein we report a kinetic analysis, primarily using USANS, on the synthesis of polymeric particles for mixed matrix membranes that can be used for electrochemical catalysis, water purification, and resource recovery. The Diallo Group developed a "one-pot" method for the preparation of polyvinylidene fluoride (PVDF) mixed matrix membranes with embedded polymeric particles. An essential aspect of these membranes is their combination of function and mechanical stability. In theory, this is achieved by the *in-situ* crosslinking of amine-containing oligomers [polyethyleneimine (PEI) or low-generation polyamidoamine dendrimer (PAMAM)] which enables interpenetration of the PVDF spherulites of the matrix. By characterizing the final structure in the mixed matrix membranes, we have determined that the amine particles range from <1–3 μm in diameter, with internal pore sizes on the order of 20 nm. However, characterization of the final solid-state structure raises questions regarding the factors that govern structure formation during processing of the membranes. To elucidate how the micro- and nanostructure develops during membrane preparation, we have conducted an integrated SANS and USANS experiment on the membrane casting solution and the functional membranes.

To our knowledge, this was the first **transient** measurement obtained using USANS. Compared to SANS, the intensities are substantially lower, requiring longer acquisition times as compensation (~minutes for SANS; ~hours for USANS). Therefore, USANS was generally only applied to equilibrated systems. However, upon examination of the intensities of the final casting solutions, we determined shorter acquisition times could be used. We ascertained the minimum acquisition time needed to capture all the features without compromising the integrity of the resulting data. For this work, the acquisition times were reduced by roughly one order of magnitude (to about 15 minutes). Using the shorter acquisition times, we observed transient structural changes in the casting solution across a q-range offered collectively by SANS and USANS.

For this experiment, we chose two variables to manipulate: amine polymer and concentration of crosslinker. We studied the "dendrimer effect" using three different polymer precursors: randomly branched PEI, zeroth generation PAMAM, and first generation PAMAM. Changing the crosslinker concentration enabled us to determine the extent to which charge-induced phase separation and crosslinking of amine polymer played a role in the overall structure of the membranes. The success of our membranes is partly attributed to the mechanical stability of the membranes, which is provided by the PVDF component. Manipulating these two variables in conjunction with the short acquisition times allowed us to test our theory on the interactions of PVDF and amine polymer as the crosslinking reaction progressed. Thus, we expanded upon the currently assumed limits of USANS—we demonstrated the capability of USANS in analyzing transient structures by studying polymeric mixed matrix membranes.

# Two Photon Polymerization for Medical Applications

Roger Narayan MD PhD
North Carolina State University

Over the past decade, two photon polymerization has been used for additive manufacturing of small-scale three-dimensional medical devices from computer designs. Two photon polymerization involves nearly simultaneous absorption of two photons within a small volume of a photosensitive material. This process leads to polymerization and hardening of the photosensitive material within a confined volume. The minimum feature size obtained using the two photon polymerization process is dependent on a variety of processing parameters, including laser power, photosensitivity, and voxel-voxel distance.

Two photon polymerization has been used to prepare many types of medical devices from acrylate-based polymers, organically-modified ceramic materials, zirconium oxide sol-gel materials, and other photosensitive materials. For example, two photon polymerization has been used for additive manufacturing of microneedles; these small-scale lancet-shaped devices may be utilized for transdermal delivery of pharmacologic agents or sampling of body fluids. Microneedles with complex shapes, including rocket-like geometries, off-center geometries, and mosquito-like geometries, have been prepared using two photon polymerization. For example, 500-700 micrometer tall microneedles were fabricated out of an acrylate-based polymer that is used in Class IIa medical devices such as hearing aid shells. A hollow microneedle was used to prepare pores in the outermost layer of porcine skin, which enabled delivery of carboxyl quantum dots to the deep epidermis and dermis within fifteen minutes. Two photon polymerization was shown to enable rapid iteration of medical device physical parameters, including geometry and length, for specific clinical applications. In addition, parallel processing of microneedle arrays has been demonstrated by means of a multi-beam approach. The biosensor applications of microneedles that were created using two photon polymerization have also been considered. For example, a device containing a two photon polymerization-fabricated hollow microneedle and a porous carbon electrode was utilized to detect potassium ions across the physiologic range and in the presence of interfering sodium ions.

Scaffolds for use in artificial tissues has also been prepared using two photon polymerization. For example, a biocompatible combination of riboflavin and triethanolamine was used a photoinitiator for two photon polymerization of tissue engineering scaffolds with small-scale features. The results of the study indicated that materials prepared using the riboflavin- triethanolamine combination had higher biocompatibility than materials prepared using common synthetic photoinitiators. For example, a genotoxicity study showed that one of the materials created using a riboflavin- triethanolamine combination was less toxic than a glass material that served as a control. A scaffold for tissue engineering was fabricated using this riboflavin- triethanolamine combination, which was subsequently used for a cell growth study involving bovine cells.

**Joshua Sangoro**

***University of Tennessee***

Abstract not yet available

Title: $^{1}H$ and $^{13}C$ NMR Spin-lattice relaxation time study of newly engineered Poly Triethylene Glycol Methyl Ether Methacrylate (PTGME)-*co*-Poly (2-vinyl-4,4-dimethylazlactone) (PVDMA) $CO_2$ capturing co-polymer

Authors: Sophia Suarez[1], Balaka Barkakaty[2], Ilia N. Ivanov,[2] Brad Lokitz[2], and Mingtao Chen[3]

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Carbon dioxide's capture and release are necessary technologies for the world today. The most applied is the liquid amine-$CO_2$-$H_2O$.[1-3] While it offers acceptable $CO_2$ capture density, this system suffers from high $CO_2$ desorption energy requirements and have unfavorable environmental impacts. Solids sorbents provide greater $CO_2$ capture density, lower energy requirements for $CO_2$ desorption, lower rates of deterioration and less environmental impact compared to the liquid amine-$CO_2$-$H_2O$. One newly developed solid sorbent is a co-polymer comprised of triethylene glycol methyl ether methacrylate with 2 vinyl-4,4-dimethylazlactone (VDMA) and amidine functional groups such as 4-(N-methyltetrahydropyrimidine) benzyl alcohol (MTHPBA). We have characterized this system using variable temperature $^{1}H$ and $^{13}C$ NMR spin-lattice relaxation times as functions of $CO_2$ content, polymers composition, and co-polymers type (random and block). Our goal is to assess its $CO_2$ absorption capability and the results will highlight its attributes.

# Oral Presentations

## *Observing and Controlling Matter at the Nanoscale*

## *Track B*

## 2016 User Meeting

**Multi-modal *in situ* characterization of dynamic processes in battery materials**

Matthew McDowell
Georgia Institute of Technology
*2016 CNMS User Meeting Abstract*

Dynamic processes such as phase transformations, ion diffusion, and side reactions often determine performance of battery materials. To engineer the next generation of batteries with higher energy density and long lifetime, a fundamental shift in the way we observe and understand materials is required: we must move beyond before-and-after experimentation and utilize *in situ* methods to probe real-time materials dynamics. The research effort here is designed to probe transformations within battery electrodes across length scales. *In situ* transmission electron microscopy (TEM) is used to reveal atomic-to-nanoscale phase transformation mechanisms in high capacity battery electrode materials. Materials that undergo alloying reactions with lithium, such as silicon and tin, are observed to undergo large volume changes during insertion and removal of lithium, and the mechanical stress that evolves during these transformations can play a significant role in determining the kinetics of the reaction. Next, the transformation mechanisms in battery materials that undergo other types of reactions (conversion and displacement mechanisms) are also observed at the nanoscale. One such material ($Cu_2S$) exhibits dramatically different reaction mechanisms when operated within sodium vs. lithium batteries, and sodium/$Cu_2S$ cells exhibit superior cycle life, with hundreds of charge-discharge cycles with > 90% capacity retention. Finally, *in situ* x-ray photoelectron spectroscopy (XPS) and x-ray diffraction reveal chemical and structural information during reaction that is complementary to *in situ* TEM studies.

# Data Mining the Graphene: Analysis of Correlation between Structure and Electronic Degrees of Freedom

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The link between changes in the material crystal structure and its mechanical, electronic, magnetic, and optical functionalities known as the structure-function relationship is the cornerstone of the contemporary materials science research. Of particular interest is a role of crystalline defects and the associated strain fields in the functionalities of the technologically relevant materials. For example, introduction of dopant atoms into the lattice of a Mott insulator can turn it into a superconductor whose properties, such as a magnitude of the superconducting gap, are sensitive to subtle variations of the inter-atomic bond lengths and bond angles in the crystal lattice structure.

The arrival of high-resolution scanning probe microscopic and spectroscopic (SPM/S) methods has recently allowed researchers performing simultaneous measurements of materials structural parameters and functional properties in a real space with a sub-nanometer precision. However, methods to cross-correlate information obtained in the structure 'channel' and function 'channel' and to describe the obtained correlation in terms of certain (linear or non-linear) physical models are very limited and yet are increasingly necessary due to the ever-growing volumes of relevant experimental data. Here, we have designed a statistics-based approach for analysis of correlation between local structure and electronic properties in atomically-resolved SPM datasets on graphene with hydrogenated and oxidized defects. Specifically, by applying a combination of the Pearson correlation matrix, linear and kernel canonical correlation analysis, we showed a presence of a non-negligible correlation between the nanoscale lattice strain and the intensities of inter-valley quasiparticle scattering at the defect sites. Our analysis also revealed that the strength of coupling to strain is altered between different scattering channels which can explain an emergence of more than one quasiparticle scattering pattern in the sample (the so-called fine structure of the electronic superlattice). Finally, application of the kernelised canonical correlation analysis allowed us extracting a non-linear component of the relationship between the lattice strain and scattering intensity in graphene. The implications of these findings to physics and chemistry of graphene will be discussed.

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# Integration of experimental and theoretical Raman scattering for characterization of 2D materials

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Raman spectroscopy is among the most useful characterization techniques to understand 2D materials, owing to its capability to identify minute structural and electronic effect. We show that the integrated experimental/theoretical Raman approach can help to determine many crucial properties of 2D materials beyond graphene, such as the number of layers, the layer-layer relative stacking, and the defect concentration. For transition metal dichalcogenides and black phosphorus, recent experimental and theoretical progress on low-frequency (LF) interlayer Raman modes has demonstrated that they are much more sensitive to the interlayer coupling, and can be more effective at determining layer thickness and stacking, compared to the typically studied high-frequency (HF) intralayer Raman modes. Establishing a map between LF modes and layer thickness/stacking could be significant for enabling rapid characterization of 2D materials in future. Of course, HF Raman modes are of no less importance, as our recent Raman measurements on defective MoS2 and MoSe2 found that HF modes exhibit unique dependence on S or Se vacancy concentration, corroborated by first-principles phonon calculations.

# Characterizing Working Catalysts with Correlated Electron and Photon Probes

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Heterogeneous catalysts often undergo dramatic changes in their structure as the mediate a chemical reaction. Multiple experimental approaches have been developed to understand these changes, but each has its particular limitations. Electron microscopy can provide analytical characterization with exquisite spatial resolution, but generally requires that the sample be imaged both *ex situ* and *ex post facto*. Photon probes have superior depth penetration and thus can be used to characterize samples in *operando* conditions (i.e when they are actively working). But they generally lack spatial resolution and thus give only ensemble average information.

We have taken advantage of the recent developments in closed-cell microscopy methods to develop an approach that allows us to successfully combine electron, x-ray and optical probes to characterize supported nanoparticle catalysts *operando*. By measuring the reaction products at each stage of the reaction, we can directly correlate the information that can be obtained from each approach, and thus gain a deep insight into the structural dynamics of the system.

I will describe how we can use this approach to correlate scanning transmission electron microscopy, x-ray absorption spectroscopy (both near-edge and extended fine structure), and infrared microspectroscopy to understand how Pt and Pd nanoparticles supported on silia undergo structural changes during the room temperature hydrogenation of the ethylene, and how we can direct measure and describe the reaction products on the surfaces of the nanoparticles as the reaction proceeds. By combining these approaches, we can track the interplay between nanoparticle reduction, coarsening, and the specific surface species at different stages of the reaction. Additionally, I will show how these techniques can also track the relationship between the reaction processes and surface chemistry, as well as how this leads to catalysts deactivation.

**Yong Chen**

***Purdue University***

Abstract not yet available

# Nanoscale Mapping of Plasmon-Emitter Coupling Energetics beyond the Jaynes-Cummings Model

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Strong plasmon-emitter coupling has received growing attention over the past decade because of the potential of engineering a plasmonic analogue to cavity quantum electrodynamics (cQED) that exploits mode volumes well below the diffraction limit. However, the demonstration of a true plasmonic cQED platform remains elusive. Here, we will use the photon statistics of strongly coupled plasmon/emitter systems excited by a scanning transmission electron microscope (STEM) in order to map nonlinear plasmon exciton interactions with nanoscale spatial resolution.

The Jaynes Cummings model has been increasingly used to model strong plasmon-emitter coupling, with appropriate substitutions for the nonlinear plasmonic dispersion, nanoscale mode volume, and poor quality factor relative to photonic systems, yielding reasonable agreement with the femtosecond dynamics of aggregates of emitters coupled to delocalized plasmon modes. However, the Jaynes Cummings model relies on a plane wave expansion of modes within the optical cavity that is invalid below the diffraction limit. In lieu of such an expansion, the local density of states can be determined from the imaginary part of the Green's function for a given plasmonic nanoresonator, calculated by finite difference time domain (FDTD) simulations. Despite the apparent experimental agreement with the Jaynes Cummings model in the limit of many coupled emitters, it makes sense to pursue a model with none of the assumptions of the Jaynes Cummings model.

By incorporating a Hanbury Brown Twiss interferometer and a spectral imaging system into a cathodoluminescence platform integrated into a STEM, we will enable the nanoscale mapping of plasmon emitter coupling. In particular, we will compare the spectra and photon statistics of individual quantum emitters strongly coupled to individual, single crystal, plasmonic nanostructures like those shown in Fig. 1 with semi-classical, pseudo-Jaynes Cummings, and novel plasmonic master equation models

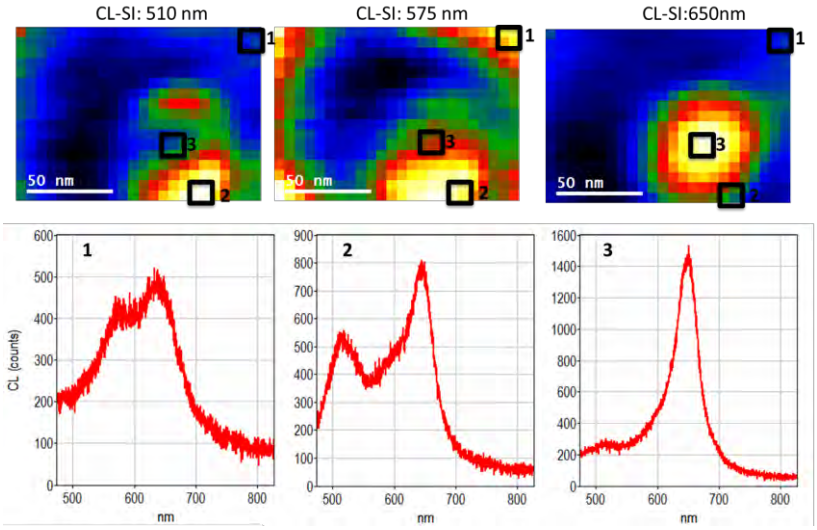


Fig. 1: Hyperspectral characterization of CL of single crystal Ag nanostructures with spectral filters applied to the spatial CL map (above), and spectra associated with three modes (below).

# Computational Design of Silicon Donor Qubits

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Recent breakthroughs in the realization of donor qubits in silicon with high gate fidelities and long qubit coherence times have increased interest in donor based quantum computing architectures in silicon. However, these proof-of-concept experimental demonstrations must be viewed as point solutions for the larger problem of designing robust quantum computing devices. Key qualities for robust device operation, including stability, reproducibility, and reliability, are currently lacking due to uncertainty in the fabrication process. Modeling and simulation has proven especially useful for the development of conventional CMOS processors where TCAD tools are standard for verifying designs generated from well characterized process models.

We address how modeling and simulation can be applied to the on-going development of quantum computing devices. Our approach addresses the performance of small-scale doped silicon nanostructures by combining models of physical layout and material designs to evaluate the operating principles of an encoded qubit. Our computational workflow exposes the ability to investigate key qualities of a device, e.g., gate fidelity, by tuning design parameters. These computational models provide a natural bridge between efforts to fabricate and characterize silicon donor systems and efforts to program future multi-qubit systems.

A representative example of the nanoscale engineering needed to control a single embedded donor atom is shown in Fig. 1(a). Simulating the electromagnetic field for this physical layout requires solving Poisson's equation over the entire device model. The process of finding the optimal mesh depends on the geometry of the device, although tools such as the COMSOL electrostatic solver provide options for automated mesh generation.

Central to the effort of modeling the donor atom as a qubit is calculating the hyperfine splitting (HFS). This is the leading term for the nuclear spin-electronic interaction in the Si:P qubit with the isotropic HFS, also known as the Fermi contact interaction, proportional to the spin density on the donor atom. The radial distribution for the spin density is shown in Fig.1(b) computed using DFT. Control over the HFS via the electron wavefunction

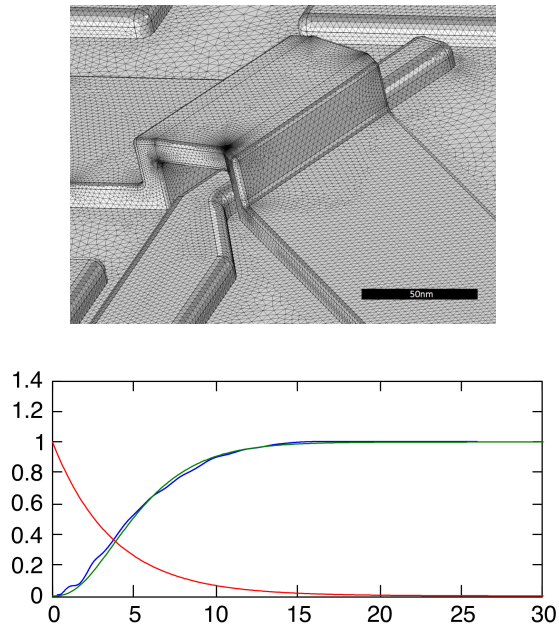


FIG. 1: (a) Closeup of the physical layout for controlling an Si:P donor systems via applied electrostatic fields; (b) Radial distribution (red) of the spin density for a 3 nm Si:P nanocrystal with cumulative density (blue) being well approximated by a Slatter-type orbital (green).

permits tuning on resonance with an applied magnetic field.

The calculated fields and orbitals provide the information necessary to simulate the expected behavior of the silicon donor device. The electron and nuclear spin dynamics of the system can be obtained by solving the Schrodinger equation, or its noisy equivalent, for the four-level system. Our computational workflow exposes both the electrostatic and material facets of these devices and enables paramteric stufies of behavior. In particular, a significant burden for future modeling of realistic devices is directly incorporating uncertainty in the fabrication or operation of the device. Variations in donor and material as well as electromagnetic noise can be taken into account by statistical sampling.

# Lab-on-a-chip devices for studies of self-organizing processes in a bacterial cell

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Cells maintain their structure and reproduce through numerous self-organizing processes. The common approach to understand how cellular organization is maintained is to perturb this organization and then observe a response from the cell. Essentially all approaches used by cell biologists in these studies enable the assessment of only ensemble-averaged responses, overlooking significant cell-to-cell variations that exist in a population. The current methods are also not suitable to study processes in cells with fast response times. Here, we describe the development of two lab-on-a-chip platforms that allow mechanical and chemical perturbation of cellular organization in bacteria while following the cellular response at single cell level in real time using a high resolution fluorescence microscope.

The platform designed for studies involving chemical perturbation consists of channels with lateral dimensions comparable to the diameter of a bacterial cell. Each channel connects to a larger flow channel allowing for controlled and rapid introduction of different chemical agents to the growth medium. While the fluidic portion of the platform functions as expected, our studies show that cells have growth limitations in the channels. We will discuss the origin of this limitation and our attempts to overcome it.

The platform designed for studies involving mechanical perturbation consists of pressure actuated microvalves. Bacteria are placed under a valve that when closed leads to bacterial deformation and shape changes. As we have shown before a long term deformation of bacterial cell leads to drastic changes in its morphology [2, 3]. The platform enables to systematically study the effect of cell shape on cellular function and probe internal organization of chromosomes and cell division proteins.

The two platforms present promising complementary approaches to probe, in a quantitative and systematic way, processes that maintain cellular functions. In addition to bacterial cells, these two platforms can also be useful in studies of yeast and other single-celled organisms.

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# Atomic-scale mapping of thermopower by ab-initio simulations and scanning tunneling microscopy

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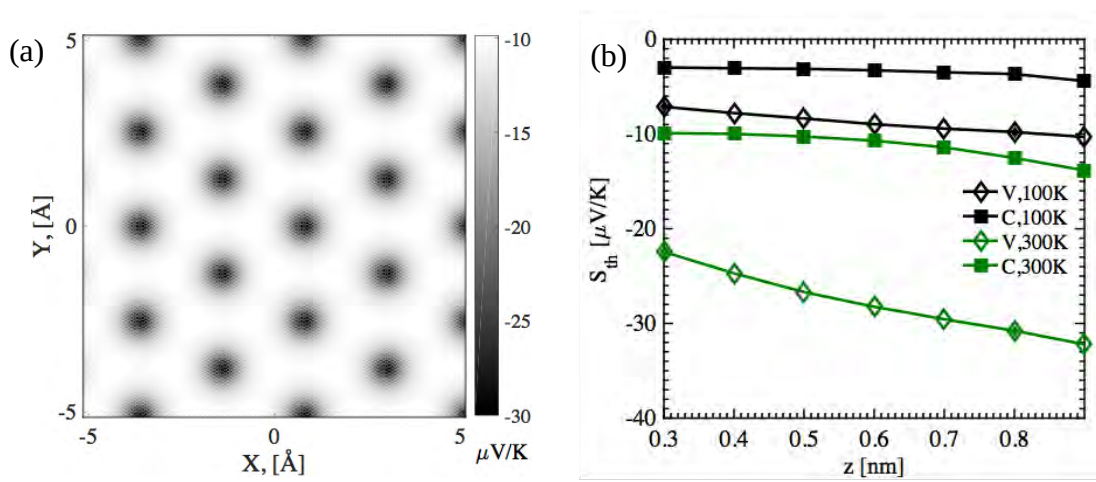
Scanning Tunneling Microscopy(STM) measurement of thermovoltage exhibits its unique capability on delivering high resolution atomic-scale mapping of the surface states, defects, and heterostructure interfaces [1-3]. The preferred theoretical Stoveneng-Lipavsky method fails to model thermovoltage at high temperature and large temperature gradient measurement conditions [1], and it cannot predict the tip-sample distance dependent thermovoltage precisely since it lacks the particular spatial wavefunctions. Here utilizing the spatial wavefunctions by first-principle calculations, we obtained the atomic scale mapping of thermovoltage at arbitrary temperature gradient and measuring distance. We applied our simulation method to pristine graphene, graphene with single carbon atom defect and graphene grain boundary interfaces. We compared the simulated topography STM images and thermovoltage images, explained and identified the key features (distance, temperature and slope of LDOS near the chemical potential) that can help enhance the resolution.




*(a) The atomic-scale thermopower image of graphene surface; (b) the tip-sample distance dependent thermopower of graphene surface. V denotes the hollow site while C denotes the carbon site.*

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# Oral Presentations

## *Exploring Electronic and Ionic Processes in Functional Materials*

## *Track C*

## 2016 User Meeting

# Scanning SQUID microscopy for studies of superconducting and magnetic materials

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Scanning Superconducting QUantum Interference Device (SQUID) microscopy is a promising technique for basic studies of superconductor hybrid devices. Although, this potential is yet to be fully explored in the future experiments, we've already performed several studies of superconductor/semiconductor Josephson junctions and ferromagnetic systems. Here, I will focus on two examples in each of the above categories.

First system, hybrid devices made of a superconductor and a 3-dimensional topological insulator where spin-momentum locking protects the charge carriers at the topological insulator surface against elastic backscattering. We use SQUID microscopy to characterize the current-phase relation of Josephson junctions composed of the 3-dimensional topological insulator HgTe.

Second system, a special class of ferromagnets called spin-ices where exotic magnetic fluctuations are predicted to emerge. Using scanning SQUID microscopy we obtain real time images of spontaneous magnetic fluctuations in the spin-ice $Ho_2Ti_2O_7$. We compare the fluctuations data to the previous susceptibility and magnetization data and theoretical models to identify the origin of the magnetic dynamics in these materials.

These two experiments demonstrate a powerful magnetic imaging approach for studies of magnetic dynamic processes on the nanoscale.

# Spin-phonon coupling in triangular lattice antiferromagnet multiferroic $CuCrO_2$

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The co-existence and interplay of ferroelectricity and magnetism in multiferroric materials is a question of fundamental scientific interest, and of technological relevance for novel low-power consumption electronics. However, long-range magnetic order and ferroelectric polarization occur at decoupled temperatures in most multiferroic materials, making it challenging to precisely control the two. In the geometrically frustrated antiferromagnet $CuCrO_2$, the ferroelectric polarization emerges concomitantly with the long-range magnetic order, revealing a direct coupling between magnetic and dielectric properties. However, the role of phonons across the magnetic and ferroelectric transition in $CuCrO_2$ remains unknown.

Here we report inelastic neutron and x-ray scattering measurements ($7 \leq T \leq 650$ K) along with first-principles simulations of the phonons in $CuCrO_2$ across the concurrent magnetic and ferroelectric transition ($T_N \sim 24$ K). The experimental measurements and *ab-initio* simulations indicate the presence of a significant spin-phonon coupling in this system. Our results show that the phonon transport is very sensitive to geometrically frustrated antiferromagnetic ordering in this system, and is strongly suppressed in the magnetic state. Also, the temperature dependence of phonon intensities and energies deviates significantly from the quasi-harmonic behavior. At high temperatures, the expected phonon intensities are recovered, and the phonon softening follows the common quasi-harmonic behavior. Furthermore, the INS data show that the magnetic scattering from short-range magnetic fluctuations persists up to ~ 300 K, far above the Neel temperature for long-range antiferromagnetic order. Our single-crystal IXS phonon measurements at 7, 35, and 300 K further further evidence of the strong spin-phonon coupling in this multiferroic compound.

This research was supported by the Office of Science Early Career Research Program (Delaire). The use of Oak Ridge National Laboratory's Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. DOE. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Theoretical calculations were performed using resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the US Department of Energy under contract no. DE-AC02-05CH11231.

## Strain response of weak ferromagnetism in $BiFeO_3$: High-throughput simulations with NEXUS

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In its rhombohedral ground-state, weak ferromagnetism (wFM) in $BiFeO_3$ (BFO) is induced from a slight canting of the collinear antiferromagnetic moments due to Dzyaloshinskii-Moria (DM) interactions. The strong coupling between atomic distortions and the DM interactions presents a route for tuning the wFM through changes in the lattice modes. Applied epitaxial strains foster changes in polar cation shifts and $FeO_6$ octahedral tilt patterns; resulting in an array of material responses such as enhanced polarization and high piezoresponse. Similarly, these distortions may alter the wFM in BFO films. Unfortunately, mapping out the influence of epitaxial strain on the underlying mechanisms that link wFM with lattice distortions requires performing a large number of non-collinear spin-polarized density functional theory (DFT) calculations including spin-orbit couplings under applied compressive and tensile strains and with different magnetic orderings. Such calculations would be tedious to perform on a one-by-one basis and are ideal for the application of high-throughput methods.

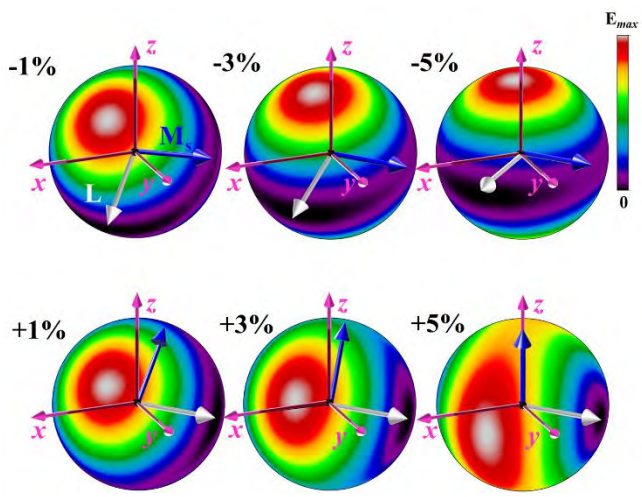


*Figure 1 Strain evolution of the magnetic energy landscape for compressive and tensile strains in BFO. Bright (red) and dark (black) region correspond to hard and easy spin axes (dashed white arrows), respectively. Under compressive and tensile strains the antiferromagnetic vector (L) is stabilized along [110] and [-110] directions, respectively. Consequently, the induced weak ferromagnetism (Ms) is also stabilized along the [-110] and [001] directions under the compressive and tensile strains, respectively.*

Using the NEXUS workflow toolkit, we systematically examined the evolution of wFM in BFO. We show that the wFM observed in the bulk rhombohedral structure persists for strain values up to ±5%. We find that the stabilization of the wFM is driven by the interplay between the DM interactions and the single ion anisotropy (SIA); with the DM interactions dominating under tensile strains and the SIA interactions having significant contributions under large compressive strains. Furthermore, we observe that at high compressive strains (≥−7%), the C- and G-type magnetic orderings compete, energetically. Group-theoretic analyses (confirmed by DFT calculations) indicate a loss of weak ferromagnetism for C-type ordering. This suggests the possibility of switching wFM "on" or "off" under external pressure. Our study offers useful insights for manipulating the distinct magnetic response of a material under epitaxial strain and has important implications towards utilizing the magnetoelectric effect in BFO thin films for future technology.

Research supported by the U.S. DOE, Office of Science, BES, MSED (J.H.L., S.O., H.D., V.R.C), and the Office of Science Early Career Research Program (V.R.C). This research used resources at NERSC, which is supported by the Office of Science of the U.S. DOE under Contract No. DE-AC02-05CH11231. Research by J.T.K. (Nexus workflows) was conducted at the CNMS, which is a DOE office of Science User Facility.

# Multi-phonon processes in solids from first-principles

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We report the construction of a comprehensive first-principles theory of inelastic scattering by defects, and apply it to study two cases of current interest, carrier capture in silicon and resonant Raman spectrum of a $MoS_2/WS_2$ heterostructure. For carrier capture, we distinguish between capture under thermal equilibrium conditions and capture under nonequilibrium conditions, e.g., in the presence of an electrical current or hot carriers where carriers undergo scattering by defects and are described by a mean free path. In the thermal-equilibrium case, capture is mediated by a nonadiabatic perturbation Hamiltonian, originally identified by Huang and Rhys and by Kubo, which is equal to linear electron-phonon coupling to first order. In the nonequilibrium case, we demonstrate that the primary capture mechanism is within the Born-Oppenheimer approximation (adiabatic transitions), with coupling to the defect potential inducing Franck-Condon electronic transitions, followed by multi-phonon dissipation of the transition energy, while the nonadiabatic terms are of secondary importance (they scale with the inverse of the mass of typical atoms in the defect complex). We report first-principles density-functional-theory calculations of the capture cross section for a prototype defect using the projector-augmented wave, which allows us to employ all-electron wave functions. We adopt a Monte Carlo scheme to sample multi-phonon configurations and obtain converged results. As a second example of the theory, we present a first-principles calculation of the Raman spectrum of $MoS_2/WS_2$ heterostructure due to electron excitation. In this case, atomic displacements between the electronic ground state and the excited states due to charge transfer between the two layers lead to finite phonon matrix elements allowing inelastic multi-phonon relaxation to accompany the emission of a photon when the excited electron returns to the ground state. For each excited state, the relative Raman intensity, peak width and shape are obtained directly from a sum over trillions of configurations of multiple phonon modes using a Monte Carlo scheme and compared to experiments.

# Applications of the Lithium Focused Ion Beam: Nanoscale Electrochemistry and Microdisk Mode Imaging

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## ABSTRACT

Laser cooling of neutral atoms provides a novel approach for realizing high brightness ion sources from many different atomic species. The first implementation of such an ion source produces a Li+ beam by photoionizing a sub-mK gas of neutral lithium held in magneto-optical trap. The ions are accelerated in an electric field and are electrostatically focused using a conventional focused ion beam column, achieving beam energies from 0.5 to 6 keV, currents up to 15 pA, and focal spots as small as 27 nm. I will discuss the essential properties of this ion source as well as two recent applications of the lithium focused ion beam including imaging of optical modes in high-Q silicon microdisk resonators and an exploratory study using ion beam implantation as a novel probe of nanoscale electrochemistry in battery-relevant materials.

# Tuning the electrical transport properties of mono and few-layer $WSe_2$ via focused helium-ion beam processing: enabling nanoscale direct write homo-junctions

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The performance of electronic and optoelectronic devices based on two-dimensional transitional metal dichalcogenides layered materials, such as tungsten diselenide ($WSe_2$) is significantly affected by the defects in the materials among others. Tuning optical and electrical properties of mono and few-layer $WSe_2$ by controlling the defects, is an intriguing opportunity to synthesize next generation two dimensional material opto-electronic devices. We report the effects of focused helium ion beam irradiation on the structural, optical and electrical properties of mono and few-layer $WSe_2$. By controlling ion dose, structural defects were controllably introduced in a mono and few-layer $WSe_2$ sample and its stoichiometry was modified by preferential sputtering of selenium at a few-nanometer scale. Localized tuning of the resistivity of $WSe_2$ was demonstrated. By selectively exposing material with the ion beam, we demonstrate a simple yet highly tunable method to create lateral homo-junctions in few-layer $WSe_2$ flakes. Furthermore, sub 10nm $WSe_2$ nanoribbon arrays with pristine quality were fabricated via gas precursor assisted focus He+ ions beam etching process. The fabricated $WSe_2$ nanoribbon arrays demonstrate high Raman anisotropy. The electrical transport measurements revel that the normalized on-currents for both electron and hole are suppressed and scale with the nanoribbon width, with the electron transport experiencing more degradation.

# Dynamic Odd-Even Effect in Multiphasic Ionic Materials

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As a compelling case of sensitive structure−property relationship, an odd−even effect refers to the alternating trend of physical or chemical properties on odd/even number of repeating structural units. In crystalline or semicrystalline materials, such odd−even effects emerge as manifestations of differences in the periodic packing patterns of molecules. Therefore, due to the lack of long-range order, such an odd−even phenomenon is not expected for dynamic properties in amorphous state. Herein, we report the discovery of a remarkable odd−even effect of dynamical properties in the liquid and glass states. In a class of glass-forming diammonium citrate ionic liquids, using incoherent quasi-elastic neutron scattering measurements, we measured the dynamical properties including diffusion coefficient and rotational relaxation time. These directly measured molecular dynamics showed pronounced alternating trends with increased number of methylene (−CH2−) groups in the backbone. Meanwhile, the structure factor S(Q) showed no long-range periodic packing of molecules, while the pair distribution function G(r) revealed subtle differences in the local molecular morphology. The observed dynamical odd−even phenomenon in ionic liquids and glasses showed that profound dynamical changes originate from subtle local structural differences.

Reference:

[1] K. Yang, Z. Cai, A. Jaiswal, M. Tyagi, J. S. Moore, **Y. Zhang*,** "Dynamic Odd-even Effect in Liquid n-Alkanes near Melting Points", submitted.

[2] K. Yang, Z. Cai, M. Tyagi, M. Feygenson, J. C. Neuefeind, J. S. Moore, **Y. Zhang*,** "Odd-even Structural Sensitivity on Dynamics in Network-forming Ionic Liquids", *Chem. Mater.* 28(9), 3227 (2016).

[3] K. Yang, M. Tyagi, J. S. Moore, **Y. Zhang*,** "Odd-even glass transition temperatures in network-forming ionic glass homologue", *J. Am. Chem. Soc.* 136(4), 1268 (2014).

**Imaging lithiation in all-solid-state batteries at the nanoscale**

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The further improvement of high performance Li-ion all-solid-state batteries requires a complete understanding and control of the chemical reactions taking place at the electrodes and electrolyte during lithiation/delithiation. While macroscopic voltammograms are extremely informative, they do not provide information about how the material composing the active layers of the battery is changing upon cycling. Therefore, we combine real-time scanning electron microscopy in ultra-high vacuum with electrochemical cycling to probe the mesoscale behavior of all-solid-state batteries. By combining this *in situ* nanoscale imaging with a detailed *ex situ* characterization of the chemical and electrical changes of the electrodes and electrolyte we develop a comprehensive model for de fast degradation of Al anodes in batteries containing LiPON as the electrolyte (deposited via sputtering) [1,2]. During lithiation, Li ions are trapped by an AlLi alloy capped by a stable Al-Li-O, leading to a rapid capacity fade, from 48.0 to 41.5 $\mu$.Ah/cm$^2$ in two cycles [1]. Unexpectedly, the addition of a Cu protective layer is insufficient to avoid the device degradation because of the ultra fast Li diffusion within Al. Yet, similar batteries containing Si anodes are extremely stable, with >92% of capacity retention after 100 cycles and Coulombic efficiency of 98% [2]. This *in situ* functional imaging platform can be extended to other materials, enabling the real-time diagnosis of degradation in all-solid-state batteries.

[1] M. S. Leite et al., *J. Mater. Chem. A.* **2**, 20552 (2014). Inside Cover.
[2] C. Gong et al., *ACS Appl. Materials and Interfaces*. **7**, 26007 (2015). Cover.

# Near-field edge fringes in nanolayer polarizability mapping

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Scattering-type scanning near-field optical microscope (s-SNOM) provides optical, chemical, and structural information of a surface and enables its imaging with nanoscale resolution [1]. Here, we investigate nanolayers of different materials and demonstrate approach to identify material type based on near fields at sample edges (Fig. 1). We develop theoretical method that combines full-wave numerical simulations and calculations of s-SNOM signal of different demodulation orders. This model allows characterization of any shape and material structures, as well as different tips, and does not include any fitting parameters. In this way, we defined that metallic edge has bright and dark fringes in near-field characterization [Fig. 1(c)-(d)], whereas an edge of dielectric material has no outside fringe. Similar behavior is observed for anisotropic material with hyperbolic dispersion (boron nitride in mid-IR range): depending on the wavelength, it shows either metal or dielectric optical properties.

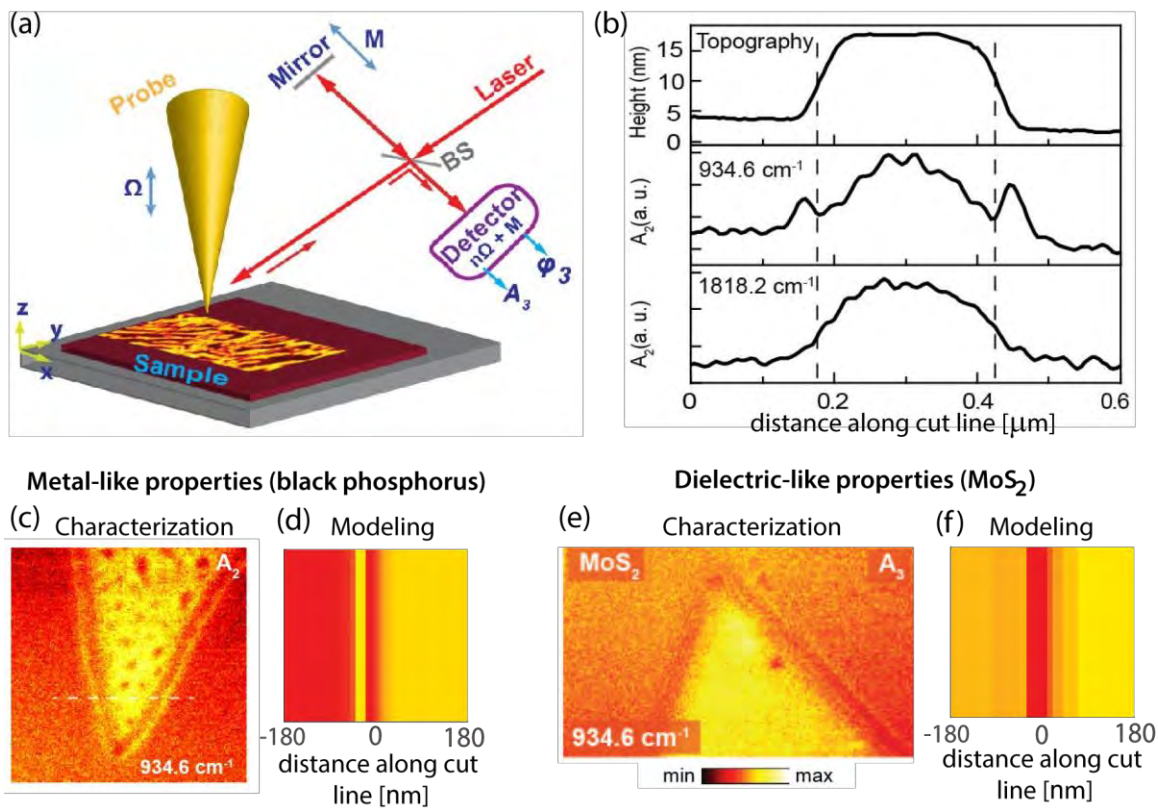


**Fig. 1**: Edge-fringe nanoscopy. (a) Experimental schematics. (b) Line profiles and topography where the broken line represents the physical boundaries of black phosphorus (BP). (c) Near-field amplitude image of BP at frequency $\omega$ = 934.6 cm$^{-1}$ (metal-like optical properties, [2]) and (d) its numerical modeling. (e) and (f) are the same as (c) and (d) but for $MoS_2$ (dielectric-like optical properties).

[1] Y. Abate, R.E. Marvel, J.I. Ziegler, S. Gamage, M.H. Javani, M.I. Stockman, and R.F. Haglund *Sci. Rep.* **5**, 13997 (2015).
[2] Y. Abate, S. Gamage, L. Zhen, S.B. Cronin, H. Wang, V. Babicheva, M.H. Javani, and M.I. Stockman, *Light: Science & Applications*, accepted (2016). http://arxiv.org/abs/1506.05431

Center for Nanophase Materials Sciences

# Poster Abstracts

## 2016 User Meeting

# Decoupling of Chain and Junction Dynamics in Associative Polymer Melts

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## Abstract

We present a detailed study of the relationship between junction dynamics and chain relaxation in associative polymer melts through the combination of dynamic mechanical spectroscopy and broadband dielectric spectroscopy. Our analysis reveals that the local relaxation of the associating junctions can be strongly decoupled from the global chain dynamics. This experimental observation is unanticipated by the classical models for associating polymers. An analogy is drawn between the observed phenomenon and the chain-segmental decoupling in polymeric liquids, where the local heterogeneities are spatially and temporally averaged out for the diffusive macromolecular relaxation. This result demonstrates the complex interplay between local and global dynamics and provides experimental support for a close connection between dynamics of associative polymers and vitrification of glass-forming liquids.

# High-Throughput Screening of Microbial Interactions on a Novel Transparent Microwell Array Platform

M. C. Halsted[1], N. Jiang[1], J. L. Wilmoth[2], A. C. Timm[2], P. A. Briggs[2], D. P. Briggs[3], K. C. Lester[3], F. E. Löffler[4] and S. T. Retterer[1,2,3]

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## Abstract

Spatial confinement affects the behavior of microbial communities that occupy critical niches in the environment. Microwell arrays can be used in the lab to study both deterministic and stochastic assembly of microbial communities *en masse*, enabling the high-throughput screening of unique biological responses to growth in confined environments. To improve resolution and expand microscopic image analyses, we developed transparent microwell arrays comprised of three-dimensional wells via negative photoresist on a glass coverslip. This design allows for shorter working distances and the added capability of bright field imaging during microscopy. The arrays incorporate a thin film of parylene for removing cells between the well boundaries and simultaneously isolating cells within well cavities. A parylene lift-off technique utilizes a low temperature atomic layer deposition of silicon dioxide that prevents adhesion of parylene to the photoresist. Successful stochastic seeding of environmentally relevant bacteria has recently been demonstrated on the new platform, including anaerobic organohalide reducer *Geobacter lovleyi SZ*, and ORNL *Populus* rhizosphere isolates *Pantoea sp. YR343* and *Pseudomonas sp. GM16*. Microbial growth and activity were investigated using autofluorescence of *c* type cytochromes in *Geobacter* and fluorescence of transformed *Populus* rhizosphere isolates expressing either GFP or mCherry. Agent based modeling of microbial interactions is being developed in parallel to inform new experimental designs and establish hypotheses that can be tested empirically using the arrays. The transparent microwells can be used to address complex environmental and industrial problems, as well as improve computational modeling, regarding microbial interactions at discrete spatial resolution on a high-throughput platform.

# USANS as a Tool for Kinetic Analysis: Polymeric Particle Growth and the Dendrimer Effect in Mixed Matrix Membranes

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2. Center for Nanophase Materials Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN
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Herein we report a kinetic analysis, primarily using USANS, on the synthesis of polymeric particles for mixed matrix membranes that can be used for electrochemical catalysis, water purification, and resource recovery. The Diallo Group developed a "one-pot" method for the preparation of polyvinylidene fluoride (PVDF) mixed matrix membranes with embedded polymeric particles. An essential aspect of these membranes is their combination of function and mechanical stability. In theory, this is achieved by the *in-situ* crosslinking of amine-containing oligomers [polyethyleneimine (PEI) or low-generation polyamidoamine dendrimer (PAMAM)] which enables interpenetration of the PVDF spherulites of the matrix. By characterizing the final structure in the mixed matrix membranes, we have determined that the amine particles range from <1–3 μm in diameter, with internal pore sizes on the order of 20 nm. However, characterization of the final solid-state structure raises questions regarding the factors that govern structure formation during processing of the membranes. To elucidate how the micro- and nanostructure develops during membrane preparation, we have conducted an integrated SANS and USANS experiment on the membrane casting solution and the functional membranes.

To our knowledge, this was the first **transient** measurement obtained using USANS. Compared to SANS, the intensities are substantially lower, requiring longer acquisition times as compensation (~minutes for SANS; ~hours for USANS). Therefore, USANS was generally only applied to equilibrated systems. However, upon examination of the intensities of the final casting solutions, we determined shorter acquisition times could be used. We ascertained the minimum acquisition time needed to capture all the features without compromising the integrity of the resulting data. For this work, the acquisition times were reduced by roughly one order of magnitude (to about 15 minutes). Using the shorter acquisition times, we observed transient structural changes in the casting solution across a q-range offered collectively by SANS and USANS.

For this experiment, we chose two variables to manipulate: amine polymer and concentration of crosslinker. We studied the "dendrimer effect" using three different polymer precursors: randomly branched PEI, zeroth generation PAMAM, and first generation PAMAM. Changing the crosslinker concentration enabled us to determine the extent to which charge-induced phase separation and crosslinking of amine polymer played a role in the overall structure of the membranes. The success of our membranes is partly attributed to the mechanical stability of the membranes, which is provided by the PVDF component. Manipulating these two variables in conjunction with the short acquisition times allowed us to test our theory on the interactions of PVDF and amine polymer as the crosslinking reaction progressed. Thus, we expanded upon the currently assumed limits of USANS—we demonstrated the capability of USANS in analyzing transient structures by studying polymeric mixed matrix membranes.

CNMS Best Student Poster: CNMS User Meeting 2016 Abstract

# Accessing Siloxane Functionalized Vinyl-added Polynorbornenes and their Development as Advanced Gas Separation Membranes

Kevin R. Gmernicki,[†] Eunice Hong,[†] Christopher R. Maroon,[†] Shannon Mahurin,[‡] Alexei Sokolov,[†‡] Tomonori Saito,[‡] Brian K. Long[†]*

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With federal mandates calling for nationwide reductions in greenhouse gas emissions over the next few decades, the U.S. power sector is in dire need of a cost effective solution to minimize carbon dioxide ($CO_2$) emissions without hindering power generation efficiency. Amongst the various methods proposed for $CO_2$ separation, polymeric membranes are extremely promising candidates that operate by a passive diffusion mechanism. This passivity requires minimal energy input and may significantly reduce operating costs as compared to other methods such as physical adsorption or cryogenic distillation. However, the ability to separate $CO_2$ from dilute gas mixtures composed mainly of nitrogen ($N_2$) (~75%) using polymeric membranes remains a grand challenge within the field due to the similar molecular sizes of $CO_2$ and $N_2$ that have kinetic diameters of 3.30 Å and 3.64 Å respectively. Towards this goal, we will demonstrate that high molecular weight, siloxane-functionalized, addition-type polynorbornenes are attractive candidates for high flux $CO_2$ separation membranes. Though these materials were previously thought unattainable, we will show that careful polymerization catalyst selection has enabled their synthesis and that large, defect-free films with remarkable $CO_2$ selectivity may be fabricated.

# Investigation of thin-film MEAs for high-efficiency energy storage

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[2] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN

## Abstract

Proton exchange membrane electrolyzer cells (PEMECs) have received much attention for energy storage and hydrogen/oxygen production due to their high efficiency even at low temperature operating conditions. By using nano fabrication methods, novel thin/well-tunable liquid/gas diffusion layers (LGDLs) have been prepared and examined. Ultra-low catalyst loaded MEAs were manufactured through advanced deposition directly on the thin/well-tunable LGDLs. The thin film catalysts with different thicknesses were investigated and the characterization of the catalyst particles between different thin film thicknesses were performed. The experimental results showed that the novel MEAs achieved superior catalyst mass activity, which greatly reduced the cost of the catalysts and the whole PEMEC.

# Electromechanical Response of Lamellar Forming Neutral-Charged Diblock Copolymer Thin Films

Yao Fu,[1] Mingtao Chen,[2] Timothy E. Long,[2] Jason Dugger,[1] Jim Browning,[3] Bobby Sumpter,[1] Brad Lokitz,[1] Rajeev Kumar[1]

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[2]Department of Chemistry, Virginia Tech, Blacksburg, VA
[3]Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge

The electromechanical responses of lamellar forming neutral-charged diblock copolymer thin films are investigated via coarse-grained molecular dynamics simulations. Effects of an applied electric field on ion transport, morphological changes, and stress build-up are studied in detail. In particular, we focus on the effects of a strong applied electric field on the degree of ionization, orientation of polymer-polymer interfaces, and ion-transport. It is found that the applied electric field leads to an increase in the degree of ionization. Furthermore, entropic stresses resulting from chain stretching and compression are found to be comparable with the electrostatic contributions originating mainly from the counter ions. This work paves the way towards establishing a modeling scheme that couples morphology to ion transport in the presence of applied electric field.

# Fabrication of Pollen Particles

**M. Matherne[1], N. Lavrik[2], D. Hu[1]**

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2. Oak Ridge National Laboratory, Center for Nanophase Materials Sciences, TN

The goal of this study is to determine the role the structure of a pollen particle has on its adhesion properties. This study will evaluate how the height and density of spikes on pollen increases its adhesion ability to natural and manmade surfaces. A 3D printed pollen grain will be used in the study to show that the structure alone creates the adhesive properties, not the material of the pollen or pollenkitt, a viscous fluid that covers the surface of many types of pollens. Understanding how the structure of pollen increases its adhesion abilities will be of interest to material scientists when designing adhesive materials, as well as to biologists to help clarify the role of the pollinator during pollination.

There are more than 350,000 known flowering plant species in the world, each with their own pollen that range in size over 3 orders of magnitude and have structures that vary between smooth to extremely echinate (spiky). It is well known that the geometry and surface morphology of a particle influences its adhesion properties, but most adhesion studies are based off of simple geometries. The vast variety of pollen geometries and morphologies, as well as their ability to adhere to surfaces in their natural environments, make pollen an ideal subject to study the adhesion properties of complex geometries. Additionally, the pollenkitt that covers many species of pollen grains has been presumed to add an extra adhesive force that aids in pollen dispersion. However, the amount of pollenkitt varies based on the structure and type of pollen. Previous studies have used atomic force microscopy (AFM) to measure the adhesive forces between defatted (no pollenkitt) and non-defatted (with pollenkitt) pollen grains and various surfaces (Lin et al., 2013). The results of that study show that pollen with a very echinate structure and high volume of pollenkitt enhance adhesion as compared to pollen with smaller surface features and less pollenkitt. Further experiments using AFM with a fabricated pollen particle could distinguish how the structure of the pollen, independent of any materials properties, influences its adhesion properties. Pollen particles have been 3D printed before at larger scales, but pollen has never before been fabricated at scale. The actual sized fabricated particles will allow accurate adhesion due to structure data to be obtained from the AFM experiments.

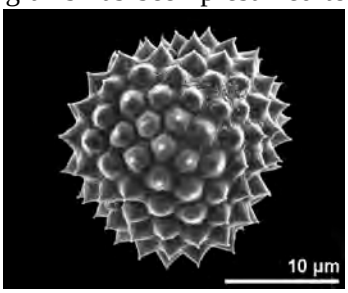


**Figure 1.** *Ambrosia artemisiifolia* pollen

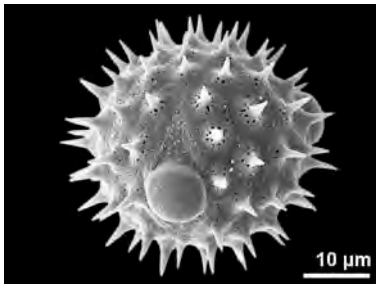


**Figure 2.** *Helianthus annuus* pollen

The CNMS facilities are required to fabricate the synthetic pollen grain due to its small size and structural complexity. According to data measured by Lin et al., *Ambrosia artemisiifolia*, or Ragweed, pollen is echinate in structure, as can be seen in Figure 1, with ~0.5 to 1.0 µm high spikes and only ~15% pollenkitt by mass. *Helianthus annuus*, or Sunflower, is echinate in structure, as can be seen in Figure 2, with ~1.5 to 2.0 µm high spikes and ~30% pollenkitt by mass. The ragweed pollen has 0.84 spikes per $\mu m^2$ and the Sunflower pollen has 0.32 spikes per $\mu m^2$. Because both pollen particles are echinate but have different heights and densities of spikes, they are good candidates to study the effects of surface morphology on adhesion properties. The AFM experiment mentioned previously will be repeated at the home institution, Georgia Tech, with the fabricated pollen grains and the results compared to those previously reported by Lin et al. It is hypothesized that the results of this experiment will prove that the adhesion properties of the pollen grain are due solely to its structure, and not to the material properties of the pollen or the pollenkitt. These experiments will elucidate the effect complex geometries have on adhesion, whereas previously only the effects of basic geometries were known. The results will influence the design of advanced materials as well as further our understanding of the pollen-pollinator interaction, which has an important influence on worldwide crop pollination.

# Anti-frosting Surfaces using Ice as Humidity Sinks

**Saurabh Nath[1], Bernadeta R. Srijanto[2], Scott T. Retterer[2], C. Patrick Collier[2] and Jonathan Boreyko[1]**

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Fig 1. Overlapping Dry Zones Between Ice Stripes

No engineered surface, to date, has been able to passively suppress in-plane growth of frost occurring in humid, subfreezing environments. A major reason for that is up until very recently it was believed during frost growth each condensate droplet freezes individually due to heterogeneous nucleation at the solid-liquid interface. However, this is not true. Very recently we have shown that condensation frosting is an inter-droplet phenomenon, where frozen droplets harvest water from their adjacent water drops and grow ice bridges that propagate through the entire population of supercooled condensate. The underlying mechanism behind the formation of ice bridges is that the saturation vapor pressure of ice is lower than that of water at the same temperature, causing ice to behave as a humidity sink. By tuning the inter-droplet distance, we can control the localized vapor pressure gradients that govern the rate of propagation of in-plane frost. Here we show that functionalized surfaces that can spatially control nucleation sites in conjunction with temporal control on the onset of freezing events can be used to passively suppress frost growth and even halt it. In such cases of halted frost growth, we see a dry zone manifest itself around ice where no condensation or frost forms. When properly controlled, in-plane dry zones can be as large as $\sim 1$ mm and sustained for hours. Finally, we demonstrate the scalability of this application. When microscopic arrays of ice are appropriately patterned onto a macroscopic surface, the in-plane dry zones around each ice stripe can overlap, enabling the surface to remain largely free of frost over time (see Fig. 1).

# Fabrication of Synthetic Moth Antennae

**T. Spencer[1], N. Lavrik[2], K. Kalaitzdou[1], D. Hu[1]**

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2. Oak Ridge National Laboratory, Center for Nanophase Materials Sciences, TN

Over 300,000 different species of Lepidoptera have evolved and thrived throughout the world. Some of those species such as the Gypsy moth, L. Dispar, wreak havoc on the vegetation the moth feeds on. The reproduction of such species is only possible with the help of an extraordinary air filtration adaptation. Moths are reported to smell each other from over 7 miles away, locating each other with just 200 airborne molecules. (Wyatt, 2015) By studying the olfactory structure of such moths, important information can be gleaned as to how such moths can filter the air with such accuracy. In this study, we investigate how the unique 3 dimensional structure of the moth's antennae influences particle capture. This information can be used to reduce the pest infestation and also be applied to create better filters.

The overall approach involves obtaining various moth species with complex antennae structures, creating mimics of antennae structures and testing the mimics in a wind tunnel to analyze fluid flow and deposition on the structures. Over 35 moth specimens have been captured from the Nantahala mountain range and their antennae have been analyzed under a confocal microscope. The structure of the antennae of these moth antennae exhibit a peak in regards to the branch angle with respect to the wind flow as shown in Figure 1.

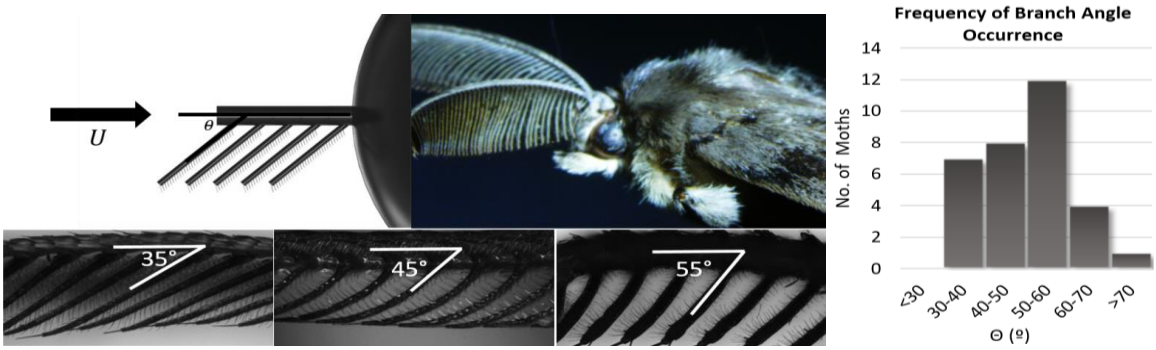


**Figure 1.** Antennae branch angles with respect to airflow across species

To create a mimic of the antennae structure, detailed fabrication is being completed in the CNMS facilities. The small scale and hierarchical nature of the antennae provide a unique fabrication challenge that cannot be solved using more traditional methods. The primary motive of the CNMS tasks is to generate an accurate antennae mimic as can withstand tests in a wind tunnel with wind speeds of up to 2 m/s. Unique fabrication challenges arise due to the small scale and the fact that the antennae structure has three levels of hierarchy. The dimensions range from 10 um in diameter up to 130 um and have very high aspect ratio features as shown in Figure 2. The fabricated mimic can then be used in wind tunnel tests at the home institution of Georgia Tech to examine the particle collection ability of the antennae.

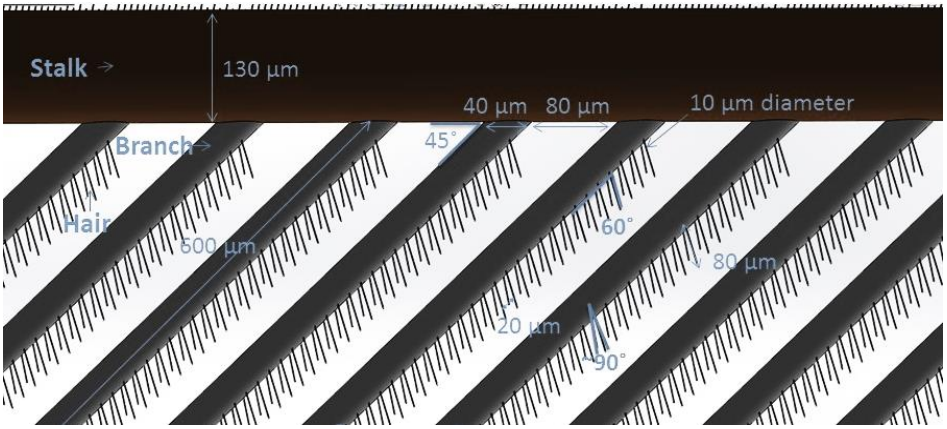


**Figure 2**. Dimensioned Schematic of hierarchical antennae mimic fabricated using stereolithographic technology available in the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory

# In Situ Mitigation of Subsurface and Peripheral Focused Ion Beam Damage via Simultaneous Pulsed Laser Heating

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Focused helium and neon ion beam induced processing has been used to improve the resolution limits of direct-write nanoscale synthesis in recent years. The ubiquitous application of $He^+/Ne^+$ beams for next-generation nanofabrication is currently limited by deleterious subsurface damage induced by the energetic ions in the underlying substrate. In this work, we demonstrate the in situ mitigation of subsurface damage created during $He^+/Ne^+$ ion exposures in silicon via a synchronized pulsed laser-assisted process. The pulsed infrared laser source delivers spatially localized photothermal energy to the near-surface region of the substrate in an in situ manner. This reduces the subsurface ion implantation and defect concentration induced during $He^+/Ne^+$ processing by as much as 90% and is dependent upon the photon/ion flux. The laser-assisted exposure technique is also shown to be effective at reducing peripheral defects in $He^+$ patterned graphene, which makes this process an attractive candidate for patterning of 2D materials. These results offer an essential solution to the substantial subsurface damage that is introduced by $He^+/Ne^+$ processing, and increase the applicability as a direct-write nanoscale material processing tool.

# Comparison of Carbon Nanotube Fiber Microelectrodes for Neurotransmitter Detection: Correlation of Electrochemical and Surface Properties

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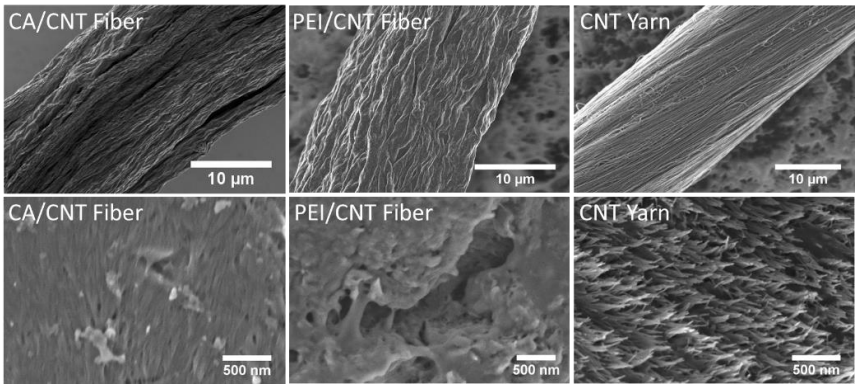
CNT fibers can be directly fabricated as electrodes with high reproducibility, but CNT fibers made by different protocols have not been compared and the surface properties that cause the outstanding electrochemical performance have not been identified. In this study, we compared three types of CNT fiber microelectrodes: CNT fibers produced by wet spinning with polyethylenimine (PEI/CNT) or chlorosulfonic acid (CA/CNT), and a CNT yarn made by solid based CNT drawing. The sensitivity scaled with conductivity as the CNT yarn microelectrode has the highest conductivity, dopamine sensitivity (290 ± 65 pA/cm$^2$) and fastest electron transfer kinetics (0.68 ± 0.02 V). CNTs yarns have well-aligned, high purity CNTs and abundant oxygen containing functional groups which are favorable for dopamine detection. The CA/CNT fiber has a smoother surface that is not as favorable for high frequency measurements, but has a negative charge due to residual chlorosulfonic acid that leads to high selectivity to dopamine over uric acid and ascorbic acid. The oxidation currents at CNT yarn and PEI/CNT fiber microelectrodes are frequency independent and the redox reaction is more reversible due to thin-layer conditions created by dopamine getting trapped in crevices. However, PEI/CNT fibers have larger crevices that trap dopamine longer, leading to a slower temporal response. The results indicate that a rough surface with small crevices and abundant oxygen groups leads to better dopamine and serotonin detection. Understanding the correlation of neurotransmitter detection with surface properties is useful for evaluating potential new carbon nanomaterial-based microelectrodes.



# Chemical Doping Enables Intermolecular Long-Range Covalent π–π Bonding

Yong-Hui Tian[†], Jingsong Huang[‡], Xiaolan Sheng[†], Bobby G. Sumpter[‡], Miklos Kertesz[§]

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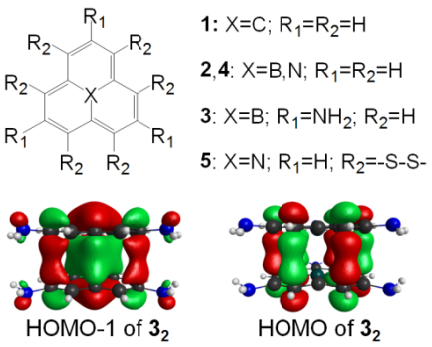
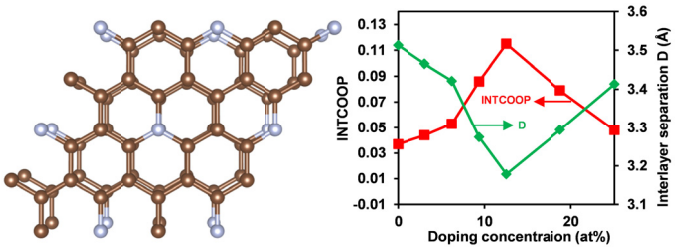
Phenalenyl (PLY), the smallest triangular graphene fragments, has long been recognized as a stable radical to construct organic conductors due to the intermolecular pancake bonding. By using quantum chemistry calculations, we demonstrated that the boron- or nitrogen-doped PLYs usually considered closed-shell molecules can form pancake-shaped 4e/all-sites double π–π bonding upon intermolecular π-dimerization, in contrast to the 2e/half-sites analogues in the parent PLY π-dimers. By extending PLY to two-dimensional (2D) systems, we show that N-doped graphenes (NGPs) with various doping levels can form an unusual 2D π–π bonding between adjacent layers substantially stronger than typical vdW interaction as reflected by the reduced interlayer separations. Electronic structure calculations indicate that the 2D interlayer pancake bonding has a covalent characteristic but occurring at a long range. The unusual π–π bonding motif induced by chemical doping in the PLY analogues and 2D graphene layers may broaden the landscape of, and find new applications for, the intermolecular covalent bonding interactions.




B- or N-doped PLYs




N-doped graphene

# Property Descriptors for Electron- and Hole-Conducting Conjugated Polymers for Organic Spin Valves Applications

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**Abstract:** Organic spin valves (OSVs) are one type of spintronic devices consisting of a non-magnetic organic spacer sandwiched between two conducting ferromagnetic electrodes. Based on two sets of key material descriptors, in this work we used ab initio theories to screen conjugated polymers in order to identify good electron-conducting n-type candidates to be used as the organic spacer materials in OSVs. Ionization potential (IP) and electron affinity (EA) were used to predict whether a conjugated polymer will be an electron donor or acceptor while the effective mass m* of the electron and hole (e and h) were used to assess the charge transport along the polymer backbone. A gamut of theories including various hybrid density functional theories (DFTs) and long-range corrected DFT were employed to calculate IP/EA. Using available experimental cyclic voltammetry (CV) data, all of the methods were validated and the material descriptors were calibrated. The effective masses $m^*_e$ and $m^*_h$ were obtained by fitting the band structures at the conduction band minimum and valence band maximum, respectively. Based on the property descriptors, two electron-conducting n-type polymers BT and F8BT were recommended for synthesis. Two hole-conducting p-type polymers PFO and P3HT on the other extreme were also recommended considering that the Fermi level may be adjusted onto the top of the valence bands by gating to create holes and that holes may also carry spin.

# Experimental and Theoretical Studies of La Filled $CoSb_3$ Skutterudites

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*Contributed equally in this work

**Abstract:** Skutterudites with a general formula of $MX_3$ (M=Co, Rh or Ir; X=P, As or Sb) constitute a promising class of thermoelectric materials via filling the dodecahedron cages with d- or f-block guest atoms. In this work, we systematically studied the effects of La filling on the thermoelectric properties of $CoSb_3$ skutterudites across a wide filling fraction range of 10-60%. Especially, the roles of La filler atoms, Sb vacancies, and their interplay have been studied by experimental pellet measurements of Seebeck coefficient, electrical conductivity, and thermal conductivity in conjunction with ab initio density functional theory calculations of spin-polarized electronic energy bands, density of states, Fermi surfaces, and magnetic properties. We found that (i) La guest atom acts as a filler, not a rattler, highlighting the key role of f-electron in the rattling scheme; (ii) the Fermi surface of La-filled $CoSb_3$ is spin polarized though there is no long-range spin ordering; (iii) Sb vacancies introduce band dispersions and modify band gaps to the electronic structure, in line with our experimental observations of semiconducting properties for skutterudites with ≤20% La filling fraction.

# Role of 2-D Materials in Photocatalytic Hydrogen Production from Water Splitting: Transition Metal Carbides (MXenes) and Transition Metal Dichalcogenides (TMDs)

*Rui Peng*[a], *Hui Wang*[a], *Zili Wu*[a],*

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Hydrogen generated by harnessing the infinite solar energy from the decomposition of water, the most abundant source on the Earth, has been reckoned as the ultimate solution for the global energy crisis and environmental issues. The blue print of this scenario was first enlightened by Fujishima and Honda using $TiO_2$ photoelectrode and Pt as a counter-electrode under UV light illumination in 1972. Since then, a myriad of semiconductors have been investigated and tested for photocatalytic hydrogen evolution reaction. However, it still remains the *Holy Grail* in photocatalytic hydrogen generation to fabricate a material that can efficiently absorb visible light and perform hydrogen evolution reaction without the company of noble metal as co-catalysts. In Recent years, a new category of materials in a 2-D fashion have arisen and attracted a wealth of research attention due to their interesting and unique physico-chemical properties and their promises to be applied as effective catalysts and/or co-catalysts in the photocatalytic reaction for photocatalytic hydrogen production from the splitting of water. In this work, $MoS_2$ and MXenes, as two distinct types (transition metal dichalcogenides and transition metal carbides) of 2-D materials, were selected to study their roles as photocatalyst and co-catalyst in photocatalytic hydrogen evolution reaction. The results suggest that these 2-D materials can carry out efficient photocatalytic hydrogen evolution reaction under visible light irradiation without the assistance of precious metal species.

# Imidazole-containing block copolymers: Towards understanding the effect of morphology on electromechanical response

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Polyelectrolytes are widely used in applications ranging from membranes for batteries and gas or water purification to stimuli-responsive actuators. The majority of research on the electromechanical response of ionic polymers has focused on macroscopic properties. Studying mesoscale morphological changes that ionic block copolymers undergo in response to an applied electrical field will provide new insight into their macroscopic properties and aid in the rationale design of new soft materials.

A novel imidazole-containing monomer was synthesized to serve as the soft blocks in di- and triblock copolymers. The hard blocks were consisted of styrene or deuterated styrene (for neutron scattering studies). Self-consistent field theory (SCFT) was employed to guide the design of model block copolymers. Reversible addition fragmentation chain transfer (RAFT) allowed the synthesis of the block copolymers and the effect of the imidazole counter ion on polymerization kinetics and thermomechanical properties was investigated. Neutron scattering and AFM of the block copolymer films revealed the morphological changes related to both ion redistribution and macroscopic response to an applied electric field. The structure-morphology-property relationship should result in a better understanding of the mesoscale changes that contribute to the macroscopic electromechanical response and aid in the rationale design of new soft materials.

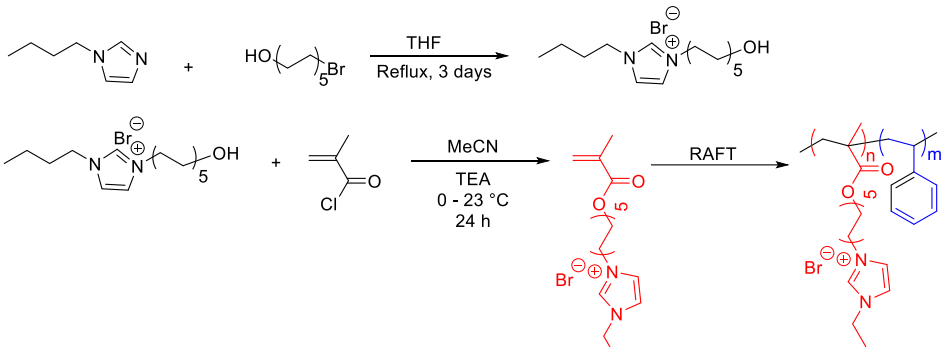


Figure 1 The synthesis of imidazole-containing monomers and block copolymers through RAFT polymerization.

# Slow Relaxations in Ionic Liquids: A Signature of Hydrophobic Aggregation

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Nanoscale aggregates arising from the 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 their special ability to solvate both polar and nonpolar molecules, however, their influence on other physicochemical properties, such as ionic conductivity and dynamics, is not yet well understood. It has been found by computation and x-ray scattering of alkyl-imidazolium ILs that the onset of long-range hydrophobic aggregation occurs when the alkyl chain contains four or more carbons. Broadband dielectric spectroscopy measurements of a series of imidazolium bis(trifluoromethylsulfonyl)imide ILs reveal the emergence of a slow relaxation and a decrease in the ionic conductivity correlating with this onset. These results are discussed within the framework of the current understanding of aggregation and dynamics in room temperature ionic liquids.

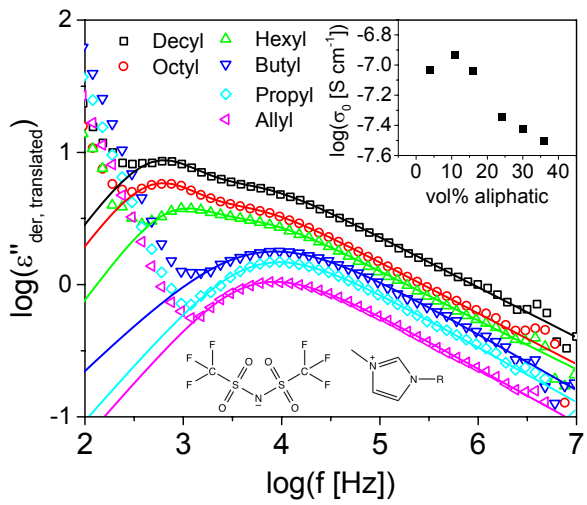


**FIG. 1:** Derivative spectra, $\varepsilon''_{der}(f) = \left(-\frac{\pi}{2}\right)\frac{\partial \varepsilon'(f)}{\partial ln(f)}$ , of a series of alkyl-imidazolium bis(trifluoromethylsulfonyl)imide ionic liquids of varying alkyl chain length. The temperature of each ionic liquid is chosen such that their structural, $\alpha$-relaxations are equal.

*Inset:* DC conductivity, $\sigma_0$, of the imidazolium ILs at the chosen temperatures *versus* volume percent of aliphatic groups. The onset of aggregation leads to a reduction of ionic conductivity.

References:

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## Origin of Fast Proton Transport in Stoichiometric Acceptor Doped Perovskites

Jilai Ding, Janakiraman Balachandran, Xiahan Sang, Wei Guo, Jonathan A. Anchell, Gabriel Veith, Craig Bridges, Yongqiang Cheng, Jonathan Poplawsky, Nazanin Bassiri-Gharb, Raymond Unocic, Panchapakesan Ganesh

Ionic transport dynamics underpin the functionality of most energy storage and conversion technologies. Yttrium doped barium zirconate (Y-BZO) has attracted significant scientific attention as a promising electrolyte in proton-conducting solid oxide fuel cells (SOFCs), due to its relatively high proton conductivity while maintaining chemical stability at intermediate operating temperatures (400-700 ℃). To reveal the fundamental role of oxygen vacancies and dopants on the proton transport mechanisms, it is vital to understand how these defects are created and distributed in the crystal at the atomic scale. A detailed understanding of local distortion in Y-BZO would help elucidate the correlation between point defects and lattice distortions and their role on proton conduction.

In this study, epitaxial Y-BZO thin films with different dopant concentrations (0%, 5% 10%, 15% and 20%Y-BZO) were prepared on (100) oriented MgO substrates by pulsed laser deposition (PLD). From the surface potential mapping by time-resolved Kelvin probe force microscopy, it was found that the activation energy for proton transport increases with increasing dopant concentration, showing a “trapping” effect. To uncover this phenomenon, a Nion UltraSTEM was used to acquire fast, frame-averaged, high-angle annular dark field (HAADF)-STEM images of the Y-BZO lattice, and distortion analysis on each B-site atom was performed on these images. Both bond angle and displacement distribution showed an increased value and variation with increasing dopant concentration, which is consistent with the density functional theory (DFT) calculation. Furthermore, DFT calculations suggest that the Y-Y pair tend to trap more protons owing to increased local lattice distortion, which lead to a monotonic increase in activation energy as a function of dopant concentration. This discovery provides new ways of improving proton conductivity by inhibiting dopant clustering and lattice distortion.

# Ion Dynamics in Ammonium-based Polymerized Ionic Liquid Diblock Copolymers

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Polymerized ionic liquids (PILs) are a class of polymers characterized by ionic liquid groups attached to polymeric chains. These materials are of interest as polymer electrolytes in electrochemical applications such as batteries, photovoltaics and field effect transistors. Block copolymers of PILs are created by directly linking two polymer chains, where at least one of the chains is a PIL. These materials have numerous potential advantages for the design of functional materials due the combination of material properties unattainable in homogenous systems. The present work provides fundamental insight into the ion dynamics of poly(ionic liquid) block copolymers using broadband dielectric spectroscopy on diblock copolymers of poly(methyl methacrylate) (PMMA) or poly(butyl methacrylate) (PBMA) with poly(methacryloyloxyethyl dimethyl ethyl ammonium) $NTf_2$ (PMAOEDMEtAm$NTf_2$). The polymers under investigation have chemically similar groups attached directly to the polymer backbone, chosen in order to probe the effect of incorporating charged groups into the polymer matrix. By varying the volume fraction of the PIL in the copolymer system, three distinct types of behavior are observed. At a low volume fraction of $\phi_{PIL}$=0.17, ion dynamics are strongly coupled to the structural relaxation of the neutral PMMA matrix. At intermediate volume fraction, $\phi_{PIL}$=0.69, ion dynamics are identical to the PIL homopolymer but conductivity is suppressed due to the influence of morphological structure and suppression of ion dissociation. In the case of high volume fraction, $\phi_{PIL}$=0.89, ion dynamics are identical to the PIL homopolymer and conductivity is enhanced due to improved ion dissociation and conducting domain interconnectivity. We demonstrate that ion transport can be enhanced in a PIL block copolymer system by incorporating a non-conducting phase and conclude that the ionic conductivities of the PIL copolymers are significantly altered by varying the volume fraction.

**Ion Dynamics in ultra-thin films of polymerized ionic liquids**

Maximilian Heres, Tyler Cosby, Joshua Sangoro, University of Tennessee, Knoxville, TN 37920

Polymerized ionic liquids combine the high ionic conductivity of ionic liquids with the mechanical properties of polymers, allowing the fabrication of ultra thin ion conducting films.[1] In applications such as dye-sensitized solar cells, field effect transistors, and electrochromic devices, the ion dynamics at the interface of such films are of vital importance to the performance of the device. While it is known that polymer dynamics are affected by one dimensional confinement on such length scale, experimental difficulty such as dielectric breakdown have previously prohibited dielectric measurements of ultra thin films of highly ion conducting polymerized ionic liquids.[2] In this work, ion dynamics in ultra-thin films of imidazolium based polymerized ionic liquids are investigated utilizing a novel nano structured electrode setup for broadband dielectric spectroscopy. By introducing a well defined, electrically insulating air gap between sample and electrode, nano-structured electrodes permit dielectric measurements of ultra thin, highly conducting polymer films.[2,3] Below the calorimetric glass transition temperature, the characteristic charge transport rates in films of polymerized ionic liquids, down to 7.5nm, remains unaltered from those in bulk. However, above the glass transition temperature of the bulk sample, a systematic slowing of ion dynamics is observed with decreasing film thickness. This effect is attributed to increasing relative contribution of the interfacial interactions between the polymerized ionic liquid and the substrate with decreasing film thickness.

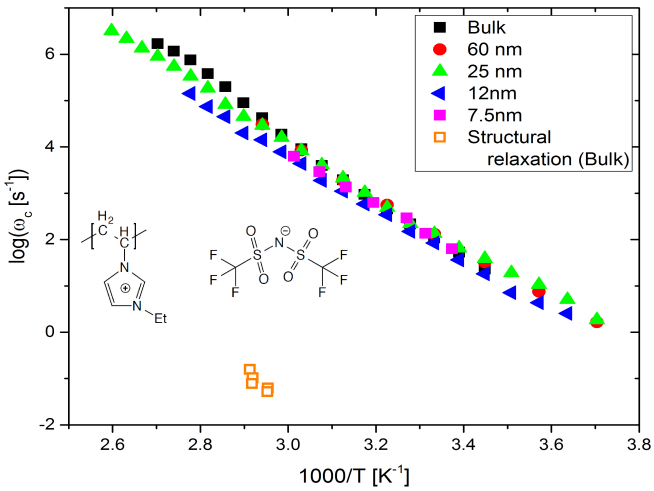


Figure 1: Characteristic ion transport rate for poly(ethylimidazolium) bis(trifluoromethylsulfonyl)imide at varying film thicknesses and bulk, as well as structural dynamics of the bulk polymerized ionic liquid with respect to inverse temperature.

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## A New, Air-Stable $Na_3SbS_4$ Solid Electrolyte for All-Solid-State Sodium Batteries

Hui Wang, Yan Chen, Zachary D. Hood, Gayatri Sahu, Amaresh Samuthira Pandian, Jong Kahk Keum, Ke An, Chengdu Liang

All-solid-state sodium batteries, those that utilize solid electrolytes and abundant sodium resources, show great promise for safe, low-cost, and large-scale energy storage applications. To achieve more-efficient all-solid-state sodium batteries, the exploration of novel highly conductive solid electrolytes is critical for room temperature operation. Ideal solid electrolytes for sodium batteries must have high ionic conductivity, employ low-cost synthetic methods, and hold outstanding chemical and electrochemical stability. Achieving the combination of these properties represents a grand challenge for most sulfide-based solid electrolytes. Herein, we report the design of a new solid electrolyte, $Na_3SbS_4$, which realizes excellent air stability and can be prepared through an economic synthesis centered on hard and soft acid and base (HSAB) theory. This new sodium-ion solid electrolyte exhibits a remarkably high ionic conductivity of 1 mS $cm^{-1}$ at 25 °C and also holds ideal compatibility with a metallic sodium anode.

# Conduction below 100˚C in nominal $Li_6ZnNb_4O_{14}$

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Lithium ion battery attracts a lot of attentions as an energy storage solution in many fields because of its high energy density and efficiency. The increasing demand for a safer rechargeable battery with a high energy density per cell is driving a search for a novel solid electrolyte with a high $Li^+$ or $Na^+$ conductivity that is chemically stable in a working Li-ion or Na-ion battery. $Li_6ZnNb_4O_{14}$ has been reported to exhibit a $\sigma_{Li} > 10^{-2}$ S cm$^{-1}$ at 250°C, but to disproportionate into multiple phases on cooling from 850°C to room temperature. Here, we report the room-temperature Li-ion conductivity in a porous pellet of a multiphase product of a nominal $Li_6ZnNb_4O_{14}$ (LZNO) composition is shown to have bulk $\sigma_{Li} \approx 3.3 \times 10^{-5}$ S cm$^{-1}$ at room temperature that increases to $1.4 \times 10^{-4}$ S cm$^{-1}$ by 50°C. $^7$Li MAS NMR spectra were fitted to two Lorentzian lines, one of which showed a dramatic increase with increasing temperature. A test for water stability and the scanning electron microscopy image indicates that $Li^+$ may move to the particle and grain surfaces to react with adsorbed water as occurs in the garnet $Li^+$ conductors. LZNO has also been made into a composite with β-$Li_3PS_4$, which showed the "filler effect" and an improved $Li^+$ conductivity. This study provides another possible solid electrolyte to further investigate and might be a potential solid electrolyte for future application.

# Computational Investigation of Half-Heusler/MgO Magnetic Tunnel Junctions

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[3)] Department of Physics and Astronomy, University of Alabama, Tuscaloosa, Alabama 35401, USA;
**Keywords:** half-Heusler alloys, MTJs, perpendicular anisotropy, half-metallicity, IV, TMR.

**Abstract body:**

Among our database of 378 half-Heusler alloys[1)] XYZ (X=Cr, Mn, Fe, Co, Ni, Ru and Rh; Y=Ti, V, Cr, Mn, Fe and Ni; Z=Al, Ga, In, Si, Ge, Sn, P, As, and Sb), 45 half-metals and 34 near-half-metals are identified with negative formation energy, and all of them follow the Slater-Pauling phase precisely. The lattice mismatch between half-metals and MgO is discussed. A list of 6 half-metal/near-half-metal half-Heusler alloys with less than 1% mismatch is found. We construct magnetic tunnel junctions (MTJ) with the six half-heusler found to create Heusler-MgO junctions. Structural relaxation is performed and the electronic and magnetic properties of those junctions are investigated. Some heuslers remain half-metallic in MTJs while other transition into near half-metallic or non half-metallic. Four types of interfacial configurations are studied and we found that the strong oxidation between metal and oxygen atoms causes the systems to choose the YY-MgO interface as the lowest energy configuration in all six cases. We have also found that the uniaxial anisotropy can be induced in Heusler layers next to MgO. The interface induced perpendicular magnetic anisotropy (PMA) combined with their half-metallicity (as in NiMnSb/MgO and CoTiSn/MgO junctions with MnMn and TiTi interface layer) makes them promising candidates for spintronics application such as spin transfer torque magnetic random access memory (STTMRAM). Finally we use DFT based Non-Equilibrium Green's Function (NEGF) method[2)] to calculate the IV characteristics of those six most stable MTJs and bring a more straightforwad view on their potential application in future spintronics devices. An example of calculations for NiMnSb-MgO is shown.

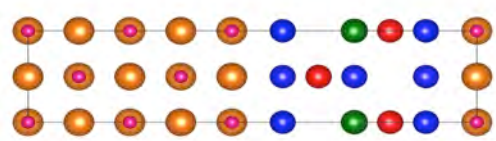

**Figure 1.** Side views of the superlattices of the half-Heusler(110)/MgO junctions with XX/OMg-terminated interface. Color note: X(red), Y(blue), Z(green), Mg(orange), O(pink).

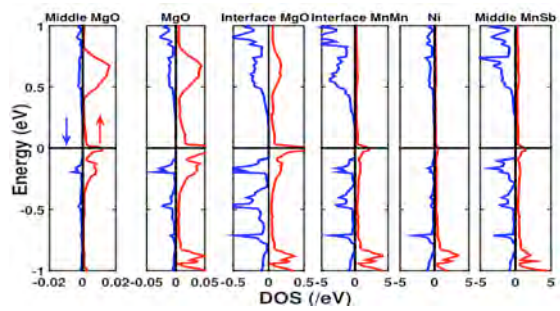


**Figure 2.** Local density of states for a NiMnSb-MgO periodic supercell with MnMn/OMg interface. The supercell stay HM (Band gap is opened in the spin-down channel).

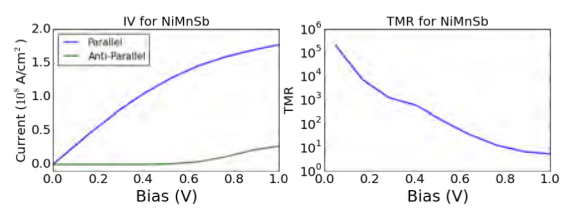


**Figure 3.** IV characteristics of NiMnSb-MgO tunnel junction from DFT-NEGF calculations.

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# Effect of Electronic Structure on Phonon Transport at the Interface of Monolayer $MoS_2$ and Metal Substrates

Zhequan Yan[1], Wenqing Shen[1], Mina Yoon[2], and Satish Kumar[1]

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**ABSTRACT**: Efficient heat removal through the interface of monolayer $MoS_2$ and metal substrates is important for high performance and reliability of $MoS_2$-based electronic devices. We have developed an atomistic framework based on the first-principle Density Functional Theory (DFT) and the Atomistic Green's Function (AGF) to elucidate the inherent connection between electronic structure and phonon properties at the interface of single-layer $MoS_2$ and metal substrates (Au and Sc). Strong chemical coupling at the interface of $MoS_2$ and Sc substrate results in a thermal boundary conductance (TBC) that is significantly higher than that of the interface of $MoS_2$/Au. The redistribution of phonon density of states (DOSs) at $MoS_2$/Sc interface, correlated with interfacial electronic structure change, enhances interfacial phonon-phonon coupling and increases phonon transmission. We find that the charge transfer caused by the introduction of a metal substrate can affect the strength of the Mo-S bond and result in the significant re-distribution of phonon DOSs and transmission at interface. The weakening of the Mo-S bond strength due to charge re-distribution and the resultant decrease in the force constant between Mo and S atoms keeps more phonons locating in low frequency region which leads to a 60 % decrease in TBC. The findings in this study demonstrate the inherent relationship among the interfacial electronic structure, the phonon distribution, and TBC, which helps us understand the mechanism of phonon transport at the $MoS_2$/metal interfaces. The results provide insights for the future design of $MoS_2$-based electronics and a way of enhancing heat dissipation at the interfaces of $MoS_2$-based nano-electronic devices.

# QUANTUM TRAJECTORY/ELECTRONIC STRUCTURE STUDY OF THE NUCLEAR QUANTUM EFFECTS IN THE GRAPHENE AND POLYMER/FULLERENE MODELS

Sophya Garashchuk [a] and Jacek Jakowski [b]

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[b]*CNMS, Oak Ridge National Laboratory, Oak Ridge, TN*

Classical dynamics of nuclei provides insight into chemical reactions under many conditions, yet at low energies quantum aspects of lighter nuclei (the zero-point energy, tunnelling and nonadiabatic behaviour) may be important. We are considering the regime when quantum-mechanical (**QM**) behaviour of a few selected nuclei influences the reactivity, while the full QM treatment of all the nuclei is unfeasible due to system size. To elucidate the role of nuclear QM effects we use the quantum trajectory (**QT**) formulation of the Schrödinger equation. The QM effects are incorporated through the quantum potential acting on the trajectory ensemble in addition to the classical potential. From practical considerations, the mean-field type approximation is made on the quantum potential. Furthermore, large molecular systems are described within the mixed quantum/classical trajectory framework with the QM correction incorporated into selected degrees of freedom [1]. This dynamics methodology is combined with the Density Functional Tight Binding approach, which allows on-the-fly computation of the electronic structure for systems of a few hundred atoms. The hybrid approach is used to study adsorption of quantum hydrogen colliding with graphene 'flakes' $C_{37}H_{15}$ and $C_{87}H_{23}$ [2]. Localization of the proton wavefunction is found to have large effect on reactivity. The approach is also used to understand experimentally observed effect of the H/D substitution on the optoelectronic properties of the P3HT/PCBM heterojunction.

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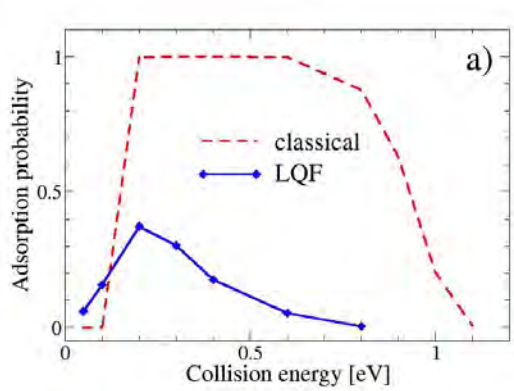


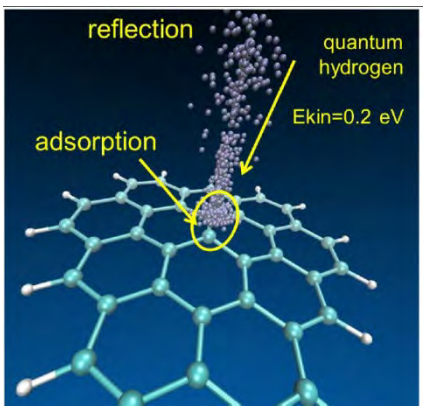


*Interaction of H with $C_{37}H_{15}$. Left: Adsorption probability obtained from dynamics with ("LQF") and without ("classical") the quantum correction for a range of collision energies. Right: the trajectory ensemble representing the protonic wavefunction.*

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Abstract Submitted
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The Oak Ridge National Laboratory

Primary Subject Area: Exploring Electronic and Ionic Processes in Functional Materials

***Ab initio* study of cross-interface electron-phonon couplings in FeSe thin films on $SrTiO_3$ and $BaTiO_3$** YAN WANG, Department of Physics and Astronomy, University of Tennessee, Knoxville, TOM BERLIJN, Oak Ridge National Laboratory, ANDREAS LINSCHEID, Department of Physics, University of Florida, Gainesville, STEVE JOHNSTON, Department of Physics and Astronomy, University of Tennessee, Knoxville — We study the electron-phonon coupling strength near the interface of monolayer and bilayer FeSe thin films on $SrTiO_3$, $BaTiO_3$, and oxygen-vacant $SrTiO_3$ substrates, using *ab initio* methods. The calculated total electron-phonon coupling strength $\lambda = 0.2$–$0.3$ cannot account for the high $T_c \sim 70$ K observed in these systems through the conventional phonon-mediated pairing mechanism. In all of these systems, however, we find that the coupling constant of a polar oxygen branch peaks at $\mathbf{q} = \mathbf{0}$ with negligible coupling elsewhere, while the energy of this mode coincides with the offset energy of the replica bands measured recently by angle-resolved photoemission spectroscopy experiments. But the integrated coupling strength for this mode from our current calculations is still too small to produce the observed high $T_c$, even through the more efficient pairing mechanism provided by the forward scattering. We arrive at the same qualitative conclusion when considering a checkerboard antiferromagnetic configuration in the Fe layer. In light of the experimental observations of the replica band feature and the relatively high $T_c$ of FeSe monolayers on polar substrates, our results point towards a cooperative role for the electron-phonon interaction, where the cross-interface interaction acts in conjunction with a purely electronic interaction. We also discuss a few scenarios where the coupling strength obtained here may be enhanced.

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# Synthesis of Indene-$d_8$, $IC_{60}BA$-$d_{16}$ and $IC_{70}BA$-$d_{16}$ for CNMS User Project 2015-053

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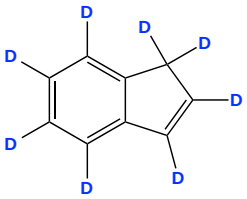
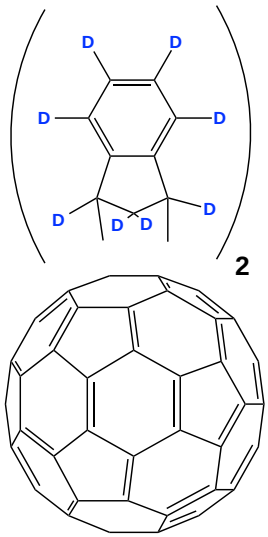
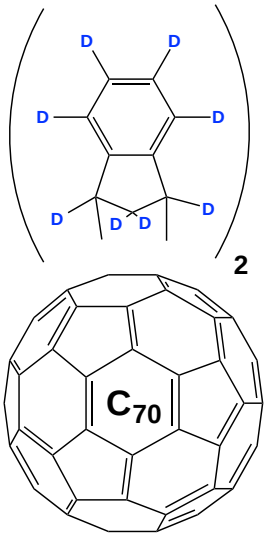
**Abstract:** The synthesis of fully deuterated indene (indene-$d_8$), needed for the preparation of $IC_{60}BA$-$d_{16}$ (Indene-$d_8$-C60 Bisadduct) and $IC_{70}BA$-$d_{16}$ (Indene-$d_8$-C70 Bisadduct) for CNMS user project 2015-053 (Tolbert, UCLA), required overcoming some interesting obstacles and challenges in organic chemistry and deuterium isotopic labeling.




**Indene-$d_8$**




**$IC_{60}BA$-$d_{16}$ mixture of isomers**




**$IC_{70}BA$-$d_{16}$ mixture of isomers**

Details of the procedures developed at the CNMS for the successful synthesis of indene-$d_8$, and the novel deuterium labeled fullerene derivatives $IC_{60}BA$-$d_{16}$ and $IC_{70}BA$-$d_{16}$, will be presented.

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

## Direct Write of 3-Dimensional Structures with Helium Ion Microscopy

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The ability to fabricate complex free-standing 3-dimensional structures at the nano-scale onto any substrate could revolutionize nanoscience and nanotechnology, opening pathways to the fundamentally new mechanical, electronic, and photonic devices. Over the last decade, electron beam deposition has been established as a technique with demonstrated ability to direct write 3-dimensional structures. Using a scanning electron microscope e-beam cracking of metallic precursor, Pt, Au and W based structures can be deposited directly onto a substrate. However, the localization of an e-beam is such that the probe size and interaction volume severely limits the minimum size of fabricated structures. Similarly, the chemical composition of the deposited materials is often limited, necessitating combined laser-e-beam methods or complex post-processing steps that often negatively impact the fidelity or final structure. In this work we demonstrate the fabrication of 3-dimensional platinum structures utilizing a helium ion microscope (HIM). Due to the nature of helium ions and stronger ion-matter interactions, this significantly limits probing volume and increases spatial localization of the reaction zone. Hence, He-ion induced deposition has the potential to deposit 3 dimensional structures faster and at smaller scales the electron beam fabricated structures. We demonstrate complex structure fabrication with the HIM and compare the efficacy with that of electron beam fabricated structures. We optimized the microscope parameters for fabrication by depositing large arrays of 3D pillars and varying the parameters at each location. Further, we demonstrate an automated process to determine the optimal deposition parameters using He-ions, which directly calculates deposition rates, thickness and angles at varying microscope parameters. Finally, the purity of these structures was analyzed with STEM-EELS and EDS.

### Acknowledgments

This work was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility.

## Termination control of magnetic coupling at a complex oxide interface

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Atomically flat interfaces between ternary oxides have chemically different variants, depending on the terminating lattice planes of both oxides. Electronic properties change with the interface termination which affects, for instance, charge accumulation and magnetic interactions at the interface. Well-defined terminations have yet rarely been investigated for oxides of $ABO_3$ type (with metals A, B). We present a strategy of thin film growth and interface characterization applied to fabricate the $La_{0.7}Sr_{0.3}MnO_3$-$SrRuO_3$ interface with controlled terminations. Ultra-strong antiferromagnetic coupling between the ferromagnets occurs at the $MnO_2$-SrO interface, whereas the other termination shows weaker coupling and exchange-bias-like behavior, in agreement with density functional calculations. X-ray magnetic circular dichroism has been measured at the Ru and Mn L edges as a function of an applied magnetic field. An unusual rigidly coupled reversal of Mn and Ru magnetic moments is observed for the $MnO_2$-SrO interface. Our results demonstrate efficient termination control of magnetic coupling across a complex oxide interface. A pathway is suggested for theoretical and experimental explorations of novel electronic interface states resulting from controlled interface termination.

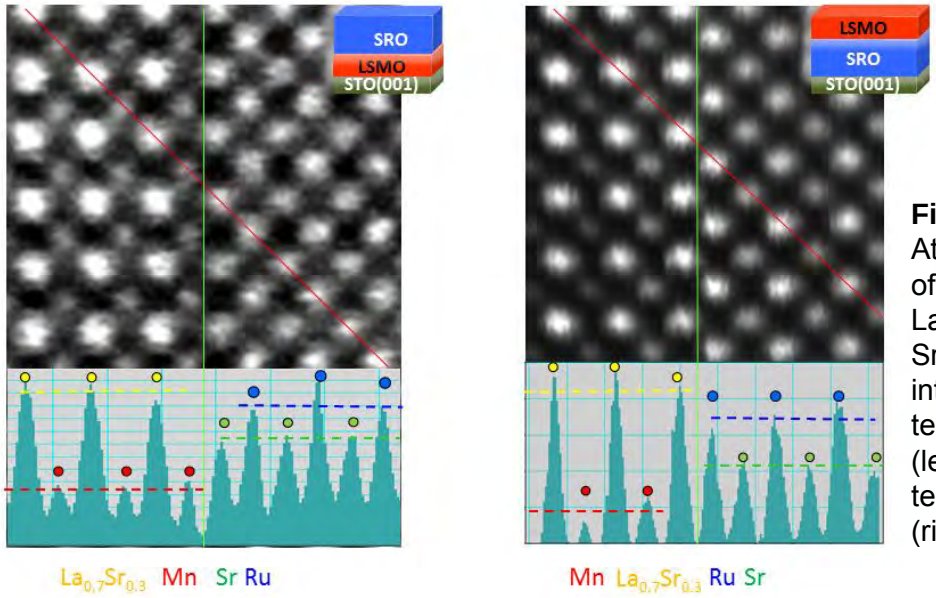


**Figure 1.** Atomic structure of the $La_{0.7}Sr_{0.3}MnO_3$-$SrRuO_3$ interface with termination 1 (left) and termination 2 (right).

# Determining the Electromechanical Response Mechanism of Nanostructured Ionic Block Copolymers

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The electromechanical response of ionic polymers to an applied electric field places ionomeric systems in a position to be of immense use to a variety of fields including flexible electronics, biomimetic devices, and nanofluidics.[1] While the use of common ionic polymers such as Nafion as actuators has been thoroughly studied,[2] the literature lacks a complete knowledge of the complex interplay of an electromechanical response and the chemical structure, morphology, and ion mobility of these ionomeric systems. The actuating behavior of ionic polymer systems results from deformation due to electric/Maxwell stress (electrostatics of ion distribution) as well as viscous/hydrodynamic stress (properties of the polymer structure and chemical identity). A fundamental understanding of how each of these parameters affects the electromechanical response would allow for the rational design of ionic polymer systems that give rise to specific functionality. To this end, we are in the early design phase of constructing a sample cell for the Liquids Reflectometer (BL-4B) at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL) that is capable of applying an electric field to a sample during neutron reflectometry measurements. While this sample cell would be of general use to a wide variety of research areas, we intend to investigate how the system morphology and chemical composition of ionic block copolymer systems affects the electrostatic interactions that occur under an applied electric field by monitoring ion and polymer migration through a thin film. The sensitivity of neutron reflectometry to scattering length density as well as subnanometer changes in thickness make it an ideal tool for investigating polymer and counterion mobility under applied fields. We have utilized raft polymerization to synthesize AB and ABA block copolymers where the ionic B block contains charged imidazolium groups to impart electromechanical responsiveness and a polystyrene A block providing structural integrity to the film. It is our hypothesis that copolymer morphologies containing conducting channels (cylindrical and gyroid) will best facilitate ion transport, leading to a more pronounced electromechanical response.

**References**

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[2] Duncan, A. J.; Leo, D. J.; Long, T. E. *Macromolecules* **2008**, *41* (21), 7765.

# How a Nanostructure's Shape Affects its Lifetime in the Environment

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Inorganic nanomaterials occupy an ever-increasing role in many technologies. Their ubiquity though can lead to environmental release of these materials, which may have harmful consequences to the natural world. To date a significant amount of research interest has been given to studying the environmental impact of the simple nanoparticle morphology of numerous inorganic compounds. However significant advances in nanomaterials synthesis have lead to the development of an extremely wide array of nanostructures, with each of these unique shapes having their own properties. Unfortunately little attention has been given to understanding how the shape effects the environmental lifetime. To this end we have begun to study the shape related effects on the environmental lifetime of Ag nanostructures in aquatic systems. Further, we focused on comparing the particle and cube morphology by placing them in synthetic hard water, seawater, and pond water. By observing their aging with a combination of UV-Vis spectroscopy and Transmission Electron Microscopy we were able to observe the vastly different aging pathways of the Ag nanoparticles and nanocubes. Specifically, the nanoparticles formed large benign aggregates where as the nanocubes maintained their nanosize domain.

# Multifunctional Probing of Electronic, Magnetic, Transport, and Thermoelectric Properties in Two-Dimensional Materials: Roles of Heterogeneities

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**and An-Ping Li**

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Two-dimensional materials are inherently heterogeneous. Both localized defects such as vacancies and dopants, and mesoscopic boundaries such as surfaces and interfaces result in compositional or structural heterogeneities. The presence of defects and boundaries can break transitional or rotational lattice symmetry, modify the energy landscape, and create quantum confinement. It is these heterogeneities that often dictate the physical properties of 2D materials by governing the electron scattering, transport, and excitation processes. Thus the study of 2D materials must go beyond “ideal” or structurally averaged systems to consider and embrace heterogeneities.

Scanning tunneling microscopy (STM) with multifunctional probing capabilities enables revealing of geometric and electronic structures as well as magnetic, thermoelectric, and transport properties of heterogeneous 2D materials. In particular, multi-probe STM can be used to map electron transport on multiple-length scales and reveal correlation between structural and electronic properties and electrical conductivity across individual defects and boundaries. Furthermore, the newly developed multi-probe transport spectroscopy method which considers both the 2D and 3D conduction channels and their interactions gives a quantitative way to differentiate surface and bulk conductivities.

# Multidimensional Probes of Complex Functional Ferroelectric Domain Structures

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Advances in the control of interface chemistry and *in situ* monitoring/control of the growth processes have provided researchers the tools necessary to design complex ferroelectric domain structures. Leveraging these approaches, researchers have produced a wealth of polar structures including: ordered ferroelastic and mixed-phase domain structures, topological defects, and others. Understanding the structure and response of these complex domain structures requires the ability to perturb and observe their responses under relevant length- and time-scales. In turn, researchers are forced to conduct multidimensional experiments which in general are difficult to analyze "by hand." Here, we discuss our recent progress using "big data" analytics to interpret multidimensional scanning transmission electron microscopy and scanning probe microscopy experiments to understand the structure and response ferroelectric materials. Particularly we focus our attention on three interesting candidate structures: a mixed-phase $PbTiO_3$ structure, collective behavior in (111)-oriented $PbZrTiO_3$, and the shape, structure, and response of "springy" ferroelastic domains in compositionally-graded $PbZr_{1-x}Ti_xO_3$.

First, we explore mixed-phase in-plane oriented $a_1/a_2/a_1/a_2$ and dense $c/a/c/a$ domain structures in highly tensile strained $PbTiO_3$ (Fig. 1a). Using band-excitation switching spectroscopy (BE-SS) we observe that it is possible to write out-of-plane oriented *c* structures using a locally bias; and explore the changes in the local switching that occur during these ferroelastic transitions. We demonstrate the local interconvertibility of in-plane and out-of-plane oriented nanoscale structures. The ability to controllably write and erase out-of-plane polarized domains in an in-plane polarized matrix creates local structures with largely varying properties (*i.e.* piezoelectric, dielectric, elastic modulus, etc.) which are readily adaptable for memory devices.

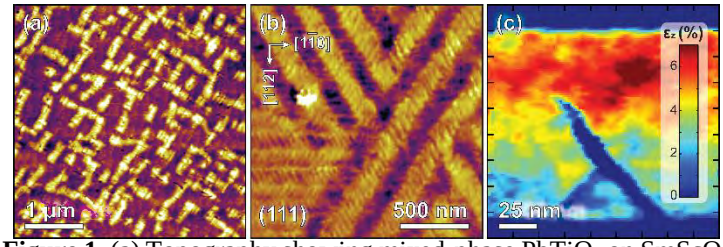


**Figure 1**. (a) Topography showing mixed-phase $PbTiO_3$ on $SmScO_3$ (110). (b) Highly ordered nanotwinned domain structure in (111)-oriented $PbZr_{0.2}Ti_{0.8}O_3$. (c) Out-of-plane strain map of compositionally-graded $PbZr_{1-x}Ti_xO_3$.

Second, using BE-SS we explore collective switching behavior in (111)-oriented $PbZr_{0.2}Ti_{0.8}O_3$ consisting of highly ordered nanotwinned domain structure (Fig. 1b). We observe a homogeneous nucleation bias inside the twin band across a number of nanodomains, different from the inhomogeneous nucleation typically observed in conventional ferroelectrics. This phenomenon suggests the presence of possible strong domain-domain coupling between nano-domains resulting in collective switching. This work provides new insights into the fundamental understanding of ferroelastic switching in ferroelectrics.

Finally, we utilize detailed nanobeam diffraction strain mapping (ND-SM) and BE-SS to explore the fine structure and response of ferroelastic domains in compositionally-graded $PbZr_{1-x}Ti_xO_3$. ND-SM reveals that the compositional and strain gradients modify the morphology of the ferroelastic domains making them appear more needle-like rather than parallelepiped-like (Fig. 1c). Subsequent studies of electric-field induced switching show that these needle-like domains are highly mobile; expanding (or contracting) from the free surface depending on the direction of the applied bias.[1] This unusual field-dependent response renders these domains highly mobile in the out-of-plane direction yet spatially localized in the plane; prompting them to be called "springy" in nature.[2] Such work highlights the ability to utilize strain gradients to finely control the structure, response, and properties of ferroelastic domains.

1. J. C. Agar, *et al*., Highly-mobile ferroelastic domain walls in compositionally-graded ferroelectric thin films. *Nature Mater.* **15**, 549-556 (2016).
2. K. Dorr, Ferroelastic domains: springy expansion. *Nature Mater.* **15**, 497-498 (2016).

**Examination of Carbon Nanostructures in Covetic Materials by Helium Ion Microscopy**

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Nanophase carbon infused base-metal alloys exhibit enhanced electrical and thermophysical properties. This new class of materials, known as covetics, have attracted increased research interest because of their superior materials performance. Covetic materials are prepared by incorporating large amount of nanophase carbon into metal matrixes using a unique melting and electrical infusion process. The enhanced electrical and thermal conductivities of covetics originate from carbon nanostructures dispersed in the metal. Understanding the nature of interfacial structure of nanophase carbon and host metal matrix is critical to elucidate the mechanics for superior material performance. Nano-carbon structures in covetic copper and aluminum alloys were examined using helium ion microscopy (HIM) at the Center for Nanophase Materials Science (CNMS). HIM provides the necessary contrast and resolution for observation of nanophase carbon structures in the convetic metal hosts. We observed unique nanophase structural characteristics that are associated with lattice infused carbon in covetics.

This work was supported by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under Contract DE-AC02-06CH11357. Helium ion microscopy was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

(Subject Area: Observing and Controlling Matter at the Nanoscale)

# Impact of Structural and Physico-chemical Differences on Catalytic Activity of Two Commercially-Sourced Platinum Nanocatalysts

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Platinum group element (PGE)-based nanocatalysts are important in a variety of industrial technological processes ranging from catalytic conversion of CO, hydrocarbons, and $NO_x$ in modern automobiles to energy production by hydrogen fuel cells. Developing a comprehensive and quantitative understanding of what controls their catalytic properties is important for further development of nanocatalysts for various applications. However, this potential cannot be fully realized without new information on how structural and chemical heterogeneity at the nanocatalyst surface, in addition to surface coatings such as enveloping hydrocarbon layers (ECL) relates to catalytic activity, especially for complex industrially produced nanocatalysts operating at realistic reaction conditions. New systematic and real-time studies are needed to produce models that link structural and physico-chemical characteristics of PGE-based nanocatalysts with their catalytic activity.

The goal of this study is to develop a comprehensive relation between the atomic structural, physical and chemical attributes of two highly reactive commercially sourced Pt nanocatalysts and their catalytic activity in the decomposition of $H_2O_2$. Previous studies of $H_2O_2$ decomposition, a reaction often used to compare nanocatalyst performance, are generally not systematic over a broad range of solution conditions. Furthermore, many of these studies lack detailed characterization of the nanocatalyst surface chemical and physical properties. To this end, my research is divided into three main parts: (1) Characterization of commercially sourced platinum black (Pt-black) and Pt-nanopowder as-received from the manufacturer; (2) Measuring the rates of $H_2O_2$ decomposition at different thermodynamic conditions and *ex situ* characterization of Pt nanocatalyst before, during and after reaction; and (3) Measuring the structural and chemical modifications at the surface of Pt-black and Pt-nanopowder - including the impact and fate of the ECL - during decomposition of $H_2O_2$ by coupling results from a benchtop electrochemical cyclic voltammetry (CV) with a liquid electrochemical fluid cell for *in situ* transmission electron microscopy (TEM) and *in situ* X-ray diffraction methods. Results from Parts 1 and 2 show that the abundance of $PtO_x$ phases at or near the surface contribute significantly to the catalytic activity of these Pt nanocatalysts in the decomposition of $H_2O_2$. These results are also allowing us to test several proposed platinum oxidation and reduction pathways for $H_2O_2$ decomposition. Our upcoming *in situ* fluid cell TEM experiments at CNMS (ORNL) at different experimental conditions will complement our bench-scale reactivity and characterization of *ex situ* samples by showing changes in nanocatalyst surface and ECL in real time. We anticipate that this systematic approach will allow me to determine what reaction pathway(s) is most important in the $H_2O_2$ decomposition by these Pt nanocatalysts as well as to link their specific catalytic activity with their different physical, chemical and structural properties.

# Local coexistence of $VO_2$ phases revealed by deep data analysis

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We report a synergistic approach of micro-Raman spectroscopic mapping and deep data analysis to study the distribution of crystallographic phases and ferroelastic domains in a defected Al-doped $VO_2$ microcrystal. Bayesian linear unmixing revealed an uneven distribution of the T phase, which is stabilized by the surface defects and uneven local doping that went undetectable by other classical analysis techniques such as PCA and SIMPLISMA. This work demonstrates the impact of information recovery via statistical analysis and full mapping in spectroscopic studies of vanadium dioxide systems, which is commonly substituted by averaging or single point-probing approaches, both of which suffer from information misinterpretation due to low resolving power.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.
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# Strengthening $Al_{0.3}CoCrFeNi$ High Entropy Alloys by B2 Precipitate

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**Abstract**

High-entropy alloys (HEAs), containing multiple metallic elements in equimolar or near-equimolar ratios, have generated great interest, because they possess a simple structure but with outstanding mechanical properties. Despite their long-range crystal order, locally the multiple elements in HEAs may occupy the lattice sites in a disordered or partially-ordered fashion, leading to phenomenal properties. Thus, it is essential to establish general relationships between microstructures and essential mechanical properties of strength, ductility, and creep resistance, applicable to several HEA systems. Suitable heat-treatment can introduce homogenous second phase, B2 phase, into the FCC matrix. The effect of B2 phase on strength, ductility, serration, and creep resistance is discussed. An in-situ neutron diffraction study is used to understand the atomic-structure evolution and deformation behaviors of the $Al_{0.3}CoCrFeNi$ at elevated temperatures. The results shows the creep behavior of $Al_{0.3}CoCrFeNi$ is superior to conventional alloys, and the heat treatment introduce secondary B2 phase into the FCC matrix, which increase the yielding strength, decrease the ductility, and diminish the serrated flow, during compression tests at high temperatures. The elemental distributions within the FCC matrix and B2 phase are predicted by thermodynamic calculations.

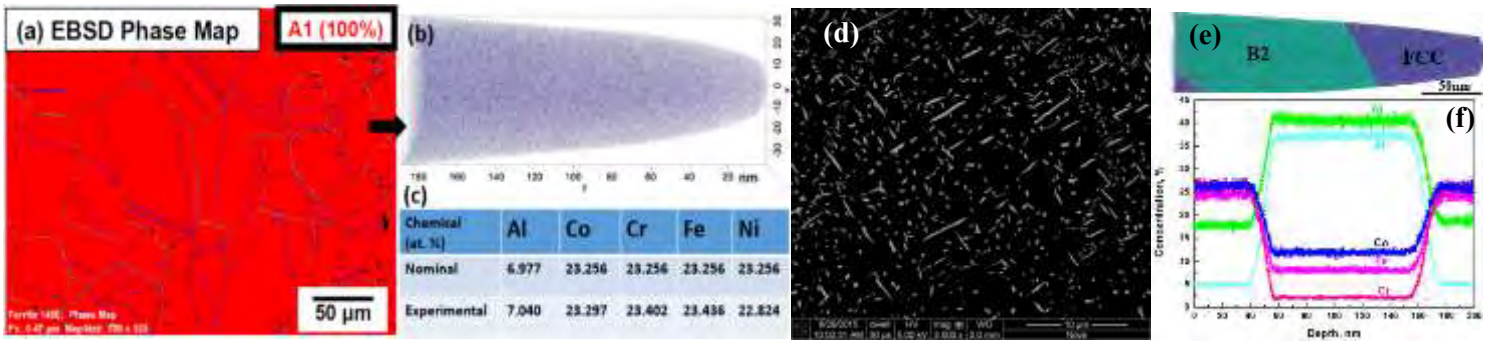


**Figure 1 (a) EBSD phase map, (b) APT, and (c) Related chemical compositions of the $Al_{0.3}CoCrFeNi$ (FCC); (d) SEM image, (e) APT, and (f) Related 1D concentration profile of the $Al_{0.3}CoCrFeNi$ (FCC + B2).**

**Acknowledgement**

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# Combining Electron Microscopy and Photonics to Study Complex Plasmonic Resonances

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Metallic nanostructures with a complex plasmonic response, such as the Archimedean nanospiral (ANS) present novel ways to utilize plasmonics in modern technology. The nanospiral can support several resonant modes, with distinct electric field profiles such as the hourglass (500-650nm) and focusing (650-980nm) modes shown in finite difference time domain (FDTD) simulations in Figure 1. In addition to the linear plasmonic response, the ANS exhibits a stronger second-order nonlinearity than other metallic nanostructured systems. A high spatial-resolution picture of the plasmonic modes is critical to understanding the interactions between plasmonic modes that drive the high non-linear efficiencies.

Cathodoluminescence (CL) experiments in a scanning transmission electron microscope (STEM) create a unique opportunity for characterizing plasmonic systems with the combined spatial and spectral resolution of electron microscopies and optical spectroscopies respectively. A significant benefit to STEM-CL in comparison with electron energy loss spectroscopy (EELS) is the flexibility of optical filtering and spectroscopy techniques for the analysis of the polarization and spectral response of nanophotonic media.

First, the focusing mode (650-980nm) is examined. Figure 1a shows a FDTD simulation of the plasmon mode. Figure 1b shows a high angle annular dark field (HAADF) image of the fabricated ANS on the SiN window. The raw CL intensity is shown in Fig 1c with no spectral filtering. Emission from all plasmonic modes, interband transitions, and any other radiative decay pathways are all simultaneously detected. However, by spectrally filtering the CL signal, individual modes can be isolated. The focusing mode is predicted to be strongest in the 650-980 nm region, so by using a 600 nm long-pass spectral filter, the radiative decay from other optical features can be eliminated, and a map of the focusing mode (Figure 1d) can be obtained.

For the hourglass mode, however, spectral filters cannot be used to observe the spatial profile of the plasmonic resonance, because unlike the focusing mode, the hourglass mode has a distinct polarization axis that is parallel to the axis of the exciting optical pulse, as shown in the FDTD simulation in Fig 1e. With no polarization selectivity on electron-optics, the hourglass plasmon modes can be excited in all in-plane axes of the ANS simultaneously within the STEM, and no individual plasmon can be isolated and detected. However, since the hourglass mode has a strong polarization dependence on the exciting pulse, it is likely that the resulting emission is similarly polarized. In Fig 1f the HAADF image of an ANS is shown, and Fig 1g shows the unfiltered CL image. Fig 1h shows CL image filtered with a linear polarizer and exhibits a similar spatial profile to the simulation in Fig 1e, demonstrating that the modes that have a have a strong dependence on the polarization of the exciting optical source also exhibit a polarization dependence on their radiative decay.

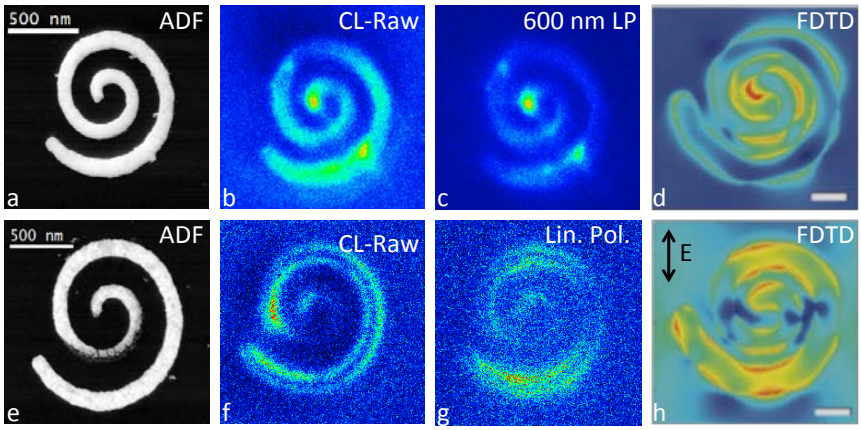


**Figure 1.** (a) Finite-difference time-domain (FDTD) simulation of the focusing mode in an Archimedean nanospiral (ANS). (b) High angle annular dark field (HAADF) image of an ANS and two cathodoluminescence (CL) images of the same ANS: (c) the unfiltered CL signal showing the total emission of the ANS, (d) the 600 nm long-pass filtered image showing the focusing mode. (e) FDTD simulation of the hourglass mode. (f) HAADF image of an ANS alongside (g) the unfiltered CL image and (h) the CL image filtered with a linear polarizer.

**Effect of Morphology on Dynamics of Poly(styrene$_2$-b-1,4-isoprene$_2$) Miktoarm Block Copolymers**

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The impact of morphology and architecture on dynamics of copolymers is of great interest in various fields from nanolithography to electrochemistry. The dynamics of poly(styrene-b-isoprene) diblock copolymers in various morphologies have been extensively studied. However, the dynamics of more complex molecular architectures is not yet well understood. In this study, dynamics of poly(styrene$_2$-b-1,4-isoprene$_2$) miktoarm block copolymers corresponding to lamellar and cylindrical morphologies were investigated by Broadband Dielectric Spectroscopy. While no change in the spectral shape of segmental relaxation mode was observed for the all the samples, systematic broadening of the poly(isoprene) chain relaxation mode was observed with increasing degree of confinement within frozen poly(styrene) domains. These results will be further discussed with respect to recent theories and models describing dynamics of confined copolymers [1, 2].

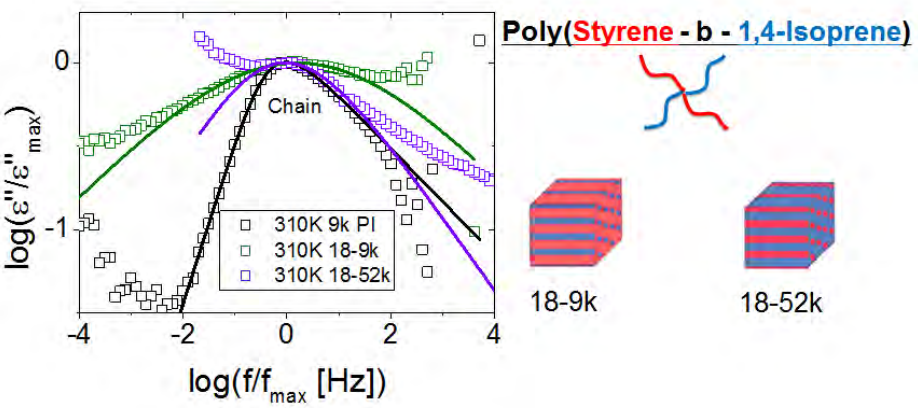


**Fig. 1:** Normalized dielectric loss spectra of chain mode relaxation peaks showing the broadening of the chain mode for 18-9k molecular weight $PS_2$-$PI_2$. Only low frequency broadening of the chain mode of 18-52k molecular weight $PS_2$-$PI_2$ is observed. Havriliak-Negami fits are shown as solid lines. Graphics to the right illustrate architecture of miktoarm polymer as well as theoretical morphological phase domains formed by the $PS_2$-$PI_2$ polymers [3].

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# In-situ Transmission Electron Microscopy Study of High-Entropy Alloys: Microstructure Transformations

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High-entropy alloys (HEAs) are composed of near-equal or equal molar metal elements. Due to the unique formation, thermodynamically, they have promising properties at elevated temperatures. In the Al-Co-Cr-Cu-Fe-Ni HEAs system, perhaps the most difficult (and interesting) structural transformation to characterize and understand is the spinodal decomposition, which occurs at temperatures near 600 °C. It is reported that the parent phase becomes unstable below 600 °C, and decomposes into two phases. These new phases share the same lattice structure as the parent phase, and co-exist within the coherent crystal grains, which were originally formed by the parent phase. Only subtle changes in the diffraction patterns could be observed. Therefore, the details of the spinodal transformation are still uncertain. Indeed, we cannot yet say for certain that the transformations are correctly classified as spinodal decompositions. In-situ high-temperature microscopy is the perfect tool for addressing this question, because this technique may be used to observe the characteristic feature of spinodal decomposition: The formation of periodic composition fluctuates, whose magnitude varies with temperature.

The $Al_{1.3}CoCrCuFeNi$ sample was heated from room temperature to 500 °C, 550 °C, and 600 °C inside the TEM chamber using the customized heating holder. Isothermal duration for each temperature is 15 min. The cross-hatched microstructures were distorted after heating, especially for chromium and iron. However, the morphology of the microstructure of copper roughly remained the same with stronger contrast, which indicates that copper is not involved in the distorting process from the matrix. The trend matched the Monte Carlo simulation for microstructure evolution for various temperatures conducted by Dr. Santodonato. Further work would be focused on the cooling process for the direct observation of the spinodal decomposition.

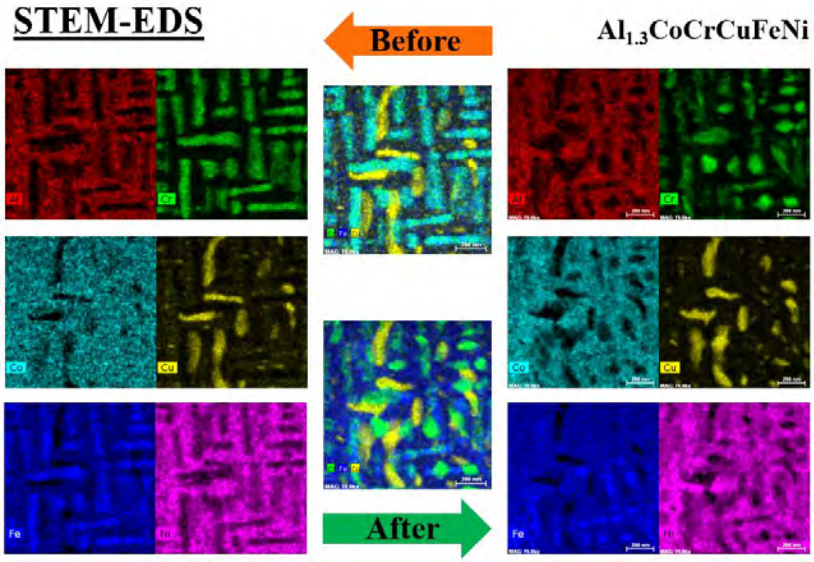


Figure 1 Energy-dispersive spectroscopy images for each element before and after in-situ heating up to 600 °C. The in-situ TEM study was conducted by Dr. Raymond R. Unocic.

**Acknowledgement**: This study is supported by National Science Foundation and Department of Energy.

# Investigation of Microstructure Evolution in NbTaTiV and NbTaTiVZr Refractory High-entropy Alloys

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Different from conventional alloys, high-entropy alloys (HEAs) have multiple principal elements, often five or more. Carefully-designed HEAs tend to form solid solutions with simple structures based on multiple principal elements. This trend results from the fact that the high mixing entropy enhances the formation of simple solid-solution phases, such as the face-centered-cubic (FCC), body-centered-cubic (BCC), and hexagonal-close-packed (HCP) structures. Due to the microstructural stability at high temperatures, HEAs are frequently considered as potential structural materials for elevated-temperature applications. The focus puts on the design and development of HEAs containing single solid-solution phases through the integration of theoretical modeling and experimental demonstration. In this study, we attempt to develop the refractory high-entropy alloys, which contain the single BCC solid-solution phase. NbTaTiV and NbTaTiVZr refractory HEAs were designed by the CALculation of PHAse Diagrams (CALPHAD) approach and investigated using the X-ray diffraction (XRD), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and atom probe tomography (APT). The as-casted NbTaTiV and NbTaTiVZr refractory high-entropy alloys exhibit the conventional dendritic structure. The systematic heat-treatment has been performed to study the microstructure evolution. The heat treatment leads to a gradual transition from the dendritic to single BCC solid-solution phase structure, as clearly revealed by APT.

Acknowledgement

We gratefully acknowledge the support of the Army Research Office through the grant of W911NF-13-1-0438 with the program managers, S. N. Mathaudhu, D. M. Stepp. We thank Dr. Michael Gao, Dr. Chuan Zhang, Fan Zhang, and Dr. P. K. Liaw for great support, ideas, suggestions, and important contributions to the present works.

# Machine Learning on Molecular Level

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The ability to utilize individual molecules and molecular assemblies as data storage elements has motivated scientist for years, concurrent with the continuous effort to shrink a size of data storage devices in microelectronics industry. One of the critical issues in this effort lies in being able to identify individual molecular assembly units on a large scale in an automated fashion of complete information extraction. Here we present a novel method of applying machine learning techniques for extraction of positional and rotational information from scanning tunneling microscopy (STM) images of π-bowl sumanene molecules on gold.

We use information from Density Functional Theory (DFT) simulations in order to form *a priori* knowledge about the system. Using this knowledge, we extract both individual molecular images and their total intensities from a large-scale STM image of molecular film. We use Markov Random Field (MRF) model to classify brightness states of each molecule based on both the simulations and experimental data. We further develop an algorithm that uses a convolutional Neural Network (cNN) combined with MRF and input from density functional theory to classify molecules into different rotational classes. Our results demonstrate that a molecular film is partitioned into distinctive rotational domains consisting typically of 20-30 molecules. In each domain, the "bright" molecules are generally surrounded by six nearest neighbor "dark" molecules, and the resultant overall structure form a periodic lattice of rotational and polar states within each domain. In addition, we also uncover the presence of peculiar dimer formations consisting of two "bright" molecules located next to each other. An example of complete decoding of a system can be seen in Fig. 1.

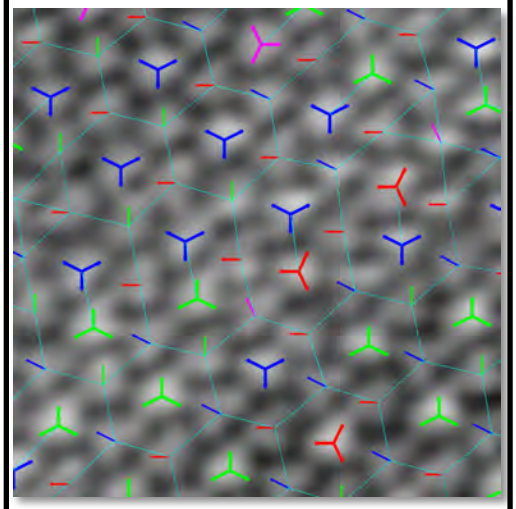

**Figure 1. A select region of STM image of sumanene with extracted information overlay. Shape of the marker denotes different brightness states, while color and direction denote different rotational states.**

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES). Fellowship support (AM) from the UT/ORNL Bredesen Center for Interdisciplinary Research and Graduate Education.

# Van der Waals heterojunctions built via an all dry-transfer method.

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## Abstract

The emergence of graphene has opened up interests in two-dimensional (2D) materials owing to their superior electronic and transport properties. The variety of individual 2D materials provides a wide range of exciting optoelectronic properties, which offers even greater functionality and scope when two or more 2D materials are combined. An all-dry transfer method provides a means to rapidly build van der Waals heterostructures with clean interfaces which are suitable for device applications. Heterostructures of dissimilar materials give rise to different types of junction behaviors, with p-n junctions serving as the basic building blocks of most semiconductor devices. Examples of such device applications include photovoltaics, photodetectors and light-emitting diodes. In addition, defects and vacancies in individual 2D materials also allows for engineering their optoelectronic properties.

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# Carbon ordering in the nanocrystalline ferrite matrix of bainitic steels

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Nanocrystalline bainite is a novel structure obtained in high-carbon high-silicon steels after transformation from austenite at temperatures below 300 ºC. As bainitic transformation proceeds, the residual austenite is enriched in carbon and further stabilized at room temperature. The resulting structure primarily consists of nano-scaled plates of bainitic ferrite embedded in carbon-enriched austenite. In the last decade a significant amount of atom probe tomography (APT) observations have been shown that large quantities of excess carbon remain in the bainitic ferrite matrix without any visible carbon segregation. Further evidences suggest that a tetragonal rather than cubic ferrite lattice increases carbon solubility in the matrix.

In this work, APT, X-ray diffraction analysis (XRD), and high resolution transmission electron microscopy (TEM) have been used to evaluate the carbon distribution in bainitic ferrite and the source of tetragonality in a nanocrystalline steel (Fe-0.98C-2.90Si-0.77Mn-0.45Cr-0.16Ni, wt.%) isothermally transformed at 250 ºC. APT reveals an ordered distribution of carbon atoms in ferrite, consisting of a carbon-poor matrix and carbon-rich clusters. The ordering of carbon into the low and high-carbon regions observed by APT may lead to the satellite spots and the modulated tweed-like structure observed by TEM (see Figure).

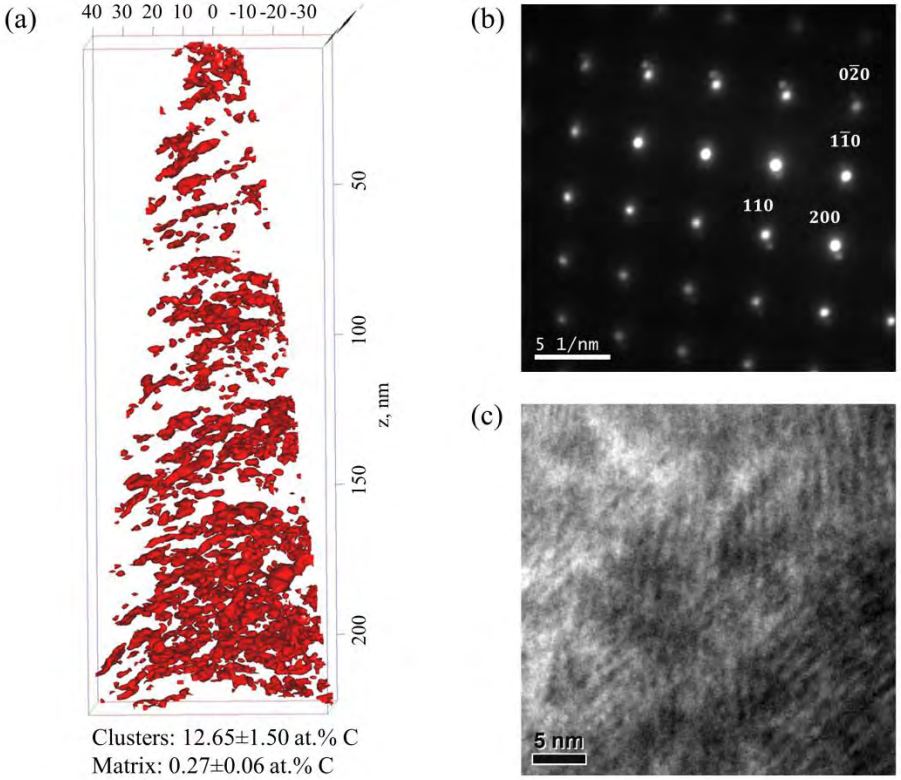


**Figure. (a) Carbon iso-concentration surfaces at 8 at. %, (b) electron diffraction pattern and (c) bright field electron micrograph in bainitic ferrite after transformation at 250ºC in a 0.98C-2.90Si-0.77Mn-0.45Cr-0.16Ni (wt.%) steel.**

# Carbon Nanospikes Grown on Metal Wires for Biosensing Applications

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Due to large number of defect sites on the surface, carbon electrodes are used for biosensing applications. The large surface area improves adsorption of biological analytes and offers high signal to noise ratios. Deposition of catalyst during carbon nanofiber growth process hampers the reproducibility of carbon nanostructured electrodes. Additionally, fabrication constraints have limited the integration of vertically aligned carbon nanostructures with CMOS. The growth process of carbon nanospikes (CNS) is catalyst free, allowing for high reproducibility among batches of electrodes. CNS also provides lower detection limits compared to other carbon nanostructures. CNS may prove to have easier integration with CMOS systems. The envisioned integration is as shown in Fig. 1. The integration between chip and CNS is easier since the interfaces can be connected efficiently using current bonding technology. PECVD is used for direct carbon deposition on metal wires. Since catalyst was not used for the growth process, direct electrical contact exists between CNS and the substrate [1-2].Fig. 2 shows the SEM images of CNS on silver, gold and titanium. The wires are chosen for compatibility with the process displayed in Fig. 1. Based on the images we can conclude that silver wire promotes more distinct spike-like structures on the metal wires compared to gold and titanium. The features on gold and titanium are more rounded than spike-like. The highest growth rate occurred for the silver wire, the lowest for the titanium wire. Fig. 3. shows the results of the Raman spectrum on the three wire types. The CNS will be characterized for sensitivity.

Fig.1. CNS CMOS integration

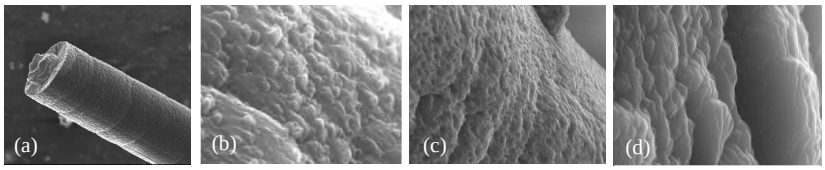


Fig.2. SEM images of CNS (a) CNS on silver (b) Zoomed-in view of CNS on silver (c) Zoomed-in view of CNS on gold (d) Zoomed-in view of CNS on titanium

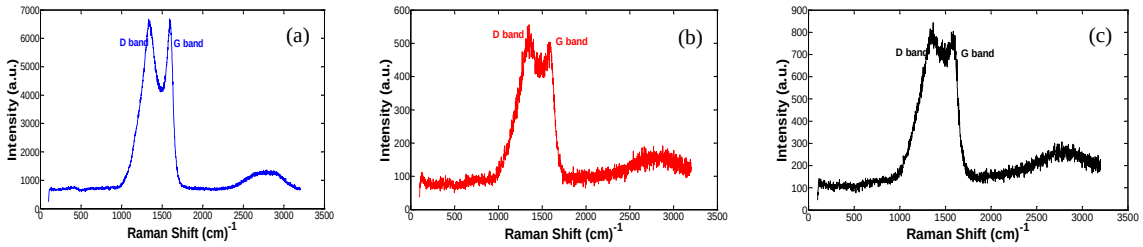


Fig.3. Raman spectrum of carbon nanospikes grown on (a) silver (b) gold (c) titanium

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# Ultra-thin layer chromatography with integrated silver colloid-based SERS detection

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ABSTRACT: Simplified lab-on-a-chip techniques are desirable for quick and efficient detection of analytes of interest in the field. The following work involves the use of deterministic pillar arrays on the micro-scale as a platform to separate compounds, and the use of Ag colloid within the arrays as a source of increased signal via surface enhanced Raman spectroscopy (SERS). One problem traditionally seen with SERS surfaces containing Ag colloid is oxidation; however, our platforms are superhydrophobic, reducing the amount of oxidation taking place on the surface of the Ag colloid. This work includes the successful separation and SERS detection of a biologically relevant compound (resorufin), fluorescent anti-tumor drugs (Adriamycin and Daunomycin), and five purine bases (adenine, cytosine, guanine, hypoxanthine, and thymine).

# Microstructural Characterization of Novel Creep-resistant Ferritic Superalloys

Shao-Yu Wang, Peter K. Liaw
The University of Tennessee, Knoxville

Ferritic superalloys containing NiAl precipitates have been investigated due to their low cost, high thermal conductivity, and low thermal expansion for applications as steam-turbine materials. However, the NiAl-strengthened ferritic superalloys are limited to operational temperatures below 621 $^{o}$C. Previously, it has been reported that the $L2_1$ phase $Ni_2TiAl$ precipitates and B2/$L2_1$ phase NiAl/$Ni_2TiAl$ precipitates have greater creep property in the temperature range of 900 to 1,156 $^{o}$C. Based on this concept, novel ferritic superalloys with hierarchical structures consisting of NiAl and $Ni_2TiAl$ precipitates in the matrix have been developed and studied.

Based upon the success of the FBB8 + 2% Ti alloy, further improvement in creep resistance is desired. Therefore in the present research, a systematic study on the microstructure of this kind of novel ferritic superalloys has been conducted. Alloys were designed and fabricated by replacing Ti content with Hf and/or Zr, to observe its capability of the formation of $L2_1$ phase precipitates, as shown in Figure 1.

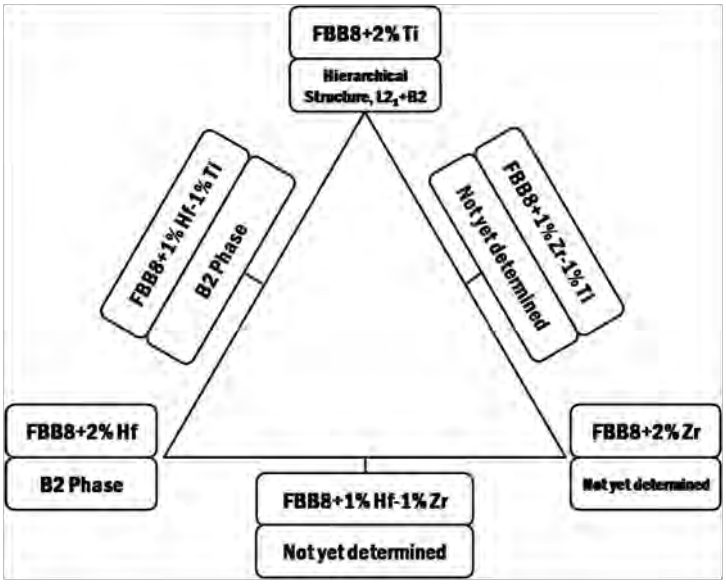


Figure 1. A systematic study plan for the ferritic alloy system.

For the microstructure characterization, scanning-electron-microscope (SEM) and transmission-electron-microscope (TEM) techniques have been utilized. Current results on the studies of FBB8+2% Hf alloy and FBB8+1% Hf-1% Ti alloy showed that there are no $L2_1$ phase precipitates presented within these alloy systems, and the Hf elements might form much larger precipitates with other heavier elements, like Mo or Zr, instead of forming a $L2_1$ phase with existing NiAl precipitates within the system. Creep test results showed the creep resistance of the FBB8+2% Hf alloy has no obvious differences compared with the FBB8 alloy, which results from no $L2_1$ phase formed as a greater strengthener. In the future, there are still more alloy systems to be investigated, and, therefore, microstructure characterization with higher efficiency and resolution techniques would be required.

# Development of Pressure-Actuated Microvalves for Studies Subcellular Organization in *Escherichia coli*

Da Yang, Branndon Jones, Scott Retterer, Jaan Männik

Microfluidics presents many new opportunities to study bacterial cells and cellular assemblies. In particular, it allows application of mechanical stresses to individual bacterial cells while observing their sub-cellular level responses in an optical microscope [1]. Here, we describe further development of microfluidic platform that allows us to mechanically manipulate bacterial shapes and to study how dynamics and organization of bacterial chromosomes changes in response to shape changes.

Our experimental design is based on pressure actuated microfluidic valves. Each pressure actuated valve consists of a flow channel and a control channel perpendicular to each other. In an experiment, an *Escherichia coli* bacterium is placed under a microfluidic valve by fluid flow. Application of external pressure to the control channel deforms the bacterium in the flow channel and perturbs its internal organization. The changes in bacteria are observed using fluorescence and phase contrast imaging.

To fabricate the valves we bond a thick layer of PDMS to a thin layer of PDMS, then bond this bilayer PDMS to a glass coverslip [2]. The valves are fabricated using replica molding. To fabricate Si molds, we used electron beam lithography and reactive ion etching (RIE). Each e-beam lithography step is combined with a Cr deposition and lift-off step for creating an etch mask used during subsequent RIE steps. Two aligned layers of electron beam lithography were necessary to obtain the specific geometry for the flow channels. We use SU8 photolithography to define the larger flow channels and the control channels.

We have fabricated microvalves with flow channel geometries that allow us to apply stress either to the whole cell [1] or just to a portion of it. In the latter case, large enough pressure can divide the cell interior into two separate compartments while the cell walls remain intact. We observe large scale chromosomal dynamics that accompanies such deformations. These data shed new light on chromosome-membrane attachments and role of entropic forces in organizing bacterial chromosomes.

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# Atomic-scale mapping of thermopower by ab-initio simulations and scanning tunneling microscopy

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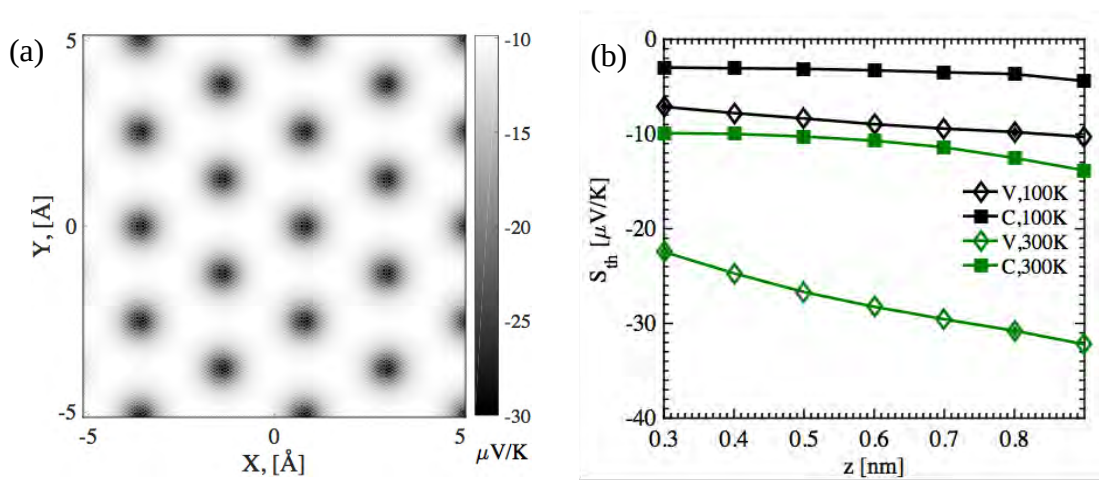
Scanning Tunneling Microscopy(STM) measurement of thermovoltage exhibits its unique capability on delivering high resolution atomic-scale mapping of the surface states, defects, and heterostructure interfaces [1-3]. The preferred theoretical Stoveneng-Lipavsky method fails to model thermovoltage at high temperature and large temperature gradient measurement conditions [1], and it cannot predict the tip-sample distance dependent thermovoltage precisely since it lacks the particular spatial wavefunctions. Here utilizing the spatial wavefunctions by first-principle calculations, we obtained the atomic scale mapping of thermovoltage at arbitrary temperature gradient and measuring distance. We applied our simulation method to pristine graphene, graphene with single carbon atom defect and graphene grain boundary interfaces. We compared the simulated topography STM images and thermovoltage images, explained and identified the key features (distance, temperature and slope of LDOS near the chemical potential) that can help enhance the resolution.




*(a) The atomic-scale thermopower image of graphene surface; (b) the tip-sample distance dependent thermopower of graphene surface. V denotes the hollow site while C denotes the carbon site.*

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# Point defects and ionic transport in solid oxides - Insights from high-throughput ab-initio modeling

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Designing and developing solid materials (such as oxides and sulfides) that can selectively transport ions have great potential in the development of next generation solid-state batteries and solid oxide fuel cells. However, development of new ion transporting materials requires us to gain a deeper understanding of point defects in material systems.

This work elucidates our recent efforts on developing a high throughput workflow framework to perform ab-initio calculations to understand point defects in material systems. The high throughput workflow framework can scale to tens of thousands of computing nodes to fully utilize the capabilities of OLCF supercomputers. We use this workflow towards understanding the role of point defects in oxide materials. In particular we employ the workflow to study the formation and interaction energies of point defects in proton conducting oxides, to understand what makes certain perovskites better proton conductors that others could enable us to develop rational design strategies for better proton conductors. We have generated data for over 100 different cubic perovskites, with Y doping, O vacancies and H interstitials. These results provide new insights on how properties of host/dopant atoms (electronegativity, ionic radius) and lattice properties (sub-lattice distortion) correlates with proton transport properties. The results obtained from this high-throughput analysis are currently being employed to fit machine-learning algorithms to predict structure-property correlations on a larger set of perovskites materials.

**Acknowledgement**
This work was sponsored by Laboratory Directed Research and Development Program of Oak Ridge National Laboratory (ORNL). Computations were performed at NERSC and OLCF supercomputing facilities. Neutron experiments were performed at Spallation Neutron Source (SNS) at ORNL. Transport measurements were performed at Center for Nanophase Materials Sciences (CNMS) at ORNL.

# One-Pot Melamine Derived Nitrogen Doped Magnetic Carbon Nanoadsorbents with Enhanced Cr(VI) Removal

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Novel nitrogen doped magnetic carbons (NMC), in-situ synthesized through facile pyrolysis-carbonization processes using $Fe(NO_3)_3$ and melamine as precursors, were demonstrated as excellent nanoadsorbents to remove Cr(VI) effectively. High removal capacity in both neutral and acidic solution, 29.4 and 2001.4 mg $g^{-1}$ respectively, were achieved, much higher than the reported adsorbents so far. The adsorbents mainly followed chemical adsorption as revealed from the pseudo-second-order kinetic study. The unprecedented high adsorption performance can be attributed to the incorporation of the nitrogen dopant, which increased the negative charge density on the surface of adsorbent thereby enhanced the interaction betweent the adsorbents and Cr(VI) ions. The density functional theory (DFT) calculation demonstrated that the nitrogen dopants can decrease the adsorption energy between the Cr(VI) ions and NMC (-3.456 kJ $mol^{-1}$), lower than the undoped sample (-3.344 kJ $mol^{-1}$), which boosted the adsorption behavior. Furthermore, the NMC showed high stability with recycling tests for the Cr(VI) removal.

# The Microstructure and Isotope Effects on Spin Response in Organic Spintronic Devices

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There is currently a strong drive to realize magnetoelectronic heterostructures with controls of magnetic ordering and electron-spin transport for use in the next generation spintronic devices. One proposed method to gain such controls is the use organic spintronics (OS). The general configuration of OS device consists of two ferromagnetic (FM) electrodes separated by an organic layer to form a sandwich structure. While basic concepts of OS device have been demonstrated, there is very little understanding about the detailed effects of the organic layer and the interface interactions within the multilayers on the physical properties of the system. Amongst the difficulties limiting high performances OS are the subtle structural variations, including *i.e.*, interdiffusion of FM electrode into the soft organic layer during the fabrication. Using the depth sensitive method of polarized neutron reflectometry we have been able to probe the fine details of the structural and magnetic properties of prototype spintronic devices (STO\\LSMO\polymer\Co\Ag). We fabricated heterostructures using two electron conducting polymers (P3HT and PFO) and their deuterated substitutions to study the isotope effect of polymer layer in the spintronic devices. While our main goal is on understanding the effect of deuterium substitution on the spin-dependent electron transport, in this presentation, we will focus the details of the structural and magnetization profiles on both LSMO\Polymer and polymer\Co interfaces and their impact on the coupling between magnetic layers.

Acknowledgements: This work was sponsored by Oak Ridge National Laboratory Directed Research and Development (LDRD 7938) and conducted at the Center for Nanophase Materials Sciences (CNMS) and Spallation Neutron Source (SNS), which are sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

# Topographical and Chemical Imaging Using a Combined Atomic Force Microscopy/Infrared Spectroscopy/Mass Spectrometry Platform

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**Abstract:**
Multimodal information is beneficial for characterizing and understanding the composition and function of chemical interfaces. Analytical tools that can provide spatially resolved sample surface morphology, or other physical information, as well as chemical information at the very low micrometer to nanometer scale, are inherently useful. Such "multimodal" information is beneficial for characterizing and understanding the composition and function of chemical interfaces in diverse fields like chemical science, material science, biology, and geology.
We report here on the use of a hybrid nanothermal analysis atomic force microscopy/infrared spectroscopy/mass spectrometry (nano-TA AFM/IR spectroscopy/MS) imaging platform for the acquisition and correlation of nanoscale surface topography and chemical images from both IR spectroscopy and MS. The basic instrumental setup, operation, and image correlation procedures are discussed and the multimodal imaging capability and utility are demonstrated using a phase separated polymer thin film. Multimodal imaging capability and utility were demonstrated by coregistered topography, IR spectroscopy and MS chemical imaging of a phase separated poly(2-vinylpyridine)/poly(methyl methacrylate) (P2VP/PMMA) polymer thin film. The spatial resolution of the mass spectral chemical images was estimated to be ~1.6 μm.
Also reported here are the fabrication, characterization and use of spatial resolution test patterns fabricated in a ~1- μm-thick PMMA film by electron beam lithography. The general utility of these test patterns is demonstrated by their use in evaluating the changing mass spectral image spatial resolution achieved as a function of the ionization interface temperature on our nano-TA AFM/MS system. The spatial resolution of MS chemical imaging of the resolution standard pure PMMA film was estimated to be 0.7 μm based on the ability to distinguish surface features in those images that were also observed in the scanning electron microscopy, energy-dispersive X-ray spectroscopy and AFM topography images of the same surface.

# Integrated nanoporous interfaces within microfluidics for imaging bacterial growth and metabolism

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The integration of nano- and microfluidic technologies enables the construction of tunable interfaces to physical and biological systems across relevant length scales. The ability to perform chemical manipulations of miniscule sample volumes is greatly enhanced through these technologies and extends the ability to manipulate and sample local fluidic environments at subcellular, cellular, and community or tissue scales. Here we describe the development of nanoporous interfaces for dosing and sampling cellular domains within microfluidic systems. We present a process for producing patterned nano-scale interfaces within microfluidics that enables supplying stimuli or tagged nutrients to the immediate community for quorum sensing or metabolic studies. Current and future efforts are focused on retrieving metabolic information from the local microenvironment surrounding cellular communities. This platform has the potential to enable chemical manipulation and multi-modal imaging for characterizing spatial organization and metabolic activity of complex microbial communities.

# Exploring the microstructure-determined corrosion behaviors of $Al_xCoCrFeNi$ high-entropy alloys through the electron-work function.

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**Abstract**

The multiple compositionally-equivalent high-entropy alloys (HEAs) have shown remarkable potential in structural and energy-related applications. Their intrinsic chemical disorder leads to a particular corrosion-resistant property, which plays one of the key roles in the practical usages. Here, a $Al_xCoCrFeNi$ HEA system is selected to present a new basis for establishing the fundamental relationship between microstructures and corrosion properties through characterizing surface-electron activities. It is revealed that the complex phase types and distinctive chemical segregations increase the variation of electron-work functions, thus weakening the corrosion-resistant ability of alloys. The annealing process at 1,250℃ has a profound effect on enhancing the chemical disorder, decreasing the electron-activity variations among phases, and evidently improving the localized corrosion resistance. The unique chemical disorder in multi-principle-elements HEAs leads to a raised confinement of valence electrons, bringing an outstanding corrosion resistant property of HEAs.

# 3D Analysis of PEM Fuel Cell Electrocatalyst Degradation by STEM Tomography: Pt Nanoparticle Dispersion & Coarsening on Alternate Carbon Supports

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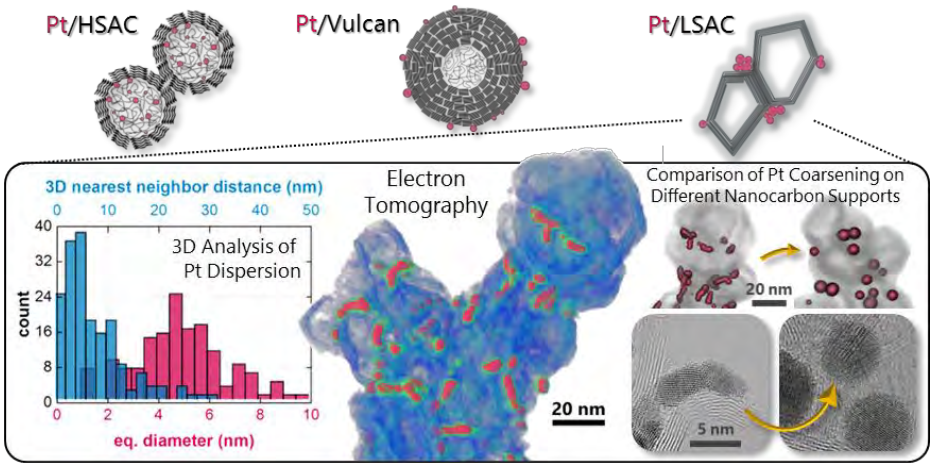
**Abstract:** The performance of catalysts for electrochemical energy conversion in PEM fuel cell devices is influenced by the electrochemical active surface area (ECSA) and the stability of this metric over the device operative lifetime. In a typical fuel cell electrocatalyst, Pt nanoparticles are distributed onto a nanocarbon support; however, the uniformity of dispersion can be varied across different metal loadings and support architectures, with agglomeration in as-prepared catalyst powders likely facilitating more rapid Pt coarsening at the beginning of their application. Furthermore, the degradation of these catalysts occurs not only through a coarsening mechanism, but from Pt dissolution, migration into the membrane, and encapsulation through carbon corrosion, with all of these pathways resulting in significant losses to ECSA. Herein, we show quantitative 3D microanalysis of the dispersion of Pt/C electrocatalysts for three different Pt loadings and three alternate carbon supports, one of which has been shown to have higher corrosion tolerance than traditional Pt/C electrocatalysts. We then compare the 3D reconstructions of the as-made catalysts with those after accelerated stress testing for Pt coarsening. We examine dispersion through analysis of distributions of Pt nanoparticle/agglomerate size, aspect ratio, and nearest neighbor distance of the different Pt/C systems, and discuss the results and implications of our study in guiding the development of alternative carbon supports.

**Graphical Abstract:**

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Title: **Computational Study of Electrostatically Tunable Band Offsets in $MoS_2$ Multilayers**

Authors: **Martin Wang, Marcelo A. Kuroda**
Affilliation: **Department of Physics, Auburn University**

The recent isolation of few-layer transition metal dichalcogenide $MoS_2$ opened promising opportunities for flexible optoelectronic applications. The 2H-phase of $MoS_2$ has a band gap in the range of 1.2 – 1.8 eV and has been proposed as a candidate for the semiconducting channel in field-effect transistors. However, similar to other two-dimensional materials, achieving low-contact resistance to this layered system is limited by Fermi level pinning and poses an important limitation in their application in electronic devices. Recently, the metallic 1T-phase of $MoS_2$ (stable at high temperatures) has been produced experimentally. Owing to the low in-plane contact resistance, it has been proposed as a solution to address the contact issue in two-dimensional materials. Alternatively, the use hybrid heterostructures combining metallic and semiconducting layers may also offer out-of-plane alternatives to the problem. In these heterostructures, the band offsets may be tuned with external electric fields altering the contact resistance. Here we study the electronic properties $MoS_2$ multilayers calculations within the density functional theory. In particular we characterize the band offsets changes in $MoS_2$ multilayers of different thicknesses (number of layers) and composition (phases of $MoS_2$) under external electric fields in field-effect device geometries. We find that introducing 1T-$MoS_2$ layers helps alleviate Fermi level pinning observed in these materials. A comparison of the results using the generalized gradient approximation and the HSE hybrid functional shows that both approaches yield similar band offsets variations despite the different band alignments. The understanding of the tunability of the band offsets based in transition dichalcogenide multilayers may prove useful for the realization of flexible two-dimensional electronics.

**Title:** Epoxy Nanocomposites with Reduced Flamability Derived From Magnesium Hydroxide-Melamine Polyphosphate Hybrids

**Author:** Alexandra M. Galaska

**Abstract:**
Epoxy resin is one of the most important and applicable thermosetting resins that is lightweight and used in a wide range of applications with high mechanical properties, and chemical resistance. However, pure epoxy has high flammability, which is one of the major concerns when used in the real life application. Flame retardants can decrease the fire hazard and make epoxy more suitable for the desired products. In this research, two flame retardants are used to reduce the flammability of epoxy. Magnesium hydroxide as an inorganic flame retardant has been used in epoxy matrix rarely, while, melamine polyphosphate is an effective phosphorus-based flame retardant commonly used in the industry, including in epoxy, and other resins. This study investigates the effects of flame retardant on polymer nanocomposites and comparison of pure epoxy and its nanocomposites through micro-combustion calorimetry (MCC), and scanning electron microscopy (SEM) studies. In this paper, the test results show that the nanofillers are dispersed very well in epoxy resin and the thermal stability and flame retardant properties of polymer nanocomposites with different loading of nanofillers are enhanced compared with pure epoxy.

**Mentor Info**: Dr. John Zhanhu Guo, Associate Professor, Chemical and Biomolecular Engineering, College of Engineering

**Assistant:** Jiang Guo, Ph.D student

# Developing Microfluidics Platforms for Single Bacterial Cell Imaging

**Anna Jennings[1], Evalynn Borrego[2], Da Yang[1], Jaana Mannik[4], Scott Retterer[3] and Jaan Mannik[1,4]**
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Traditionally, bacteria cells have been imaged on agarose pads allowing them to grow in steady conditions for only a few doubling times. In recent years several microfluidic platforms have been designed that allow bacteria to grow in log-phase in micron-size channels and pockets for over one hundred generations. One of the most promising approaches has been the so-called mother machine design[1]. The mother machine has a single main channel with dead-end pockets where bacteria grow in single files (Fig. 1, Left). The fluid flow in the main channel flushes away extra cells and metabolic waste products from pocket entrances. It also constantly resupplies nutrients providing steady cell growth. The mother machine chips are made of PDMS and are easy to assemble and usable over long periods of time. However, the cell loading process is time consuming and the chips do not enable high resolution phase contrast imaging. Our measurements also show a growth limitation for the cells deeper in the pockets limiting reproducibility of measurements.

Here, we investigate two extensions to mother machine platform to overcome these shortcomings. The first platform, which we refer to as the flow through chip (Fig. 1, Right), allows the liquid to flow past the cells in the pockets. The flow provides fresh nutrients to all cells in the pockets. This platform also significantly decreases the time it takes to load the cell into pockets (from about two hours to 15 minutes). However, the flow may push cells out of the pockets to the opposite end of the channel and thereby disrupt the measurements. The second platform follows the original mother machine design but is made of agarose. This chip produces a good quality phase contrast image of cells since the index of refraction of agarose is similar to that of water. Agarose also allows quick diffusion of nutrients to all cells in the pockets. However, agarose is a structurally more challenging material to work with. Nevertheless we have been able to grow cells for about 10 hours while medium is being flowed through the chip.

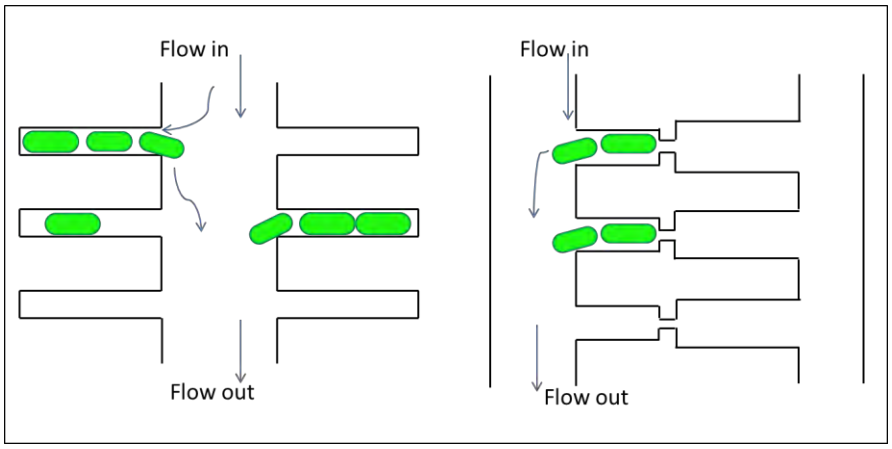


**Figure 1: Left: Schematics of mother machine chip. Right: Mother machine with flow through pockets.**

[1] Wang, P., Robert, L., Pelletier, J., Dang, W.L., Taddei, F., Wright, A., and Jun, S. (2010). Robust growth of *Escherichia coli*. Curr. Biol. 20, 1099–1103.

CNMS User Meeting 2016, August 9-12, Oak Ridge, TN

# Bio-inspired optimization of flow network accommodation around obstacles

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Bronchial trees, root systems, sedimentary basins and ducts embedded in plant leaves present a fractal topology. The constructal theory (Bejan, 1997) can explain the optimality of fractal flow networks with configuration and purpose. However, not all networks found in nature are fractal, and models that can predict the processes of accommodation, adaptation and competition of biological networks are currently lacking. Moreover, no systematic method exists in geotechnical engineering to optimize the efficiency, resiliency and versatility of utilities networks (e.g. sewage systems, buried cables). Biological and geotechnical networks found in constrained environments present similarities (Fig.1). Could natural network topologies be optimal for engineering design? Is it practical, sustainable and efficient for engineers to deploy networks like living organisms do? Is adaptive design resilient, safe and sustainable? To answer these questions, we plan to model the formation of various natural networks under topological, environmental and biological constraints and use these biological analogs to optimize: (1) The accommodation of water and gas supply networks in the presence of obstacles and geological heterogeneities; (2) The adaptation of utility networks to variable demand, supply defects and disconnections; (3) The competition of water and electricity cable networks in the same space.

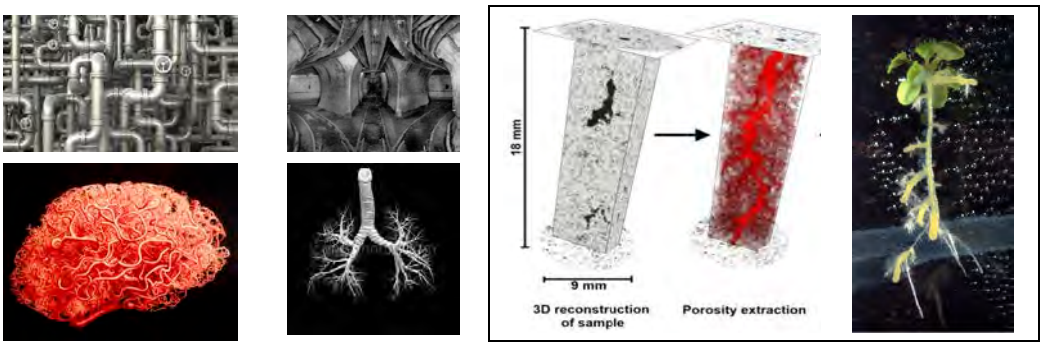


**Figure 1.** Bio-mimicry in geotechnics: pipelines vs. blood capillaries (left); metro vs. bronchial tree (center); fracture pattern vs. roots (right).

The collaborative project done between Georgia Tech (GT) and Oak Ridge National Laboratory (ORNL) focuses on topological adaptation. We plan to extend the set up of Dr. Retterer (2016) to study the density, length and orientation of root hair that develops out of plant stems in 2D, with and without solid obstacles. In a selected set of experiments, we will allow the stem to grow into a root system and we will monitor the evolution of the root architecture system and that of root hair. We will simulate these experiments with a Finite Element Method – based program (FEM) dedicated to root growth (Somma et al., 1997). To this end, we will enrich the program with new growth rules to differentiate hairs and stems. We will describe the graph formed by the root architecture system in order to compare the numerical predictions to the experimental results and calibrate our model (Fig. 2).

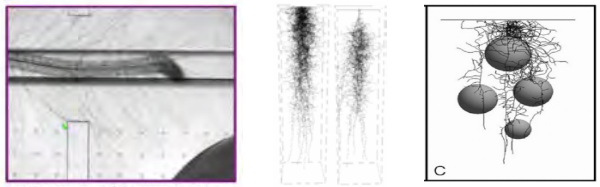


**Figure 2:** Planned study of root system accommodation in the presence of obstacles. Left: Imaging of root stems and root hair in 2D (ORNL). Center: FEM modeling of the development of root architecture with stems and hair (GT). Right: comparison of numerical and experimental root systems with obstacles (ORNL, GT).

Then, we will predict fluid flow in a fracture network with equations analog to those of our root model. We will perform sensitivity analyses with a numerical code that couples FEM and cohesive Zone Models (Jin et al., 2016) in order to test the optimality of root-inspired fracture network for fluid injection.

# A radial thermoelectric generator based on n- and p-type conducting polymers

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The abundance of heat at temperatures < 150 °C indicates there is a lot of potential for low temperature waste heat recovery. Thermoelectric generators (TEG) enable direct conversion of this waste heat into electricity without moving parts and are projected to have long lifetimes, which make them attractive for energy harvesting applications. Electrically conducting polymers are attractive for TEGs because of their low thermal conductivity and thin-film solution processability. Here, we report the performance of a radial TEG made from n- and p-type polymers printed on paper substrates. Our thermoelectric models predict an optimized geometry for a radial device that operates under natural convective cooling alone, and herein we report the fabrication and performance of this new organic TEG. We use poly[$K_x$(Ni-ett)] blended with PVDF/DMSO as the n-type material, and PEDOT:PSS with Te nanowires as the p-type materials, coated on paper to evaluate the thermoelectric performance. The radial TEG produced an open-circuit voltage of 85 mV and a power density of 15 nW/cm$^2$ under a 45 K temperature difference. This proof-of-concept is the first demonstration of a polymer-based radial TEG that accommodates a hot pipe as the heat source and does not require active cooling due to heat spreading. This is promising for scalable and low $/W cost thermoelectric devices for self-powered sensor networks.

**Alberto Nocera**
Computer Science & Mathematics Division and
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## Dynamical response functions with the Density Matrix Renormalization Group method

Computing the dynamical response functions of quantum magnets, superconductors, and transition metal oxides is of paramount importance in helping experimental efforts in neutron scattering and photo-emission spectroscopy.
In this talk, I summarize how dynamical response functions are calculated with the Density Matrix Renormalization Group method. I will then present and discuss the dynamical response functions of widely used models of strongly correlated electronic materials. Calculated with the Density Matrix Renormalization Group method, these dynamical response functions include the spin structure factor and the spectral function.
I will show that the approach is general, and applicable to complex geometries beyond chains, and discuss applications of interest to neutron scattering. Finally, I will explain how the approach can be extended to finite temperature.

# Ultratrace Plasmonic Sensing below the Shot Noise Limit

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With growing interest in ultratrace sensing, the ability to exploit quantum statistics in real-world sensors is increasingly critical. Here, we utilize two-mode intensity difference squeezing to reduce the noise floor in a well-known surface plasmon resonance (SPR) sensing platform below the photon shot noise limit (SNL). SPR sensors utilizing the Kretschmann geometry, illustrated schematically in Fig. 1, rely on metal films several 10's of nm thick, and are capable of resolving changes in refractive index units of $10^{-7}$ by monitoring the plasmon-polariton resonance angle. However, the SNL limits classical sensors from reducing the noise floor any further, and as a result, trace signals are obscured by shot noise. By introducing a quantum noise reduction, or "squeezing" on the probe field prior to using it to optically transduce the SPR sensor, we demonstrate a 2.5 dB improvement in sensitivity compared to the best possible classical SPR sensor relying on intensity modulation.

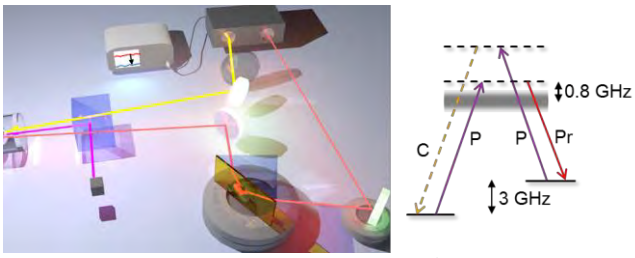


Fig. 1 A two mode squeezed state is generated by four-wave-mixing in $^{75}$Rb vapor (left). The four-wave-mixing is the result of a weak probe (Pr) stimulating the coherent emission of a conjugate (C) photon for every emitted probe photon in a double lambda system (right). The probe field is used as the readout field for a Kretschmann sensor comprised of a 43.5 nm Au film on a right angle prism.

Figure 1 illustrates the experiment schematically. A four-wave-mixing process in $^{85}$Rb vapor was used to generate 5.5 dB of quantum noise reduction below the SNL. After modulating the probe at 2 MHz with an acousto-optic modulator and using it as the optical readout for a Kretschmann sensor designed to offer maximal sensitivity at a wavelength of 795 nm, a variable neutral density filter was used to proportionately attenuate the conjugate field. Measuring the SPR response at an RF sideband effectively eliminates classical noise at DC. When off-resonance, this configuration yielded 4.5 dB of quantum noise reduction near the 2 MHz modulation frequency. The prism was swept across the critical angle for plasmon polariton absorption as the variable neutral density filter was simultaneously controlled to balance the probe and conjugate fields. The sensitivity of this quantum plasmonic sensor was characterized by varying the index at the Au film surface with index matching oils.

Figure 2 illustrates the shift in the SPR absorption angle as the index of refraction on the SPR sensor interface increased from n=1.3 to n=1.301 to n=1.305. In each case, the amplitude of the 2 MHz sideband modulation on the probe field was used as the signal. A spectrum analyzer was used to record the modulation amplitude and the noise floor simultaneously as the incidence angle was swept. The raw spectra associated with the data points marked b) and c) in Fig. 2a are shown in Figs. 2b and 2c. In each case, the SNL is indicated by the red line above the measured noise floor, indicating 4.5 dB of squeezing in Fig. 2b and 2.5 dB of squeezing in Fig. 2c. Furthermore, as shown in Fig. 2d, squeezing was shown at all angles, even when >90% of the probe field was attenuated by the SPR sensor. Because it has been previously shown that SPR sensors can be operated at the inflection point of the absorption curve in order to enable real-time biochemical sensing without loss of sensitivity, it is possible to maintain 2.5 dB of quantum noise reduction for a real-time quantum enhanced biochemical sensing platform. The optical power in the probe field is consistent with the powers typically used in SPR sensing platforms, but the power could be further increased while maintaining quantum noise reduction if thermoplasmonic effects could be mitigated.

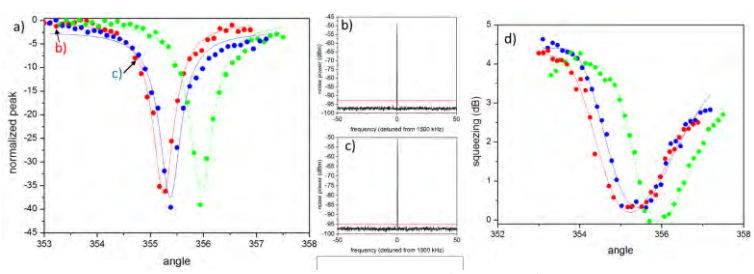


Fig. 2 (a) SPR 2 MHz sideband signal strength as a function of (uncorrected) incident angle for n=1.3, 1.301, 1.305 (red, blue, green). The noise floor for each data point in (a) is below the SNL, with representative data points illustrated in b) and c). The recorded quantum noise reduction, or squeezing, is plotted for all data points in d).