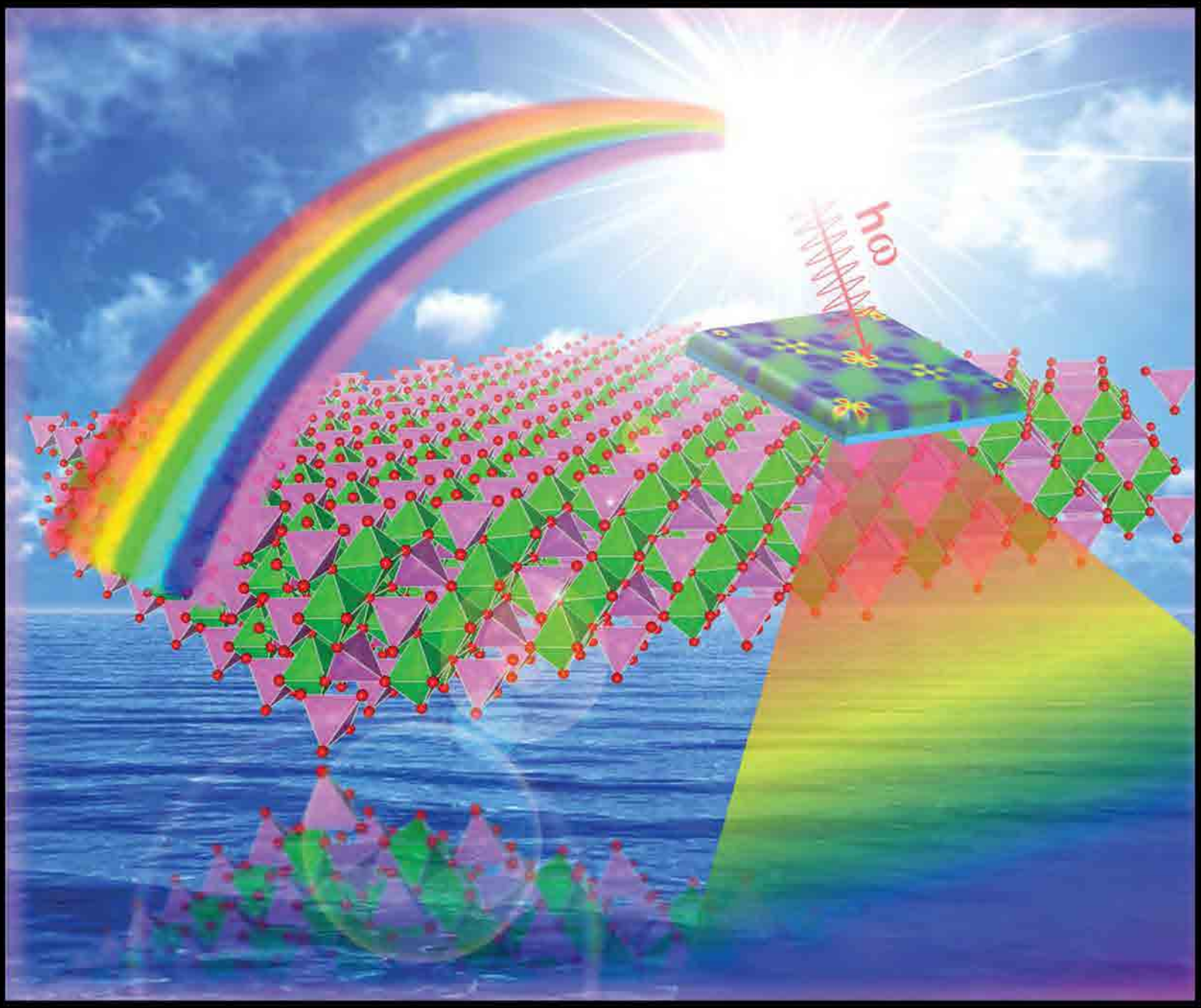
2015 CNMS USER MEETING

Planning CNMS Science for Its 2nd Decade



OAK RIDGE National Laboratory | CENTER FOR NANOPHASE MATERIALS SCIENCES

Table of Contents

2015 CNMS User Meeting Agenda **1**

List of Posters **5**

Plenary Session **13**

Roundtable Sessions

- **Buried Interface Structure and Effects on Properties** **17**
- **Elucidating Materials Functionality with Operando Characterization** **21**
- **Emerging Areas in the Synthesis of Organic Molecules and Polymers** **25**
- **Materials Genome-Materials by Design** **33**
- **Full Information Recovery and Advanced Data Analytics in Scanning Probe Microscopy** **37**

Poster Abstracts **41**

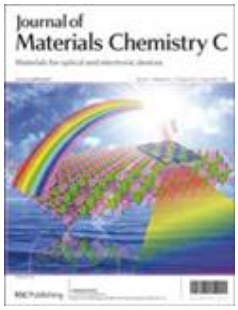
Denotes Student Poster

Cover Image

In memoriam, Mike Biegalski, 1976 - 2014

Image adapted from "Nature of the band gap and origin of the electro-/photo-activity of Co_3O_4" by L. Qiao, M. D. Biegalski, *et al.*, *J. Mater. Chem. C*, 2013, 1, 4628.

Reproduced from *Journal of Materials Chemistry C* with permission from the Royal Society of Chemistry.



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

2015 CNMS User Meeting
Planning CNMS Science for Its 2nd Decade
Oak Ridge National Laboratory
Oak Ridge, Tennessee

3:00p	**Tuesday, September 1**	**Registration Opens**	
4:00	**Poster Session and Student Poster Competition** – SNS Atrium		
5:30	Celebrating 10 years at CNMS with ***RidgeDance IX, a Retrospective*** – Iran Thomas Auditorium, SNS		
7:30a	**Wednesday, September 2**	**Registration -** Posters available for viewing	
	PLENARY SESSION *Iran Thomas Auditorium, SNS*		
8:00	**WELCOME AND ANNOUNCEMENTS** **Thomas Zacharia**, ORNL Deputy Director for Science and Technology **Hans Christen**, CNMS Director		
8:20	**PLENARY LECTURE I** *"Dynamics of Chain Exchange in Block Copolymer Micelles"* **Timothy P. Lodge**, *University of Minnesota*		
9:05	Break		
	Buried Interface Structure and Effects on Properties *SNS Auditorium*	**Elucidating Materials Functionality with *Operando* Characterization** *Room C-152*	**Emerging Areas in the Synthesis of Organic Molecules and Polymers** *Room C-156*
9:15	**Michael Demkowicz**, MIT	**Deborah Kelly**, Virginia Tech	**Donghui Zhang**, Louisiana State U.
9:35	**Jeffery Aguiar**, NREL	**Adam Rondinone**, ORNL	**April Kloxin**, U. Delaware
9:45	**Erica Corral**, U. Arizona	**Beth Guiton**, U. Kentucky	**Robert Mathers**, Penn State U.
9:55	**Gabriel Veith**, ORNL	**Jamie Hart**, Drexel U.	**Y. Elaine Zhu,** U. Notre Dame
10:05	**Featured Poster Summaries**	**Featured Poster Summaries**	**Featured Poster Summaries**
10:25	Poster Viewing	Poster Viewing	Poster Viewing
10:45	Discussion	Discussion	Discussion
11:30	Lunch on your own; Posters available for viewing		
	Materials Genome-Materials by Design *SNS Auditorium*	**Full Information Recovery and Advanced Data Analytics in Scanning Probe Microscopy** *Room C-152*	**Emerging Areas in the Synthesis of Organic Molecules and Polymers** *Room C-156*
1:00p	**Rampi Ramprasad**, U. Connecticut	**Roger Proksch**, Oxford Inst.	**Michael Hickner**, ORNL
1:20	**Olivier Delaire**, ORNL	**Gabriele Ferrini** U. Cattolica del Sacro Cuore	**Shannon Yee**, Georgia Tech.
1:30	**Alexey Kolmogorov**, Binghamton U.	**Jason Killgore**, NIST	**Daniel Hallinan, Jr.**, Florida State U.
1:40	**Anatole von Lilienfield**, U. Basel	**Laurene Tetard**, U. Central Florida	**William Gramlich**, U. Maine
1:50	**Featured Poster Summaries**	**Featured Poster Summaries**	**Featured Poster Summaries**
2:10	Poster Viewing	Poster Viewing	Poster Viewing
2:30	Discussion	Discussion	Discussion
3:15	Break		
3:30	**Strategic Planning Meeting** – Iran Thomas Auditorium, SNS *including announcement of Student Poster winners*		
4:15	**PLENARY LECTURE II** *"High-Throughput Materials Discovery and Development: Breakthroughs and Challenges in the Mapping of the Materials Genome"* **Marco Buongiorno Nardelli**, *University of North Texas*		
5:00	Adjourn / Closing Comments		

ROUNDTABLE SESSIONS

Buried Interface Structure and Effects on Properties

Michael Demkowicz, Massachusetts Institute of Technology
Self-Assembly of Helium Cluster Networks Enabled by Interfaces in Metal Nanocomposites

Jeffery Aguiar, National Renewable Energy Laboratory

Erica Corral, University of Arizona
Microstructure and Mechanical Properties of Ultra-High Purity ZrB_2 Using Thermodynamic Assisted Spark Plasma Sintering

Gabriel Veith, Oak Ridge National Laboratory
Liquid-Solid Interfaces within Energy Storage Devices

FEATURED POSTER SUMMARIES

Poster 11: Sanjib Das, University of Tennessee
Correlating High Power Conversion Efficiency of Inverted Organic Solar Cells to Nanoscale Structure

Poster 12: Zhiqi Liu, Oak Ridge National Laboratory
Intermetallic Alloys Facing Functional Oxides: An Emerging Opportunity for Multiferroics

Poster 01: Beihai Ma, Argonne National Laboratory
Structural Characteristics of Nanophase-Carbon in Covetic Materials

Poster 02: Steven Brewer, Georgia Institute of Technology
Effects of Radiation Exposure on Ferroelectric Material Stacks in Piezoelectric MEMS/NEMS

Elucidating Materials Functionality with Operando Characterization

Deborah Kelly, Virginia Tech Carilion Research Institute
In Situ TEM of Macromolecules

Adam Rondinone, Oak Ridge National Laboratory
Direct-Write Nanofabrication using Ion Beams

Beth Guiton, University of Kentucky
Linking the Forward and Reverse Vapor-Liquid-Solid Mechanisms in Metal Oxide Nanostructures

Jamie Hart, Drexel U.
Predictive Microstructural Evolution in Extreme Environments Using In Situ TEM

FEATURED POSTER SUMMARIES

Poster 17: Lei Yu, University of Kentucky
Exploring a Simple Synthetic Route to Metal Oxide Nanowires with the Spinel Crystal Structure

Poster 18: B. M. Hudak, University of Kentucky
Direct Observation of Phase Transformations in Individual Hafnia Nanorods

Poster 19: Matthew McDowell, Georgia Institute of Technology
Characterization of Dynamic Materials Interfaces in Electrochemical Energy Systems

Poster 20: Bin Yang, Oak Ridge National Laboratory
Perovskite Solar Cells with Near 100% Internal Quantum Efficiency Based on Large Single Crystalline Grains and Vertical Bulk Heterojunctions

ROUNDTABLE SESSIONS

Emerging Areas in the Synthesis of Organic Molecules and Polymers (Morning Session)

Donghui Zhang, Louisiana State University
Design, Synthesis and Characterization of Peptidomimetic Polymers towards Biomedical Applications

April Kloxin, University of Delaware
Responsive Biomaterials for Controlling the Cell Microenvironment

Daniel Hallinan, Jr., Florida State U.
Simultaneous Organic Ligand Grafting and Self-Assembly of Nanoparticles at Liquid-Liquid Interfaces

Y. Elaine Zhu, University of Notre Dame
Single Chain Conformation and Complexation of Annealed Polyelectrolytes in Dilute Aqueous Solution

FEATURED POSTER SUMMARIES

Poster 28: Oluyemi O. Daramola, Federal University of Technology
Influence of Submicron Agro Waste Silica Particles and Vinyl Acetate on Mechanical, Diffusivity and Thermal Properties of High Density Polyethylene Matrix Composites

Poster 31: Brian Long, University of Tennessee
Accessing Next-Generation Polyolefins and Gas Separation Membranes via Coordination-Insertion Polymerization

Poster 34: Chau D. Tran, Oak Ridge National Laboratory
Organic-Organic Amorphous Nanocomposites

Poster 35: Da Yang, University of Tennessee
Cellular Organizations in Escherichia coli Mechanically Probed by a Novel Microfluidic Device

Materials Genome-Materials by Design

Rampi Ramprasad, University of Connecticut
Rational Computation-Guided Design of Polymer Dielectrics

Olivier Delaire, Oak Ridge National Laboratory
Thermodynamics and Thermal Transport Near Lattice Instabilities

Alexey Kolmogorov, Binghamton University
Acceleration of Materials Discovery with Bio-Inspired Algorithms

Anatole von Lilienfield, University of Basel
Machine Learning Methods for the Rapid yet Accurate Sampling of Chemical Compound Space

FEATURED POSTER SUMMARIES

Poster 52: Janakiraman Balachandran, Oak Ridge National Laboratory
Role of Disorder in Proton Conduction in Oxide Materials

Poster 54: Changwon Park, Oak Ridge National Laboratory
Predictive Power of Density Functional Theory in Finite-Temperature Hydrogen Adsorption/Desorption Thermodynamics with Corrective Energies and Potential Surfaces

Poster 53: Wenmei Ming, Oak Ridge National Laboratory
Theoretical Predication of Two-Dimensional Electrides

ROUNDTABLE SESSIONS

Full Information Recovery and Advanced Data Analytics in Scanning Probe Microscopy

Roger Proksch, Oxford Instruments Company
Quantifying Electromechanical Scanning Probe Microscopy

Gabriele Ferrini, Università Cattolica del Sacro Cuore
A Perspective for Multi-Dimensional Ultrafast Scanning Probe Microscopy

Jason Killgore, National Institute of Standards and Technology
Dynamic Contact AFM with Photothermal Excitation

Laurene Tetard, University of Central Florida
Multi-Frequency Atomic Force Microscopy for Subsurface and Chemical Mapping

FEATURED POSTER SUMMARIES

Poster 46: Nicholas Cross, University of Tennessee
Statistical Thermodynamics with Point Defects in 2-Dimensional Materials

Poster 48: Todd Sulchek, Georgia Institute of Technology
Direct Measurement of Biological Energy Landscapes using Boltzmann's Equation

Poster 47: Suhas Somnath, Oak Ridge National Laboratory
A Novel Spectroscopy Technique for Ultrafast Polarization Switching in Ferroelectrics

Poster 45: Alex Belianinov, Oak Ridge National Laboratory
Scalable Analysis of Multidimensional Imaging and Spectral Data in Material Science

Emerging Areas in the Synthesis of Organic Molecules and Polymers (Afternoon Session)

Michael Hickner, Oak Ridge National Laboratory
Synthesis of Cationic Polymers for Membrane Applications

Shannon Yee, Georgia Institute of Technology
Polymer-Based Thermoelectrics: New Directions

Robert Mathers, Pennsylvania State University
Predicting Hydrophobicity in Polymers

William Gramlich, University of Maine
Creating Hierarchically Structured Sustainable Materials using Modular Synthesis Strategies

FEATURED POSTER SUMMARIES

Poster 32: Xinyi Lu, University of Tennessee
Improved Carbon Nanotube Yarns through Crosslinking

Poster 30: Andrew Goodwin, University of Tennessee
Mechanical Behavior of All-Acrylic Multigraft Copolymers Based on Side Chain Molecular Weight and Volume Fraction

Poster 29: Ryan Murphy, University of Delaware
Gelation of Anisotropic Silica Nanoparticles with Thermoreversible Short-Range Interactions

Poster 33: Tomonori Saito, Oak Ridge National Laboratory
Development of Passive Polymer Membranes for Carbon Dioxide Separation

Center for Nanophase Materials Sciences

List of Posters

2015 User Meeting

Center for Nanophase Materials Sciences
2015 User Meeting
Poster Session

**denotes Student Poster*

Tuesday, September 1, 2015
4:00 – 5:30p

Poster Locations
Main Hallway: 01-63

Posters will also be available for viewing on Wednesday, September 2

01. Structural Characteristics of Nanophase-Carbon in Covetic Materials

Beihai Ma,[1] Uthamalingam Balachandran,[1] Jianguo Wen,[2] Dean J. Miller,[2] Robert P. Winarski,[2] Carlo U. Segre,[3] David C. Joy[4]

[1]Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439
[2]Nanoscience and Technology Division, Argonne National Laboratory, Argonne, IL 60439
[3]Department of Physics, Illinois Institute of Technology, Chicago, IL 60616
[4]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

02. *Effects of Radiation Exposure on Ferroelectric Material Stacks in Piezoelectric MEMS/NEMS

S. J. Brewer,[1] M. K. Paul,[1,2] K.J. Fisher,[1,2] J. E. Guerrier,[4] R. Q. Rudy,[5] E. R. Glaser,[6] C. D. Cress,[6] R. G. Polcawich,[5] J. L. Jones,[4] N. Bassiri-Gharb[1,7]

[1]G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332
[2]Woodward Academy, Atlanta, GA 30337, USA
[3]Riverwood International Charter School, Sandy Springs, GA 30328
[4]Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695
[5]Army Research Laboratory, Adelphi, MA 20783
[6]Naval Research Laboratory, Washington, D.C. 20375
[7]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332

03. *Quantitative Effects of Textures and Grain Sizes on Short Fatigue Crack Growth in High Strength Aluminum Alloys by a 3-D Microstructure-Based Model

Pei Cai,[1] Yan Jin,[1] Wei Wen,[1,3] Donovan N. Leonard,[2] Tongguang Zhai[1]

[1]Chemical and Materials Engineering Department, University of Kentucky, Lexington, KY 40506
[2]Microscopy Group, Materials Sciences and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[3]Novelis Global Research and Technology Center, Kennesaw, GA 30144

04. *Using *in situ* Microscopy and Spectroscopy to Link Synthesis and Self- Assembly with Plasmon Coupling in Ordered Metal Nanoparticle Heterostructures

Yao-Jen Chang,[1] Bethany M. Hudak,[1] Taha Rostamzadeh,[2] John B. Wiley,[2] Nicholas A. Merill,[3] Marc R. Knecht,[3] Raymond R. Unocic,[4] and Beth S. Guiton[1,4]

[1]Department of Chemistry, University of Kentucky, Lexington, KY 40506
[2]Department of Chemistry and Advanced Materials Research Institute, University of New Orleans, New Orleans, LA 70148
[3]Department of Chemistry, University of Miami, Coral Gables, FL 33146
[4]Materials Science and Technology Division, Oak Ridge National Lab, Oak Ridge, TN 37831

05. *Manipulating Inter Pillar Gap in Pillar Array Ultra-Thin Layer Planar Chromatography Platforms

Nichole A. Crane,[1] Nickolay V. Lavrik,[2] Michael J. Sepaniak[1]

[1]University of Tennessee, Knoxville, TN 37996
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

06. *Plasmonic Behavior and Optical Transmission of Silver-Cobalt Thin Film Hole Arrays

A. E. Farah,[1] R. Davidson,[2] B. Lawrie,[2] R. Pooser,[2] R. Kalyanaraman[1]
[1]University of Tennessee, Knoxville, TN 37996
[2]Oak Ridge National Laboratory

07. *Engineered Exciton Localization in Colloidal Cadmium Chalcogenide Quantum Well Heterostructures

Qiuyang Li, Kaifeng Wu, Tianquan Lian
Emory University, Atlanta, GA 30322

08. *An Iron Oxide Based Transparent Amorphous Semiconductor with Extraordinary Electronic Conductivity and Mobility

A. Malasi,[1] H.Taz,[2] A. Farah,[3] M. Patel,[3] B. Lawrie,[4] R. Pooser,[4] A. Baddorf,[5,6] G. Duscher[3,6] and R. Kalyanaraman[1,2,3]
[1]Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee, 37996
[2]Bredesen Center, University of Tennessee, Knoxville, Tennessee, 37996
[3]Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee, 37996
[4]Quantum Information Science Group, Computational Sciences & Engineering Division, Oak Ridge National Laboratory
[5]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
[6]Material Sciences and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831

09. *Crowding α-Hemolysin in a Functional Model Membrane

Bill McClintic[1] and Pat Collier[2]
[1]University of Tennessee, Knoxville, Tennessee, 37996
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

10. *Diffusional Response of Layer-by-Layer Assembled Polyelectrolyte Chains to Salt Annealing

Victor Selin,[1] John F. Ankner,[2] Svetlana A. Sukhishvili[1]
[1]Department of Materials Science & Engineering, Texas A&M University, College Station, TX 77843
[2]Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

11. Correlating High Power Conversion Efficiency of Inverted Organic Solar Cells to Nanoscale Structure

Sanjib Das,[1] Jong Keum,[2,3] James Browning,[3] Gong Gu,[1] Bin Yang,[2] Ondrej Dyck,[4] Changwoo Do,[3] Jihua Chen,[2] Ilia N. Ivanov,[2] Kunlun Hong,[2] Adam J. Rondinone,[2] Pooran C. Joshi,[5] David B. Geohegan,[2] Gerd Duscher,[4] Kai Xiao[2]
[1]Department of Electrical Engineering and Computer Science, University of Tennessee, Knoxville, TN, 37996
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
[3]Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
[4]Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee, 37996
[5]Material Sciences and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831

12. Intermetallic Alloys Facing Functional Oxides: An Emerging Opportunity for Multiferroics

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

13. *Biosensing and Optical Modulation on a Silicon Platform

K. J. Miller, G. A. Rodriguez, Y. Zhao, P. Markov, S. Hu, R. E. Marvel, R. F. Haglund, & S. M. Weiss
Vanderbilt University

14. *Multimodal PEDOT:PSS/QCM-Based Humidity and Pressure Sensor Using Artificial Neural Network

Eric Muckley,[1,2] James Lynch,[2] and Ilia Ivanov[2]
[1]Bredesen Center, University of Tennessee, Knoxville, Tennessee, 37996
[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831

15. *Helium Ion Induced Patterning of sub-10 nm Structures in Liquid Cell

Nathan Philip,[3] Vighter Iberi,[1,2] Ray Unocic,[1,4] Adam J. Rondinone,[1] David C. Joy,[1,2] Alex Belianinov,[1,4] Olga S. Ovchinnikova[1,4]

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

[2]Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee, 37996

[3]Bredesen Center, University of Tennessee, Knoxville, Tennessee, 37996

[4]The Institute for Functional Imaging of Materials, Oak Ridge National Laboratory, Oak Ridge, TN 37831

16. *Nanoscale Characterization of Zinc Electrodeposition using in situ Electrochemical STEM

Reed M. Wittman,[1,2] Raymond R. Unocic,[3] Thomas A. Zawodzinski[2,4]

[1]Bredesen Center, Energy Science and Engineering Department, University of Tennessee, Knoxville, Tennessee, 37996

[2]Physical Chemistry of Materials Group, Oak Ridge National Laboratory, Oak Ridge, TN, 37831

[3]Microscopy Group, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831

[4]Chemical and Biomolecular Engineering Department, University of Tennessee, Knoxville, Tennessee, 37996

17. *Exploring a Simple Synthetic Route to Metal Oxide Nanowires with the Spinel Crystal Structure

Lei Yu,[1] Amita Patel,[1] Yan Zhang,[1] Bethany M. Hudak,[1] Damon K.Wallace,[1] Doo Young Kim,[1] Beth S. Guiton[1,2]

[1]Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

[2]Materials Science and Technology Division, Oak Ridge National Laboratory , Oak Ridge, TN 37831

18. Direct Observation of Phase Transformations in Individual Hafnia Nanorods

B. M. Hudak,[1] S. W. Depner,[2] G. Waetzig,[3] S. Banerjee,[3] B. S. Guiton[1,4]

[1]Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

[2]DEMIEN LLC, Amhurst, NY 14228

[3]Department of Chemistry, Texas A&M University, College Station, TX 77842

[4]Materials Science and Technology Division, Oak Ridge National Laboratory , Oak Ridge, TN 37831

19. New *in situ* Measurements of Local Atomic Structure Response to Electric Fields using Pair Distribution Functions

Jacob L. Jones,[1] Tedi-Marie Usher,[1] Igor Levin,[2] John E. Daniels,[3] Elena Aksel,[4] Jenny Forrester[4]

[1]Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695

[2]Ceramics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

[3]School of Materials Science and Engineering, UNSW Australia, Sydney 2052, Australia

[4]Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611

20. Perovskite Solar Cells with Near 100% Internal Quantum Efficiency Based on Large Single Crystalline Grains and Vertical Bulk Heterojunctions

Bin Yang,[1] Ondrej Dyck,[2] Jonathan Poplawsky,[1] Jong Keum,[1] Alexander Puretzky,[1] Sanjib Das,[3] Ilia Ivanov,[1] Christopher Rouleau,[1] Gerd Duscher,[2] David Geohegan,[1] Kai Xiao[1]

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

[2]Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee, 37996

[3]Department of Electrical Engineering and Computer Science, University of Tennessee, Knoxville, TN, 37996

21. Polymer Membranes for Large-Scale Energy Conversion and Storage

Michael A. Hickner

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

22. *Charge Transport and Hydrogen-Bonding in Imidazole/Carboxylic Acid Mixtures

Tyler Cosby,[1] Adam Holt,[2] Phillip Griffin,[3] Yangyang Wang,[4] Joshua Sangoro[1]

[1]Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee, 37996

[2]Department of Physics and Astronomy, University of Tennessee, Knoxville, TN 37902

[3]Department of Material Science, University of Pennsylvania, Philadelphia, PA 19104

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

23. *Charge Transport and Structural Dynamics in Ammonium Based Polymerized Ionic Liquids and their Monomeric Analogues

Maximilian Heres
University of Tennessee, TN 37996

24. *Design of a Polymer Thermoelectric Generator using Radial Architecture

Akanksha K. Menon, Shannon K. Yee
G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology Atlanta, GA 30332-0405

25. *Carbon Nanotube Based Dosimetry of Neutron and Gamma Radiation

Tony Nelson
[1]Virginia Tech

26. *Electrical Characteristics of InSe-WSe_2 Van der Waals Heterojunctions

Akinola Oyedele,[1,2] Ming-Wei Lin,[2] Kai Wang,[2] David B. Geohegan,[2] Kai Xiao[2]
[1]Bredesen Center, University of Tennessee, Knoxville, TN 37902
[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

27. *Carbon Nanotubes Grown on Metal Microelectrodes for the Detection of Dopamine

Cheng Yang,[1] Christopher B. Jacobs,[1] Mallikarjunarao Ganesana,[1] Michael D. Nguyen,[1] Alexander G. Zestos,[1] Ilia N. Ivanov,[2] Alex A. Puretzky,[2] Christopher M. Rouleau,[2] David B. Geohegan,[2] B. Jill Venton[1]
[1]Department of Chemistry, University of Virginia, McCormick Road, Box 400319, Charlottesville, Virginia 22904-4319
[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

28. *Influence of Submicron Agro Waste Silica Particles and Vinyl Acetate on Mechanical, Diffusivity and Thermal Properties of High Density Polyethylene Matrix Composites

Oluyemi O. Daramola,[1] Isiaka O. Oladele,[1] Benjamin O. Adewuyi,[1] Rotimi Sadiku,[2] Stephen C. Agwuncha[2]
[1]Department of Metallurgical and Materials Engineering, Federal University of Technology, PMB 704, Akure, Ondo State, Nigeria
[2]Division of Polymer Technology, Department of Chemical, Metallurgical, & Material Engineering, Tshwane U. Technology, South Africa

29. *Gelation of Anisotropic Silica Nanoparticles with Thermoreversible Short-Range Interactions

Ryan Murphy
[1]University of Delaware

30. Mechanical Behavior of All-Acrylic Multigraft Copolymers Based on Side Chain Molecular Weight and Volume Fraction

Andrew Goodwin,[1] Weiyu Wang,[1] Nam-Goo Kang,[1] Yangyang Wang,[2] Kunlun Hong,[2] Jimmy Mays[1,3]
[1]Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
[3]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

31. Accessing Next-Generation Polyolefins and Gas Separation Membranes via Coordination-Insertion Polymerization

Brian Long
University of Tennessee, Knoxville, TN 37902

32. Improved Carbon Nanotube Yarns through Crosslinking

Xinyi Lu
University of Tennessee, Knoxville, TN 37902

33. Development of Passive Polymer Membranes for Carbon Dioxide Separation

Tao Hong, Sabornie Chatterjee, Shannon Mahurin, De-en Jiang, Brian Long, Jimmy Mays, Alexei Sokolov, Tomonori Saito[1]
[1]Chemical Sciences Division, Oak Ridge National Laboratory , Oak Ridge, TN 37831

34. Organic-Organic Amorphous Nanocomposites

Chau D. Tran,[1] Tony Bova,[1] Jihua Chen,[2] Jong K. Keum,[2,3] Amit K. Naskar[1]
[1]Materials Science and Technology Division, Oak Ridge National Laboratory , Oak Ridge, TN 37831
[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[3]Neutron Science Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37831

35. Cellular Organizations in *Escherichia coli* Mechanically Probed by a Novel Microfluidic Device

Da Yang,[1] Branndon Jones,[1] Scott Retterer,[2] Jaan Männik[1]
[1]University of Tennessee, Knoxville, TN 37902
[2]Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

36. Big Data Techniques for Investigation of the Tip-Induced Ferroelectric Switching

Anton Ievlev and Sergei Kalinin
Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

37. Extraction and Analysis of Dynamic Information in SPM

Alexei Belianinov, Suhas Somnath, Sergei Kalinin, Stephen Jesse
Institute for Functional Imaging of Materials and the Center for Nanophase and Materials Sciences, ORNL, Oak Ridge, TN 37831

38. TBD

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

39. Advanced Understanding of Bias-Induced Dynamic Phenomena in SPM

Nina Balke, Qian Li, Stephen Jesse, Petro Maksymovych, Sergei Kalinin
Center for Nanophase and Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

40. *Electron Energy Loss Spectrum Analysis for Van der Waals Heterostructures

Nicholas Cross,[1] Lei Liu,[2] Ali Mohsin,[2] Gong Gu,[2] Gerd Duscher[1,3]
[1]Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee, 37996
[2]Department of Electrical Engineering and Computer Science, University of Tennessee, Knoxville, TN, 37996
[3]Materials Science and Technology Division, Oak Ridge National Laboratory , Oak Ridge, TN 37831

41. *Proton Conduction Mechanisms in Yttrium-doped Barium Zirconate

Jilai Ding,[1] Evgheni Strelcov,[3] Gabriel Veith,[2] Craig Bridges,[3] Janakiraman Balachandran,[4] Panchapakesan Ganesh,[4] Sergei Kalinin,[4] Nazanin Bassiri-Gharb,[1] Raymond Unocic[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

42. *Elucidation of Rare Pathways Sampled during Biomolecular Binding Events

Ahmad Haider, Daniel Potter, Todd Sulchek
G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology Atlanta, GA 30332-0405

43. *Enhanced Thermal Excitation of AFM Cantilevers to Improve Sampling of Rare States during Energy Landscape Reconstruction

Daniel Potter, Ahmad Haider, Todd Sulchek
G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology Atlanta, GA 30332-0405

44. *Formation Mechanism of Mn Containing Precipitates during Homogenization in 6xxx Series Aluminum Alloys

Gongwang Zhang,[1] Yi Han,[2] Yi Xu,[2] Hiromi Nagaumi,[2] Sha Gang,[3] Chad M. Parish,[4] Donovan Leonard,[4] Tongguang Zhai[1]
[1]Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506
[2]Suzhou Research Institute for Nonferrous Metals, Shenhu Road 200, Suzhou Industrial Park, Suzhou, China
[3]School of Materials Science and Engineering, Nanjing U. Science & Technology, No. 200 Xiaolingwei, Nanjing, Jiangsu, 210094, China
[4]Microscopy Group, Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

45. Scalable Analysis of Multidimensional Imaging and Spectral Data in Material Science

A. Belianinov,[1,2] E. J. Lingerfelt,[3] S. Jesse,[1,2] E. Endeve,[3] O. Ovchinnikov,[5] M. B. Okatan,[1,2] C. T. Symons,[4] M. Shankar,[4] R. K. Archibald[3]

[1]The Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

[2]Institute for Functional Imaging of Materials, Oak Ridge National Laboratory, Oak Ridge, TN 37831

[3]Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

[4]Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

46. Statistical Thermodynamics with Point Defects in 2-Dimensional Materials

Nicholas Cross,[1] Lei Liu,[2] Ali Mohsin,[2] Wolfgang Windl,[3] Gong Gu,[2] Gerd Duscher[1,4]

[1]Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA

[2]Department of Electrical Engineering and Computer Science, University of Tennessee, Knoxville, TN, 37996

[3]Department of Materials Science Engineering, Ohio State University, Columbus, Ohio 43210, United States

[4]Materials Science and Technology Division, Oak Ridge National Laboratory , Oak Ridge, TN 37831

47. A Novel Spectroscopy Technique for Ultrafast Polarization Switching in Ferroelectrics

Suhas Somnath, Alexei Belianinov, Sergei V. Kalinin, Stephen Jesse

Institute for Functional Imaging of Materials, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37931

48. Direct Measurement of Biological Energy Landscapes using Boltzmann's Equation

Todd Sulchek, Daniel Potter, Ahmad Haider

G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology Atlanta, GA 30332-0405

49. Van der Waals Epitaxial Growth of Two-Dimensional Single-Crystalline GaSe Domains on Graphene

Xufan Li,[1] Leonardo Basile,[1,2] Bing Huang,[1] Cheng Ma,[1] Jaekwang Lee,[1] Ivan V. Vlassiouk,[3] Alexander A. Puretzky,[1] Ming-Wei Lin,[1] Mina Yoon,[1] Miaofang Chi,[1] Juan C. Idrobo,[1] Christopher M. Rouleau,[1] Bobby G. Sumpter,[1] David B. Geohegan,[1] Kai Xiao[1]

[1]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37931

[2]Departamento de Física, Escuela Politécnica Nacional, Quito, Ecuador

[3]Energy & Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

50. Uncover the Template Effect in the Synthesis of Gigantic Molecular Clusters

Panchao Yin

Oak-Ridge National Laboratory, Oak-Ridge, TN 37831, USA

51. *First Principle Study of Thermal Transport at Graphene and Hexagonal Boron Nitride Interfaces

Zhequan Yan,[1] Liang Chen,[1] Mina Yoon,[2] Satish Kumar[1]

[1]G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology Atlanta, GA 30332-0405

[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37931

52. Role of Disorder in Proton Conduction in Oxide Materials

Janakiraman Balachandran,[1] Craig Bridges,[3] Yongqiang Cheng,[2] Ganesh Panchapakesan[1]

[1]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37931

[2]Neutron Science Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37831

[3]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

53. Theoretical Predication of Two-Dimensional Electrides

Wenmei Ming and Mina Yoon

Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37931

54. Predictive Power of Density Functional Theory in Finite-Temperature Hydrogen Adsorption/Desorption Thermodynamics with Corrective Energies and Potential Surfaces

Changwon Park, Bobby Sumpter, Mina Yoon

Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

55. Tailoring the Growth of Organic Thin Films by Selective Orbital Coupling

Sean R. Wagner,[1] Bing Huang,[2] Changwon Park,[2] Jiagui Feng,[1] Mina Yoon,[2] Pengpeng Zhang[1]

[1]Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824-2320

[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37931

56. *High-Performance Flexible Perovskite Solar Cells by Using a Combination of Ultrasonic Spray-Coating and Photonic Curing

Sanjib Das,[1] Bin Yang,[2] Gong Gu,[1] Pooran C. Joshi,[3] Ilia N. Ivanov,[2] Christopher M. Rouleau,[2] Tolga Aytug,[4] David B. Geohegan,[2] Kai Xiao[2]

[1]Department of Electrical Engineering and Computer Science, University of Tennessee, Knoxville, TN, 37996

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

[3]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

[4]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

57. *Quantum Model of Plasmon-Quantum Emitter Interaction in the Strong-Coupling Regime

Roderick B Davidson II,[1,2] Pavel Lougovski,[1] Ben J. Lawrie[1]

[1]Quantum Information Science Group, Oak Ridge National Laboratory, Oak Ridge, TN, 37830

[2]Department of Physics and Astronomy, Vanderbilt University, Nashville, TN, 37235

58. *All-Optical-Field-Induced Second-Harmonic Generation

Roderick B Davidson II,[1,2] Anna Yanchenko,[3] Jed Ziegler,[1] Sergey M. Avanesyan,[1] Richard F. Haglund Jr.[1]

[1]Department of Physics and Astronomy, Vanderbilt University, Nashville, TN, 37235

[2]Oak Ridge National Laboratory, Oak Ridge, TN, 37830

[3]Department of Physics, University of Virginia, Charlottesville, VA, 22904

59. Na-ion Conducting Membranes for Non-Aqueous Redox Flow Batteries: Vibrational Spectroscopy Studies

Jagjit Nanda, Rose Ruther and Frank Delnick

Oak Ridge National Laboratory, Oak Ridge, TN, 37830

60. *The Development of Lanthanum Phosphate Based Magnetic-Luminescent Nanocomposites

Austin Plymill

University of Tennessee, Knoxville, TN, 37996

61. *Probing Synaptic Activity through Graphene Optoelectronic Platforms

Rui Wang,[1] Bryson M. Brewer,[2] Mingjian Shi,[3] Deyu Li,[2] Donna J. Webb,[3,4] Ya-Qiong Xu[1,5]

[1]Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235

[2]Department of Mechanical Engineering, Vanderbilt University, Nashville, TN 37235

[3]Department of Biological Sciences and Vanderbilt Kennedy Center for Research on Human Development, Vanderbilt University, Nashville, TN 37235

[4]Department of Cancer Biology, Vanderbilt University, Nashville, TN 37235

[5]Department of Electrical Engineering, Vanderbilt University, Nashville, TN 37235

62. Transduction of Entangled Images by Localized Surface Plasmons

A. M. Marino,[1] M. Holtfrerich,[1] R.C. Pooser,[2] B.J. Lawrie,[2] R. Davidson[2]

[1]Homer L. Dodge Department of Physics and Astronomy, The University of Oklahoma, Norman, Oklahoma 73019

[2]Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

63. Molecular Dynamics Simulations of Leidenfrost Droplets on a Vibrating Nano-Ratchet

Kumar Abhishek,[1] Nickolay V. Lavrik,[2] Miguel Fuentes-Cabrera[2]

[1]Computer Science and Mathematics Division, Oak Ridge National Laboratory

[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Center for Nanophase Materials Sciences

Plenary Session

2015 User Meeting

Dynamics of Chain Exchange in Block Copolymer Micelles

Timothy P. Lodge

Department of Chemistry and
Department of Chemical Engineering & Materials Science
University of Minnesota, Minneapolis, MN 55455, USA

Block copolymers provide a remarkably versatile platform for achieving desired nanostructures by self-assembly, with lengthscales ranging from a few nanometers up to several hundred nanometers. In particular, block copolymer micelles in selective solvents are of great interest across a range of technologies, including drug delivery, imaging, catalysis, lubrication, and extraction. While block copolymers generally adopt the morphologies familiar in small molecule surfactants and lipids (*i.e.*, spherical micelles, worm-like micelles, and vesicles), one key difference is that polymeric micelles are very rarely at equilibrium. The primary reason for this is the large number of repeat units in the insoluble block, N_{core}, which makes the thermodynamic penalty for extracting a single chain ("unimer exchange") substantial. As a consequence, the critical micelle concentration (CMC) is rarely accessed experimentally; however, in the proximity of a critical micelle temperature (CMT), equilibration is possible. We have been using time-resolved small angle neutron scattering (TR-SANS) to obtain a detailed picture of the mechanisms and time scales for chain exchange, at or near equilibrium. The model system is poly(styrene-*b*-(ethylene-*alt*-propylene)) (PS-PEP), in the PEP-selective solvent squalane ($C_{30}H_{62}$). Equivalent micelles with either normal (hPS) or perdeuterated (dPS) cores are initially mixed in a blend of isotopically substituted squalane, designed to contrast-match a 50:50 hPS:dPS core. Samples are then annealed at a target temperature, and chain exchange is revealed quantitatively by the temporal decay in scattered intensity. The rate of exchange as function of concentration, temperature, N_{core}, added PEP homopolymer concentration, and chain architecture (diblock versus triblock) will be discussed.

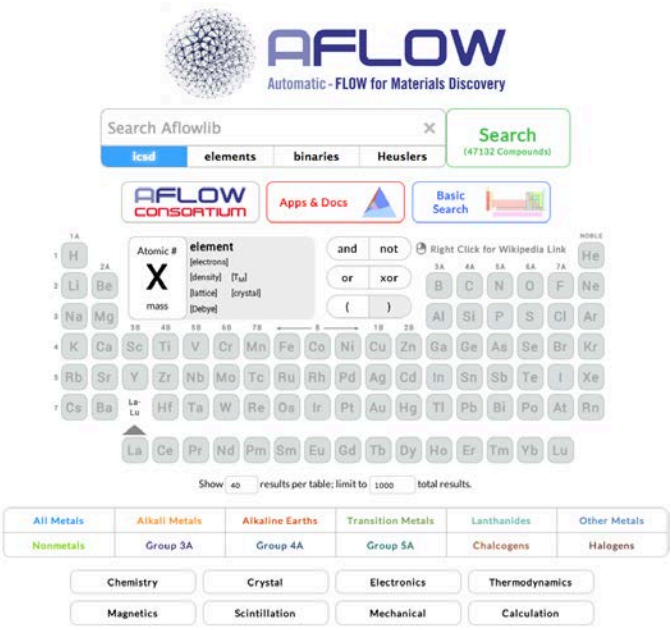
High-throughput materials discovery and development: breakthroughs and challenges in the mapping of the materials genome.

Marco Buongiorno Nardelli

Department of Physics and Department of Chemistry, University of North Texas

High-Throughput Quantum-Mechanics computation of materials properties by ab initio methods has become the foundation of an effective approach to materials design, discovery and characterization.[1,2] This data driven approach to materials science currently presents the most promising path to the development of advanced technological materials that could solve or mitigate important social and economic challenges of the 21st century. In particular, the rapid proliferation of computational data on materials properties presents the possibility to complement and extend materials property databases where the experimental data is lacking and difficult to obtain.

Enhanced repositories such as AFLOWLIB, open novel opportunities for structure discovery and optimization, including uncovering of unsuspected compounds, metastable structures and correlations between various properties. The practical realization of these opportunities depends on the the design effcient algorithms for electronic structure simulations of realistic material systems,[3,4] the systematic compilation and classification of the generated data,[5,6] and its presentation in easily accessed form to the materials science community, the primary mission of the AFLOW consortium.



[1] S. Curtarolo, G. L. W. Hart, M. Buongiorno Nardelli, N. Mingo, S. Sanvito, and O. Levy, *The high-throughput highway to computational materials design*, Nat. Mater. **12**, 191 (2013).
[2] K. Yang, W. Setyawan, S.Wang, M. Buongiorno Nardelli, and S. Curtarolo, *A search model for topological insulators with high-throughput robustness descriptors*, Nat. Mater. **11**, 614 (2012).
[3] L. A. Agapito, A. Ferretti, A. Calzolari, S. Curtarolo, and M. Buongiorno Nardelli, *Effective and accurate representation of extended Bloch states on finite Hilbert spaces*, Phys. Rev. B **88**, 165127 (2013).
[4] L.A. Agapito, S. Curtarolo and M. Buongiorno Nardelli, *Reformulation of DFT+U as a pseudo-hybrid Hubbard density functional for accelerated materials discovery*, Phys. Rev. X **5**, 011006 (2015).
[5] Curtarolo, S.; Setyawan, W.; Wang, S.; Xue, J.; Yang, K.; Taylor, R. H.; Nelson, L. J.; Hart, G. L. W.; Sanvito, S.; Buongiorno Nardelli, M. et al. *AFLOWLIB.ORG: A distributed materials properties repository from high-throughput ab initio calculations*. Comp. Mat. Sci. **58**, 227–235 (2012).
[6] Taylor, R. H.; Rose, F.; Toher, C.; Levy, O.; Yang, K.; Buongiorno Nardelli, M.; Curtarolo, S. *A RESTful API for exchanging Materials Data in the AFLOWLIB.org consortium*. Comp. Mat. Sci. doi=10.1016/j.commatsci.2014.05.014 2014,

Center for Nanophase Materials Sciences

Roundtable Sessions

2015 User Meeting

Self-assembly of helium cluster networks enabled by interfaces in metal nanocomposites

M. J. Demkowicz
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge MA, 02139

Helium (He) is a major cause of damage in materials envisioned for future fusion reactors. If the dream of limitless clean energy from fusion is to be realized, then new, He-resistant materials must be developed. We have proposed a disruptive solution to the He damage problem: design layered nanocomposite materials where heterophase interfaces cause He precipitates to interact, coalesce, and ultimately self-assemble into an interconnected network of clusters. Any additional He introduced into such a material would diffuse through this network and eventually outgas to the environment, preventing damage. This talk will describe progress towards the development of He damage-resistant materials following this new paradigm.

Jeffery Aguiar

National Renewable Energy Laboratory

Abstract not yet available

Microstructure and Mechanical Properties of Ultra-High Purity ZrB_2 Using Thermodynamic Assisted Spark Plasma Sintering

David Pham and Erica L. Corral
Materials Science and Engineering Department, The University of Arizona, Tucson, Arizona 85748, Unites States

Abstract

Zirconium diboride is an ultra-high temperature ceramic (UHTC) with attractive material properties for use in extreme hypersonic flight environments and energy applications. The diboride phase is the basis for high temperature oxidation resistant UHTC composites using secondary phase reinforcements that also enhance high temperature properties of ZrB_2-based composites. However, the mechanical properties are limited by the impurity content found in the diboride source powder. Thus our work focuses on developing a methodology to process the highest purity ZrB_2 using spark plasma sintering (SPS) and computational thermodynamics analysis coupled with high resolution atomic scale electron microscopy. A clear path towards processing ultra-high purity ZrB_2 ceramics is presented using a combined experimental and thermodynamically assisted processing method through thermal treatments and oxide reducing agents carbon and boron carbide (B_4C). Computational thermodynamic phase diagrams consisting of the Zr-O-C ternary and Zr-B-C-O quaternary are developed to predict and explain the microstructures found after SPS. ZrB_2+C results in low oxygen content, but retains oxygen after SPS (0.12 wt%O) as predicted by the thermodynamic model. ZrB_2+B_4C contains minimal oxygen (0.06 wt%O) with the highest purity after SPS. Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) analysis shows evidence of SPS-unique grain boundary cleaning and the potential to use current to further improve ZrB_2+B_4C purity. Current density applied during SPS is optimized to provides the lowest oxygen content with a fine grained microstructure (~3 μm) and superior mechanical properties with a flexure strength of 660 MPa and fracture toughness of 3.4 $MPa \cdot m^{½}$.

Liquid-Solid Interfaces within Energy Storage Devices

Gabriel M. Veith
Materials Science and Technology Division; Oak Ridge National Laboratory
veithgm@ornl.gov

Controlling liquid-solid interfacial reactions is the most critical challenge confronting battery researchers. Bad interfaces result in batteries that fail in a short period of time (like those old laptop batteries) or worse catch on fire. Good interfaces enable your devices to cycle reliably for years. Despite this importance our understanding of battery interfaces is primitive and confined to *ex situ* characterization reports. This presentation will discuss some recent *in situ* characterization studies which reveal the interfaces are dynamic with cycling and potential.

In Situ TEM of Macromolecules

Madeline Dukes[1] and Deborah F. Kelly[2]

[1]Protochips, Inc., Raleigh NC 27606
[2]Virginia Tech Carilion Research Institute
Virginia Tech
Roanoke, VA 24016
Phone: (540) 526-2031; Fax: (540) 985-3373
Email: debkelly@vt.edu

Understanding the fundamental properties of macromolecules has enhanced the development of emerging technologies used to improve biomedical research. Currently, there is a critical need for innovative platforms that can illuminate the function of biomedical reagents in a native environment. To address this need, we have developed an *in situ* approach to visualize the dynamic behavior of biomedically-relevant macromolecules at the nanoscale. Newly designed silicon nitride devices containing integrated "microwells" were used to enclose active macromolecular specimens in liquid for TEM imaging purposes. We were able to successfully examine novel MRI contrast reagents, micelle suspensions, liposomes carrier vehicles and transcribing viral assemblies. With each specimen tested, the integrated microwells could adequately maintain macromolecules in discrete local environments while enabling thin liquid layers to be produced for high-resolution imaging purposes.

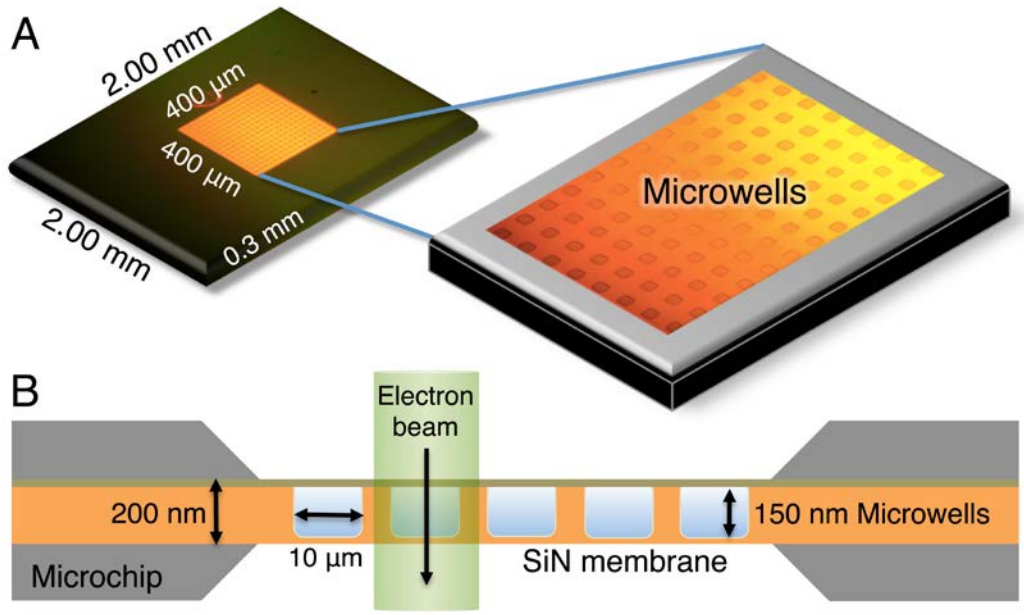


Figure 1. Specifications of SiN chips with integrated microwells. (**A**) SiN microchips having frame dimensions of 2.00-mm x 2.00-mm x 0.3-mm were produced with integrated microwells. (**B**) Side view of the liquid cell chamber composed of a 200-nm thick SiN membrane containing microwells (10 µm x 10 µm) that can accommodate liquid layers of 150-nm thick in the path of the electron beam within a TEM.

Direct-write nanofabrication using ion beams

Adam Rondinone, Olga Ovchinnikova, Alex Belianinov, Vighter Iberi and David Joy

Direct-write nanofabrication may revolutionize the fabrication of sub-micron devices in a manner similar to that achieved by 3D printing for manufacturing and rapid prototyping. Focused helium-ion beams have demonstrated unparalleled control and energy transfer resulting in high milling precision, as well as outstanding control of beam-deposited material. However, other strategies for submicron structure formation are available. In this talk we present strategies for direct write nanofabrication based on ion beam/solid interactions which result in structures difficult to achieve using other methods, including localized substitutional chemistry and localized electrochemical deposition from a solution. These approaches yield structures or functional modifications with precise localization and lateral resolutions in the 10-50nm range.

Linking the Forward and Reverse Vapor-Liquid-Solid Mechanisms in Metal Oxide Nanostructures

B. M. Hudak,[1] L. Yu,[1] Y.-J. Chang,[1] M. Park,[1] B. S. Guiton[1,2]

[1]*Department of Chemistry, University of Kentucky, Lexington, KY 40506*
[2]*Materials Science and Technology Division, Oak Ridge National Lab, Oak Ridge, TN 37831*
E-mail: beth.guiton@uky.edu

The vapor-liquid-solid (VLS) nanowire growth mechanism is ubiquitous in semiconductor nanowire synthesis. These one-dimensional nanostructures are important for applications such as solar cells, Li-ion batteries, and gas sensors. VLS synthesis is known to produce single-crystalline nanowires with diameters, lengths, dopant concentrations, and interfaces that can be tuned throughout the growth process. Theoretical predictions suggest that VLS growth is governed by steady-state kinetics, and that the crystal chemistry important for the reverse process may be different from that which governs nanowire growth. We have developed a technique to directly observe the reverse process of Au-catalyzed SnO_2 VLS nanowire growth – namely the etching of SnO_2 nanowires by the Au nanoparticles at their tip – using *in situ* heating in a transmission electron microscope (TEM).[1] This process is the opposite of the growth mechanism, and has been dubbed SLV. By utilizing energy dispersive x-ray spectroscopy (EDS), we can track the Sn content of the Au catalyst particle as the nanowire dissolves at the solid-liquid interface, and evaporates at the liquid droplet surface. This method provides an experimental platform to explore the VLS nanowire growth mechanism, including measuring the saturation concentration of a reactant within a VLS catalyst droplet. This technique is further extended to combine SLV with VLS growth, to produce integrated metal oxide heterostructures.

References

(1) Hudak, B. M.; Chang, Y.-J.; Yu, L.; Li, G.; Edwards, D. N.; Guiton, B. S. *ACS Nano* **2014**, *8*, 5441.

Abstract:

"Predictive Microstructural Evolution in Extreme Environments Using In Situ TEM"

James Hart, Andrew Lang, Michael Jablonski, Christopher Barr, Osman El-Atwani, Asher Leff, and Mitra L. Taheri

Hoeganaes Associate Professor

Drexel University, Department of Materials Science & Engineering

Abstract:

To gain a greater understanding of the mechanisms that control material properties, researchers often turn to in situ TEM. In situ TEM techniques have improved considerably in recent years with respect to their ability to understand materials behavior with high temporal and spatial resolution. While significant advances have been made in elucidating atomic-scale mechanisms that control properties of polycrystalline materials for a wide range of applications, the need for a more predictive understanding of material response exists. This talk discusses the coupled use of in situ TEM techniques in "extreme environments" of high temperature, strain, electrical bias, and irradiation with analytical and quantitative TEM methods, such as precession diffraction and strain mapping in conjunction. Case studies of in situ TEM exploration of radiation damage in nanocrystalline iron-based materials, strain-based twin evolution in copper and steel, and finally, ferroelectric domain switching in multiferroics, will be presented. The multi-scale characterization techniques presented will help provide a connection of the role of structure and interfaces in developing materials for various applications where environments pose a threat to material damage and failure, such as those found in the energy, data storage, and defense sectors.

Design, Synthesis and Characterization of Peptidomimetic Polymers towards Biomedical Applications

Donghui Zhang
Department of Chemistry, Macromolecular Studies Group,
Louisiana State University, Baton Rouge, LA 70803

Polypeptoids are a class of psudo-peptidic polymers featuring *N*-substituted polyglycine backbones with proteinogenic or synthetic side chains on the nitrogen atoms. Because of the *N*-substitution, polypeptoids exhibit enhanced protease resistance, tunable backbone conformation (via sidechain structures) and thermos-processability in contrast to polypeptides. In addition, polypeptoids are cyto-compatible and can be degraded under oxidative conditions that mimic inflammation, suggesting the potential use of polypeptoids for *in vivo* biomedical applications.

This presentation will focus on our recent efforts in the development of controlled polymerization methods towards well-defined polypeptoids and polypeptides as well as the design, synthesis and characterization of polypeptoid block copolymers for targeted biomedical applications (i.e., drug delivery and tissue engineering). Specifically, a redox responsive micellar system and thermos-reversible hydrogels based on block copolypeptoids will be discussed.

Donghui Zhang is an associate professor in the Chemistry Department of Louisiana State University. She obtained B.S. in Chemistry from Peking University in 1998 and Ph.D. in organometallic chemistry from Dartmouth College in 2003. After conducting postdoctoral research at University of Minnesota on the synthesis and characterization of polymers from biorenewable source materials, she moved to New Mexico State University as a research faculty. She joined LSU in 2007. Her current research interests focus on polymer catalysis, design and synthesis of functional polymeric materials by incorporating biomimetic principles.

Responsive biomaterials for controlling the cell microenvironment

Lisa A. Sawicki,[a] Prathamesh M. Kharkar,[b] Chen Guo,[a] Amber M. Hilderbrand,[a] and April M. Kloxin[a,b]*

a, Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy Street, Colburn Laboratory, Newark, DE, 19716, U. S. A.

b, Department of Materials Science and Engineering, University of Delaware, 201 DuPont Hall, Newark, DE, 19716, U. S. A.

Biomaterials are effective as tools to probe and direct the complex interplay between mammalian cells and their microenvironments, an array of chemical and physical cues that dictate cell fate (e.g., extracellular matrix modulus and biochemical content).[1] For this, materials are needed that afford property control at specific locations and times in response to different stimuli (e.g., light, enzymes, reducing conditions), all executed in the presence of live cells. Enabling technologies to achieve this level of property control are *i)* 'click' chemistry that often provides rapid, cytocompatible, and orthogonal reactions for material formation and modification and *ii)* cleavable chemistries for material degradation.[2] Here, we have sought to create hydrogel-based materials for controlling cellular microenvironments using select thiol–ene click chemistries and degradable moieties for programmed, responsive, or triggered changes in material properties on the benchtop (*in vitro*) and in the body (*in vivo*).

For *in vitro* microenvironments, building blocks that are accessible and allow the formation and modification of the base hydrogel are needed toward the widespread use of synthetic extracellular matrix mimics. To address this, we designed a hydrogel formed by the reaction of allyloxycarbonyl-functionalized peptides and thiol-functionalized poly(ethylene glycol), monomers that are modular and created using straightforward syntheses.[3] These monomers were polymerized with cytocompatible doses of light (~ 1 min, 10 mW/cm^2 at 365 nm) to form hydrogels with moduli mimicking a range of soft tissues (E ~ 1-10 kPa). Additionally, by polymerizing hydrogels with excess thiol functional groups, a biochemical cue (e.g., RGDS) modified with an allyloxycarbonyl group was added after hydrogel formation using photolithographic techniques, where good pattern fidelity was observed using Ellman's reagent, a simple and cost effective assay. Human mesenchymal stem cells remained viable and spread after encapsulation and photopatterning within enzymatically degradable matrices, demonstrating the utility of this approach for three-dimensional cell culture. Further, we are investigating the incorporation of assembling peptides within these materials to impart hierarchical structures that better mimic tissues.

For *in vivo* applications, chemistries that respond to stimuli found within cellular microenvironments (e.g., enzymes, pH, reducing conditions) are desirable for controlling material properties. Harnessing the power of reversible click reactions, we created injectable hydrogels that form under cytocompatible conditions and degrade in response to thiol-rich reducing conditions found in tissues containing cells with high metabolic activity (e.g., increased glutathione [GSH] present in tumors).[4] Specifically, the reaction between multifunctional monomers decorated with maleimides and thiols was utilized for hydrogel formation, and the selection of thiol dictated the degradability of the resulting linkage under thiol-rich reducing conditions (10 μm-10 mM GSH). In a reducing environment, arylthiol-based thioether succinimide linkages underwent degradation by thiol exchange (short time scales) and ester hydrolysis (long time scales), whereas alkylthiol-based thioether succinimide linkages only underwent ester hydrolysis. Building upon this, we recently incorporated a photolabile moiety within these responsive materials to enable material degradation and therapeutic release in response to both microenvironmental and externally-applied stimuli toward patient-specific treatment regimens.[5] These unique chemistries are promising for controlling the delivery of proteins and other therapeutics within tumor microenvironments.

References

1. M. S. Rehmann, A. M. Kloxin, *Soft Matter*, 2013, **9**, 6737-6746.
2. P. M. Kharkar, K. L. Kiick, A. M. Kloxin, *Chemical Society Reviews*, 2013, **42**, 7335-7372.
3. L. A. Sawicki , A. M. Kloxin, *Biomaterials Science*, 2014, **2**, 1612-1626.
4. P. M. Kharkar, A. M. Kloxin, K. L. Kiick, *Journal of Materials Chemistry B*, 2014, **2**, 5511-5521.
5. P. M. Kharkar, K. L. Kiick, A. M. Kloxin, *Polymer Chemistry*, 2015, **6**, 5565-5574.

Predicting Hydrophobicity in Polymers

Robert T. Mathers

Pennsylvania State University, New Kensington PA

Although hydrophobicity is intuitively recognized, quantifying hydrophobicity prior to a polymerization or comparing functional groups represents a challenging task. Using partition coefficients, a combined experimental and computational approach has been investigated to predict hydrophobicity of monomers and polymers. Based on these partition coefficients, new insights have been made for two monomer libraries. The ability to design monomers has many implications for understanding hydrophobicity as well as polymer swelling behavior and degradation of polyesters.

Single Chain Conformation and Complexation of Annealed Polyelectrolytes in Dilute Aqueous Solution

Y. Elaine Zhu
Department of Chemical and Biomolecular Engineering
University of Notre Dame

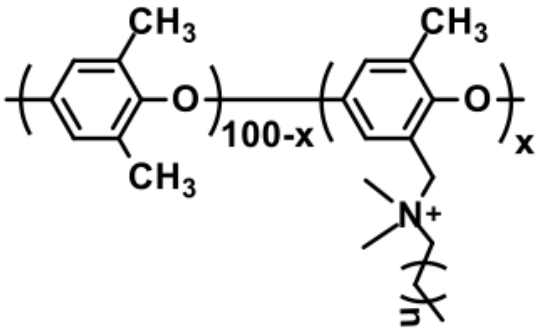
Polyelectrolytes, including many biopolymers, have emerged as building blocks to create new intelligent functional materials with properties tunable by pH and salt concentrations. Such stimuli-response polyelectrolyte materials have promising applications in batteries, protective coatings, nanomaterial synthesis, drug delivery, and separation membranes. Of extreme importance in designing and engineering new applications for polyelectrolyte materials is detailed understanding of electrostatic effect and structural dynamics of polyelectrolytes and their complexes in aqueous solution. In this talk, I will discuss our recent experimental study of the effects of multivalent ions and chain architecture on the single chain conformations and complex formation of annealed polyelectrolyte, poly(2-vinyl pyridine) (P2VP) of tunable charge density in dilute aqueous solutions. Swollen linear P2VP chains in dilute aqueous solution can abruptly collapse by increasing pH due to decreased P2VP charge fraction as confirmed by measured local pH in close vicinity to a P2VP chain. Start-like branched P2VP exhibits distinct features from the linear one due to topological complexity. For both linear and branched PVPs, multivalent ions and macroions can effectively alter the pH range to control the swollen and collapsed states of P2VP chains in an opposite trend to monovalent ions. Distinct from simple ions, inorganic nanocluster macroion of 1-5 nm in diameter can form dense complexes with P2VP, whose dimension becomes independent of solution pH.

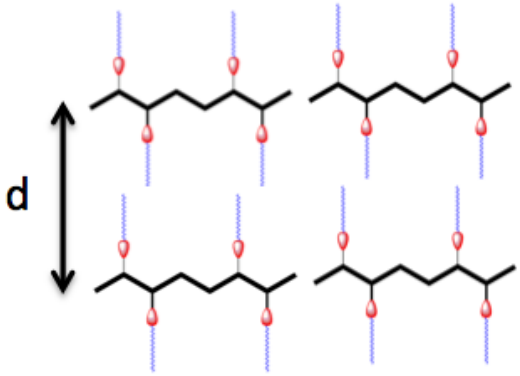
Synthesis of Cationic Polymers for Membrane Applications

Michael A. Hickner
Center for Nanophase Materials Sciences
Oak Ridge National Laboratory

Ion transport in polymeric membranes plays an important role in many energy-focused applications including fuel cell and large-scale battery technologies. The synthesis of sulfonated polymers has been widely investigated over the last 20 years and a number of innovative strategies for creating new proton exchange membranes have been demonstrated. Their counterparts, anion exchange membranes with backbone-tethered cations and free anions, are not as well studied. Anion exchange membranes pose interesting synthetic challenges due to the large number of polymeric backbones and organic cations that remain unexplored for use as high-performance materials. However, the hydroxide stability and anion conductivity of these polymeric membranes remain challenges in the field.

In this talk, I will discuss insights into the stability of anion exchange membranes and give an overview of the synthetic diversity that is possible with cationic polymers that may be candidates as next-generation membrane materials. We have developed syntheses that are adaptable to producing materials at large scale and that have been tested in operating fuel cells and water electrolyzers. We have found that functionalized poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is an electron rich, stable backbone that shows low degradation under hydroxide attack, a key attribute for long-lived device lifetimes. Additionally, using PPO as a synthetic platform, we have employed a number of different side chain functionalization strategies to drive phase separation in random copolymers. This strategy is useful for boosting the conductivity of the material through formation of nanophase segregated, ion-rich domains. Additional functionality such as crosslinking and non-ionic hydrophilicity has been imparted to these materials through modification of the side chains on the PPO backbone or the formation of semi-interpenetrating networks. Our synthetic strategies and insights for materials exploration and optimization of anion exchange membranes will be discussed.





Polymer-Based Thermoelectrics: New Directions

Shannon Yee, Assistant Professor
Georgia Institute of Technology

The capital cost of many thermoelectric generator (TEG) systems, including those used for vehicle waste heat recovery and for CSP bottoming cycles, are often dominated by the cost of the cold-side heat exchanger, where cost scaling "laws" for heat exchangers are not favorable. Following the cost scaling "laws" to their logical conclusion points to materials with thermal conductivities < 0.5 W/m-K, such as polymers. Polymers afford new fabrication techniques and architectures that are inaccessible to many inorganic thermoelectrics warranting a renewed look into TEG architectures specifically for polymer and polymer-based materials. Polymer thermoelectrics also offer new transport physics dominated by electron-phonon coupling that lead to enhanced power factors making them competitive with their inorganic counterparts. However, suitable n-type and p-type polymers have limited compelling device demonstration and therefore the realization of a polymer-based TEG. This talk will discuss our progress in developing n-type and p-type polymer thermoelectric thin-films in collaboration with ORNL. We will also present our new radial device architecture and the results of our first polymer-based TEG device, where the device is passively cooled by natural convection. This circumvents the heat exchanging cost-scaling problem and provides a compelling demonstration for the potential of polymer-based TEGs for bottoming cycles and low temperature waste-heat recovery.

Simultaneous Organic Ligand Grafting and Self-Assembly of Nanoparticles at Liquid-Liquid Interfaces

Daniel Hallinan, Jr.
Florida State University

Precise grafting of organic ligands to nanoparticles can be challenging. This is particularly true for hydrophobic organic ligands, such as alkyl amines, and aqueous gold nanoparticles. Organic ligands are used to stabilize nanoparticles, to compatibilize them with polymer matrices, or to control particle spacing. Self-assembled monolayers of nanoparticles are of interest for electronic, photonic, and sensing applications. However, large-scale assembly of nanoparticle monolayers is challenging with existing preparation techniques. A new approach, using liquid-liquid interfacial ligand grafting and simultaneous assembly will be presented. Gold nanoparticles with 13 nm diameter and polydispersity index less than 1.1 were synthesized by reducing gold salt in aqueous solution. Alkyl amine ligands ranging in length from 6 to 18 carbons were grafted to gold nanoparticles at a hexane/water interface, which induced the formation of a large-scale monolayer that could be deposited on a variety of substrates. The monolayer structure was characterized with grazing incidence small angle X-ray scattering and transmission electron microscopy. The electronic and photonic properties of the monolayer film both have an exponentially decaying dependence on particle spacing. Future research directions that could be enabled by this synthesis technique will be discussed.

Creating hierarchically structured sustainable materials using modular synthesis strategies

Will Gramlich, University of Maine Department of Chemistry

Nature, through billions of years of evolution, has developed hierarchical material structures that span several orders of magnitude to accomplish numerous tasks such as efficiently transporting fluids, providing mechanical support, and preventing biofouling. Previous research has targeted mimics of these hierarchical structures for applications such as cell scaffolds, anti-bacterial coatings, and tough materials using synthetic polymers. Current work aims to create these materials sustainably using plant based raw materials as monomers or biopolymers. To implement these sustainable polymers into nanometer- and micrometer- scale phase separated hierarchical systems, complex polymer architectures such as block and graft copolymers are needed. Synthetic strategies have been developed to functionalize these sustainable materials with reactive groups, providing molecular handles to attach or polymerize other polymer chains and yielding complex polymer architectures that phase separate on the nanometer-scale. Further research is focused on providing functional groups for micrometer-scale organization. In our group, we have functionalized renewable polymer chains with pendant reactive groups for modular graft synthesis. These materials have been used to create toughened renewable plastics and stimuli responsive hydrogels that phase separate on the nanometer scale. Using similar modular chemistry, work is ongoing to combine block copolymer phase separation and hierarchically structured nanofibrillated cellulose to create polymer toughening agents. By incorporating these functional groups on renewable polymers that undergo specific and efficient reactions, these polymers may be modularly assembled to create a variety of future hierarchical materials without developing new chemistry.

Rational Computation-Guided Design of Polymer Dielectrics

Rampi Ramprasad
University of Connecticut, Storrs, CT 06269, USA

To date, trial and error strategies guided by intuition have dominated the identification of materials suitable for a specific application. We are entering a data-rich, modeling-driven era where such Edisonian approaches are gradually being replaced by rational strategies which couple predictions from advanced computational screening with targeted experimental synthesis and validation. Consistent with this emerging paradigm, we propose a strategy of hierarchical modeling with successive down-selection stages to accelerate the identification of polymer dielectrics that have the potential to surpass `standard' materials for a given application. Specifically, quantum mechanics based combinatorial searches of chemical space are used to identify polymer repeat units that could lead to desirable dielectric properties, followed by configurational space searches to determine the 3-dimensional arrangement of polymers (and their properties) built from the desirable repeat units. Successful synthesis and testing of some of the most promising identified polymers and the measured attractive dielectric properties (which are in quantitative agreement with predictions) strongly supports the proposed approach to material selection [1].

While the above success is indeed exciting, it leaves open the question that the chemical space of even the subclass of polymers studied may not have been searched exhaustively. This is because the search process had to be significantly restricted as expensive quantum mechanical calculations were used. Extensive expansion of the search space requires other strategies, e.g., machine-learning algorithms trained on the already available quantum mechanical data [2]. The most critical step in this process is the identification of descriptors or fingerprints that represent the materials effectively, intuitively and uniquely. Several strategies have been developed to handle this, including atomic level and building unit level fingerprints. A critical assessment of different flavors of these choices in predicting properties will be discussed. Appropriately crafted fingerprints can also permit “inverse design”, i.e., identification of specific groups of materials that meet a certain property requirement. Large-scale searches made possible by these machine or statistical learning strategies have helped identify a rich variety of newer polymer dielectrics worthy of further studies. Harnessing such learning paradigms extends recent efforts to systematically explore and mine vast chemical spaces, and can significantly accelerate the discovery of new application-specific materials.

[1] V. Sharma, C. C. Wang, R. G. Lorenzini, R. Ma, Q. Zhu, D. W. Sinkovits, G. Pilania, A. R. Oganov, S. Kumar, G. A. Sotzing, S. A. Boggs, R. Ramprasad “Rational design of all organic polymer dielectrics”, Nature Communications 5, 4845 (2014).

[2] G. Pilania, C. C. Wang, X. Jiang, S. Rajasekaran, R. Ramprasad, “Accelerating materials property predictions using machine learning”, Sci. Rep., 3, 2810 (2013).

Thermodynamics and Thermal Transport Near Lattice Instabilities

Olivier Delaire
Oak Ridge National Laboratory, Materials Science and Technology Division

In this presentation, I will present some results from our combined computational and experimental investigations of lattice dynamics in complex functional materials. In particular, I will highlight the importance of deviations from the textbook model of harmonic lattice vibrations in solids (phonons), which can arise through a variety of effects such as: anharmonicity in the interatomic potential leading to phonon-phonon interactions [1,2], or electron-phonon [3] and spin-phonon interactions [4], all of which may be exploited to design materials with enhanced functional properties. In particular, lattice instabilities impact functional properties in many materials, including ferroelectrics, thermoelectrics, phase-change materials, and superionic conductors. Phase transitions are central in much of condensed matter physics and materials science, and the phonon entropy can sometimes have a large effect on thermodynamics and structural phase transitions [5,6]. Near soft-mode lattice instabilities, the usual quasiharmonic approximations can fail spectacularly, showcasing the need to account for strong anharmonic phonon-phonon interactions. Strong anharmonic phonon scattering also plays a critical role in thermal transport properties, for example in thermoelectrics [1,2,3]. Using a combination of experimental scattering techniques (neutron and x-ray scattering) and first-principles computer simulations, we carefully probe and quantitatively rationalize these interactions, providing insights for the design of improved materials. I will review some of our recent studies investigating phonon anharmonicity near lattice instabilities in connection with thermal transport in thermoelectrics, and phase stability in ferroelectrics and related oxides.

Funding from US-DOE/BES/MSED, Office of Science Early-Career-Award, and as part of the S3TEC-EFRC.

[1] O. Delaire, J. Ma, K. Marty, A. F. May, M. A. McGuire, M.-H. Du, D. J. Singh, A. Podlesnyak, G. Ehlers, M. Lumsden, and B. C. Sales, "Giant Anharmonic Phonon Scattering in PbTe", **Nature Materials** 10, 614 (2011).

[2] C.W. Li, O. Hellman, J. Ma, A.F. May, H. Cao, X. Chen, A.D. Christianson, G. Ehlers, D.J. Singh, B.C. Sales, and O. Delaire, "Phonon self-energy and origin of anomalous neutron scattering spectra in SnTe and PbTe thermoelectrics", **Phys. Rev. Letters** 112, 175501 (2014).

[3] O. Delaire, K. Marty, M. B. Stone, P. R. C. Kent, M. S. Lucas, D. L. Abernathy, D. Mandrus, and B. C. Sales, "Phonon softening and metallization of a narrow-gap semiconductor by thermal disorder", **Proc. Nat. Acad. Sci. USA** 108, 4725 (2011).

[4] O. Delaire, M.B. Stone, J. Ma, A. Huq, D. Gout, C. Brown, K.F. Wang, and Z.F. Ren, "Anharmonic Phonons and Magnons in $BiFeO_3$", **Phys. Rev. B** 85, 064405 (2012).

[5] J. D. Budai*, J. Hong*, M. E. Manley, E. D. Specht, C. W. Li, J. Z. Tischler, D. L. Abernathy, A. H. Said, B. M. Leu, L. A. Boatner, R. J. McQueeney, and O. Delaire, "Metallization of vanadium dioxide driven by large phonon entropy", **Nature** 515, 535–539 (2014).

[6] O. Delaire, M. Lucas, J. Muñoz, M. Kresch and B. Fultz, "Adiabatic Electron-Phonon Interaction and High-Temperature Thermodynamics of A15 Compounds", **Phys. Rev. Letters** 101, 105504 (2008).

Acceleration of materials discovery with bio-inspired algorithms

Alexey Kolmogorov

With growing number of theory-guided discoveries, the focus of *ab initio* materials prediction research has shifted from demonstrating the feasibility to improving the efficiency and reliability of the search methods. The success of identifying new synthesizable materials depends largely on the extent of configurational space sampling and the accuracy of the thermodynamical stability calculation. A number of advanced strategies have been developed in recent years to address the first problem – to efficiently screen the space of structures and compositions. I will share my experience with using a combination of high-throughput screening [1], targeted evolutionary search [2], and rational design [3]. Successful examples of this work include the prediction and discovery of an unexpected Fe-based phonon-mediated superconductor [4,5] and a new compound with complex boron building units [6]. A variety of density functional theory (DFT)-based methods and classical interaction models have also been introduced to address the second problem – to calculate material's stability with sufficient accuracy at an affordable cost – but the desired balance has yet to be achieved. The focus of ongoing research in my group [7] is to automate the construction and use of artificial neural networks (NNs) for calculating interatomic interactions. Compared to traditional classical potentials, NNs are flexible enough to describe different interaction types and have tuneable accuracy but their parameterization may require large DFT datasets. Our first tests illustrate that NNs trained on moderate DFT datasets can accelerate the search for complex ground state structures by orders of magnitude while providing near-ab-initio accuracy.

[1] A.G. Van Der Geest and A. N. Kolmogorov, CALPHAD 46, 184 (2014)
[2] A.N. Kolmogorov, Module for Ab Initio Structure Evolution (2009-), http://maise-guide.org
[3] A.N. Kolmogorov *et al.*, Phys. Rev. B 78, 094520 (2008)
[4] A.N. Kolmogorov *et al*., Phys. Rev. Lett. 105, 217003 (2010)
[5] H. Gou *et al.*, Phys. Rev. Lett., 111, 157002 (2013)
[6] A.N. Kolmogorov *et al.*, Phys. Rev. Lett., 109, 075501 (2012)
[7] A.N. Kolmogorov, NSF award 1410514 (2014-2017)

Machine Learning Methods for the Rapid yet Accurate Sampling of Chemical Compound Space

Anatole von Lilienfeld
Chemistry Department
University of Basel, Switzerland

Many of the most relevant chemical properties of matter depend explicitly on atomistic details, rendering a first principles approach mandatory. Alas, even when using high-performance computers, brute force high-throughput screening of compounds with electronic structure theory is beyond any capacity for all but the simplest systems and properties due to the combinatorial nature of chemical space, i.e. all the compositional, constitutional, and conformational isomers. Consequently, efficient exploration algorithms should exploit all implicit redundancies present in high-throughput approaches. In this talk, I will describe recently developed statistical approaches for interpolating (Kriging) quantum mechanical observables in composition space. Examples will be presented for predicting properties of out-of-sample molecules and solids with high accuracy and small computational cost.

Quantifying Electromechanical Scanning Probe Microscopy

Liam Collins,[1] Haidong Lu, [2] Aleks Labuda,[3] Alexei Gruverman,[2], and Roger Proksch[3]

[1]Irish Gentleman Farmer, Environs of Knoxville, TN
[2] University of Nebraska, Lincoln, NE
[3]Asylum Research, an Oxford Instruments Company, Santa Barbara, CA

One of the ongoing challenges in the field of Atomic Force Microscopy (AFM) has been quantitative measurement of the motion of the cantilever probe. This is certainly the case for electromechanical force microscopies such as piezoresponse force microscopy (PFM) and electrochemical strain microscopy (ESM) where accurate quantification of the piezo-electric sensitivities (d33, d15, etc…) has been a longstanding goal. Conventional PFM systems almost exclusively use a "beam bounce" optical detection system[1] where a laser is focused on the back of the cantilever and the angle of the reflected light is used to deduce the cantilever deflection or torsion. Even with careful calibration, non-ideal cantilever motion such as buckling, torsion and combined movement between different vibrational modes may lead to crosstalk in the measurements of normal and lateral components of the electromechanical motion and between long and short-ranged interactions between the cantilever and sample.

Here we describe results from a metrological AFM, based on a commercial Cypher S AFM that combines highly sensitive and advanced PFM imaging and spectroscopies based around an optical lever with a separate quantitative Laser Doppler Vibrometer (LDV) system that allows displacement and velocity measurement of the cantilever probe response[2]. The motorized LDV spot position is independent of the conventional optical lever. This combined instrument allows a host of quantitative measurements to be performed including measuring a variety of in-situ PFM cantilever oscillation modes. In addition, parameters such as the optical lever sensitivity and spring constant can readily be measured without the cantilever touching the surface. We will present metrological data on a variety of ferroelectric materials, including vector-PFM[3] images where three-dimensional maps of the surface strain are measured. We will also present a series of novel ESM measurements where we attempt to tease out the source of electromechanical contrast for this new technique.

[1] S. Alexander et al., J. Appl. Phys., **65**, 1 (1989).

[2] A. Labuda and R. Proksch, Appl. Phys. Lett., **need ref** (2015).

[3] L. M. Eng et al., Appl. Phys. Lett., **74**, 233 (1999).

A perspective for multi-dimensional ultrafast Scanning Probe Microscopy

Gabriele Ferrini

Interdisciplinary Laboratories for Advanced Materials Physics (iLAMP),
Università Cattolica del Sacro Cuore, I-25121 Brescia, Italy

Recent developments in scanning probe microscopies (SPM) enabled high throughput instruments with enhanced sensibility and big output volumes of multi-dimensional data. The traditional approach to the analysis of such data sets are no longer sufficient to extract the most meaningful information. The next nanoscience grand challenge calls for the integration of advanced data analytics and theory into a unified view for such multichannel data complexes.

One important example of multi-dimensional analysis is related to the evolution of transient tip-sample interactions in time, frequency and space. Convolution and Fourier transform, the signal analysis tools predominantly used in SPM, are mathematically sufficient to handle linear time invariant systems. However, new tools are necessary to face the complexity of transient signal processing. I will focus on the opportunity of harnessing information from signals generated by ultrafast interactions of a mechanical probe with a sample surface. To develop this program we need ideas coming from ultrafast laser optics, series analysis techniques from meteorology and geophysics, wavelet transform techniques developed in the past decades.

The ultimate goal is to provide visualization and analysis techniques that are able to reduce the data dimensionality, display data correlations in the most effective way to capture the essential trends, help to make sense of unstructured data. Such task is a prerequisite for physical modelling or for a qualitative understanding of the relevant processes at the nanoscale.

Dynamic Contact AFM with Photothermal Excitation

Jason P. Killgore
National Institute of Standards and Technology
Applied Chemicals and Materials Division, MS 647
Boulder, CO 80304
(303)497-4729

The atomic force microscope (AFM) has achieved widespread success for applications ranging from polymer science to biology. One of the premier capabilities of the AFM is the ability to measure local mechanical properties of a surface with nanoscale spatial resolution. In dynamic contact AFM methods, the cantilever sensor is brought into feedback at a constant force while a small oscillation is applied to the sample or cantilever. By characterizing properties of the cantilever response such as resonance frequency or sub-resonance amplitude, many properties of the surface can be determined. Two of the most common types of dynamic contact AFM methods are force modulation microscopy (FMM) and contact resonance force microscopy (CR-FM). Conventionally, the drive force in both methods has come from a piezoelectric element placed at the base of the cantilever, or beneath the sample. Such an approach has limitations when operating in fluid environments and across broad frequency ranges where spurious vibrations result in erroneous or even impossible data interpretation.

Here, we apply photothermal excitation to FMM and CR-FM measurements. The photothermal excitation places a laser with sinusoidally modulated power onto the cantilever to provide a smoothly varying drive force as a function of frequency. For FMM, photothermal excitation is used to provide broadband excitation across a range of frequencies. Rank order stiffness maps are obtained on a microbridge sample with stiffness varying along its length. Certain drive and detect laser positions result in a non-monotonic amplitude versus stiffness relation, suggesting that the photothermally induced cantilever motion varies substantially from the end-loaded models for which FMM analysis has been conventionally derived. By rastering the detection laser to measure the shape of the oscillating cantilever, we are able to apply a rederived FMM analysis to determine tip-sample stiffness for photothermal or acoustically drive AFM systems.

In CR-FM, the photothermal excitation is used to obtain measurements of viscoelastic loss tangent while operating in a liquid environment. Operation in a liquid environment significantly complicates viscoelastic CR-FM measurements because the fluid damping masks the dissipative properties of the material, while also introducing substantial noise into acoustically driven measurements. We have developed a new analysis that subtracts out the fluid damping effect in the system, leaving behind only the properties of the test-material. The photothermal excitation provides a clean Lorentz resonance response in the cantilever, which enables an accurate analysis of damping for point-by-point and contact-mode scanning measurements. Accuracy is found to depend on eigenmode selection and the magnitude of the material's loss tangent. By comparing viscoelastic measurements made in air and water on materials not affected by the water, we show that liquid contact resonance is an accurate method for measuring the loss tangent of nanostructured materials.

Multi-frequency Atomic Force Microscopy for subsurface and chemical mapping

L. Tetard
NanoScience Technology Center, University of Central Florida, Orlando, FL, USA.

Although exploring new dimensions of complex systems properties at the nanoscale remains an outstanding challenge, it was recently facilitated by the emergence of multi-frequency atomic force microscopy (AFM). Hence, using multiple simultaneous mechanical actuations of the AFM cantilever-sample system, with two frequencies or more, improvements in spatial resolution and quantitative studies of surface and subsurface properties could be achieved.

Here we will highlight how such dynamic attributes, implemented on a platform coined Mode Synthesizing Atomic Force Microscopy (MSAFM), can be used to resolve previously uncharted features lying below the surface, with high lateral and depth resolution. We will present new developments to detect variations in physical properties at the nanoscale, and reconstruct a three dimensional (3D) representation of the sample volume. Furthermore, we will introduce how the “mode synthesizing” concept can be extended to a combination of mechanical and photonic actuations, to offer high resolution chemical mapping and localized infrared spectroscopy.

Finally, we will discuss how these new capabilities can provide new insights into nanoscale features of complex systems, such as unraveling the physical and chemical traits of subcellular structures of plant cells to support the biomass deconstruction efforts in biofuel research, and the development of new disease management treatments in agriculture.

Center for Nanophase Materials Sciences

Poster Abstracts

2015 User Meeting

Structural Characteristics of Nanophase-Carbon in Covetic Materials*

Beihai Ma[1], Uthamalingam (Balu) Balachandran[1], Jianguo Wen[2], Dean J. Miller[2], Robert P. Winarski[2], Carlo U. Segre[3], and David C. Joy[4]

[1]Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439
[2]Nanoscience and Technology Division, Argonne National Laboratory, Argonne, IL 60439
[3]Department of Physics, Illinois Institute of Technology, Chicago, IL 60616
[4]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Recent advancement in nanophase materials science and engineering had made it possible to incorporate carbon nanostructures into metal matrixes to achieve enhanced physical properties. This new class of materials, known as covetics, may be a game-changer for materials scientists and engineers who have long sought to combine light-weight and high-conductivity carbon with metal in their pursuit to improve materials performance. Covetic materials are prepared by having large amount of nanophase carbon infused into metal matrixes using a unique electrical process. The enhanced electrical and thermal conductivities of covetics originate from carbon nanostructures dispersed in the metal. Understanding the buried interfacial structure of nanophase carbon and host metal matrix is critical to elucidate the mechanics for superior material performance. Electron microscopy and X-ray imaging were applied to study covetic copper and aluminum alloys. Details of the results will be presented in this talk.

This work was supported by the U.S. Department of Energy, Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under Contract DE-AC02-06CH11357.

(Topics: Buried interface structure and effects on properties)

Effects of Radiation Exposure on Ferroelectric Material Stacks in Piezoelectric MEMS/NEMS

S. J. Brewer[1], M. K. Paul[1,2], K.J. Fisher[1,3], J. E. Guerrier[4], R. Q. Rudy[5], , E. R. Glaser[6], C. D. Cress[6], R. G. Polcawich[5], J. L. Jones[4], N. Bassiri-Gharb[1,7],
[1]G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology
Atlanta, GA 30332, USA
[2]Woodward Academy, Atlanta, GA 30337, USA
[3]Riverwood International Charter School, Sandy Springs, GA 30328, USA
[4]Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA
[5]Army Research Laboratory, Adelphi, MA 20783, USA
[6]Naval Research Laboratory, Washington, D.C. 20375, USA
[7]School of Materials Science and Engineering, Georgia Institute of Technology
Atlanta, GA 30332, USA

Ferroelectric films and devices enable numerous applications such as precision positioners and optics, MEMS sensors and actuators, non-volatile memories, and energy harvesting systems. Additionally, the multifunctional properties of ferroelectric materials such as lead zirconate titanate (PZT)--i.e. excellent ferroelectric, piezoelectric, pyroelectric and electrocaloric properties-- make it an ideal candidate for enabling a “More-than-Moore” paradigm in microelectronic devices. Of specific interest are millimeter-scale robotics for performing tasks at locations that are either difficult to reach or otherwise dangerous for humans in energy and security applications, such as nuclear power plants and aerospace. It is thus necessary to investigate and characterize the response of ferroelectric thin films as a function of exposure to radiation dose in the context of functional devices.

Prior research has primarily concentrated on the effects of polarization degradation for ferroelectric memory devices. This work addresses the mechanisms of radiation interaction with the material resulting in degradation of dielectric and electromechanical response upon exposure to radiation. The effects of irradiation are studied on a ferroelectric material stack consisting of PZT (Zr:Ti=52:48) deposited on platinized Si wafers, with either Pt or IrO_2, as top electrode, as well as prototype MEMS devices in cantilever and relay formats. All samples are irradiated with a Cobalt-60 gamma radiation source at a dose rate of approximately 602 rad (Si)/sec at the Naval Research Laboratory (NRL), and the ferroelectric and piezoelectric response of the material stack and devices are characterized. Electron spin resonance (ESR) is used to identify and differentiate between native defects in the films compared to those produced by exposure to ionizing radiation. Additionally, the effects of oxygen vacancies and defect migration at the interface between the electrode and oxide dielectric will be studied, using Pt vs. oxide (IrOx) electrodes. It is expected that the metallic/oxide electrode is a primary contributor to the defect creation and accumulation sites, due to the photoelectric effect.

Preliminary results of irradiation experiments performed at 2.5 Mrad (Si) show a degradation of approximately 15% of the low-field dielectric permittivity, and up to 6% degradation in remanent polarization compared to the same samples before irradiation. Additional characterization of dielectric and electromechanical response will further elucidate the effect of radiation and electrode material on PZT and prospective MEMS/NEMS devices.

Quantitative Effects of Textures and Grain Sizes on Short Fatigue Crack Growth in High Strength Aluminum Alloys by a 3-D Microstructure-Based Model

Pei Cai [1], Yan Jin [1], Wei Wen [1,3], Donovan N Leonard [2] and Tongguang Zhai [1]
[1] Chemical and Materials Engineering Department, University of Kentucky, Lexington, KY 40506
[2] Microscopy Group, Materials Sciences & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[3] Novelis Global Research & Technology Center, Kennesaw, GA 30144

A 3-D microstructural based model was developed to quantify the growth behaviors of short fatigue cracks by taking into account both the driving force and local resistance in high strength Al alloys. Focused Ion Beam (FIB) cross-sectioning (Fig.1) verified that the crack plane followed a {111} plane within each grain in these alloys. The twist angle (α) between two crack planes across a grain boundary was the key parameter controlling the resistance of the boundary to crack growth. The resistance was experimentally determined to be a Weibull function of α (Fig.2). By reconstructing a digital microstructure from EBSD measurement, the microstructure-based model was used to simulate the crack propagation behaviors in 3-D in an Al-Li alloy (Fig.3). The simulated da/dN curve was in good agreement with the experimentally measured one. It could statistically predict short fatigue crack growth behaviors in alloys with different grain sizes and textures (Fig.4). It was found that there were two characteristic peaks in the simulated life spectra, and the shorter-life peak was always associated with a smaller α angle at the very first grain boundary that the short crack encountered, while the longer-life peak was related to a larger α angle at the first grain boundary. The model could also quantitatively predict the life of a short crack in terms of the grain size in the alloys (Fig. 4(d)).

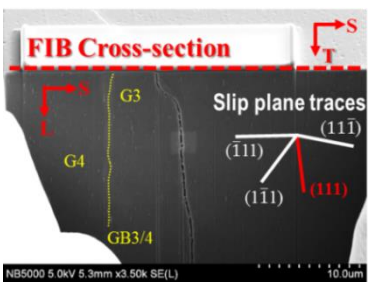


Fig.1 FIB cross-section for determination of twist angle.

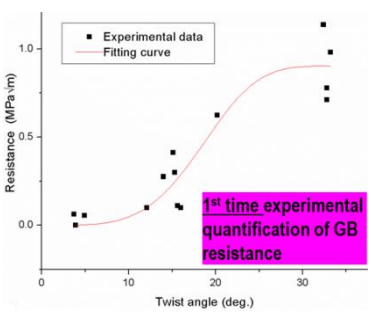


Fig. 2 The first time experimental quantification of GB resistance as.

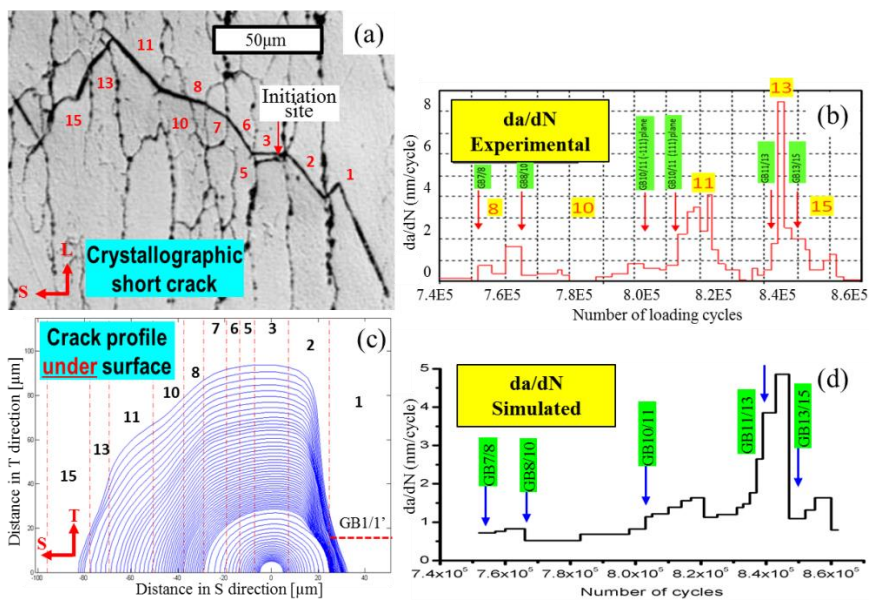


Fig.3 Comparison between experimental and simulated results for Al-Li 8090 alloy. (a) Crystallographic short fatigue crack observed on sample surface, and (b) experimentally measured da/dN curve. (c) Simulated crack profile under surface in the reconstructed grains, and (d) simulated crack growth rate.

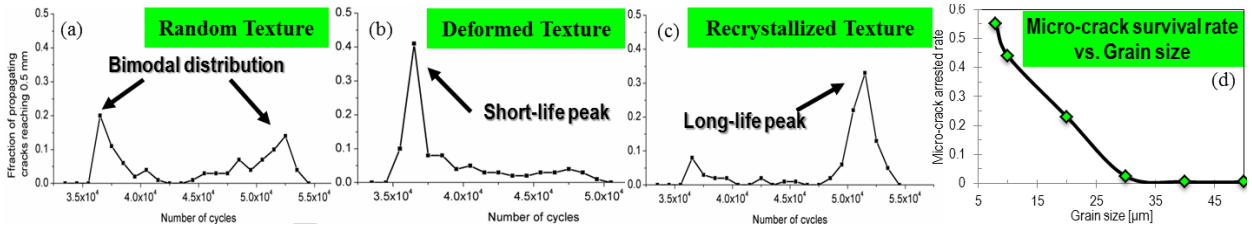


Fig.4 Simulated short fatigue life distribution under (a) random, (b) deformed and (c) recrystallized texture. And (d) Micro-crack arrested rate under different grain sizes.

Using *in situ* microscopy and spectroscopy to link synthesis and self-assembly with plasmon coupling in ordered metal nanoparticle heterostructures

Yao-Jen Chang[1], Bethany M. Hudak[1], Taha Rostamzadeh[2], John B. Wiley[2], Nicholas A. Merill[3], Marc R. Knecht[3], Raymond R. Unocic[4], and Beth S. Guiton[1,4]

[1]Department of Chemistry, University of Kentucky, Lexington, KY 40506
[2] Department of Chemistry and Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana 70148
[3]Department of Chemistry, University of Miami, Coral Gables, FL 33146
[4]Materials Science and Technology Division, Oak Ridge National Lab, Oak Ridge, TN 37831

The localized surface plasmon resonance (LSPR) is the collective oscillation of conduction electrons on the surface of a metallic nanostructure, and is known to depend on the shape, size, and surrounding environment of the nanostructure. The plasmonic characteristics can further be manipulated when multiple similar nanoparticles are organized in an ordered array, such that coupling may occur, resulting in additional and tunable LSPR modes, and the ability to direct and even propagate electromagnetic radiation. These tunable characteristics have the potential for a wide range of energy and optical applications. Though noble metal particles arranged on a surface, with coupling propagated through a vacuum, have been widely investigated, less attention has been focused by the plasmonics community on metal particles embedded within a solid matrix; embedded particles have several potential advantages, however, such as the ability to develop spontaneously as part of the synthetic process, and the versatility of a variety of dielectric environments which further act to protect the particles. We are investigating several composite systems in which noble metal nanoparticles assemble as part of the synthesis process, including Au and Ag particles encased in hexaniobate scrolls, and Au particles embedded in metal oxide nanowires, using *in situ* liquid cell and heating experiments in the transmission electron microscope, *in situ* helium ion microscopy, and low energy electron energy loss spectroscopy, to elucidate the relationship between the synthetic processes and the resulting plasmonic coupling.

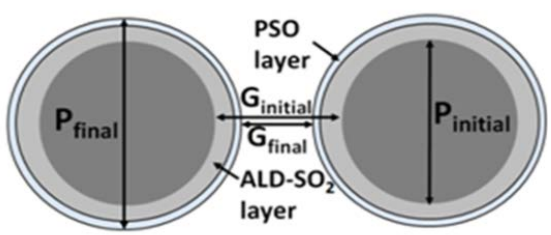
Manipulating inter pillar gap in pillar array ultra-thin layer planar chromatography platforms

Nichole A. Crane, Nickolay V. Lavrik, Michael J. Sepaniak

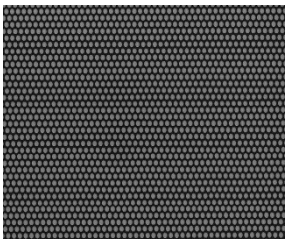
Abstract

An advantage of separation platforms based on engineered deterministic micro- and nano-fabrication, relative to traditional systems based on packed beds of particles, is exquisite control of all morphological parameters. For example, with planar platforms based on lithographically - prepared pillar arrays the size, shape, height, geometric arrangement, and inter-pillar gap can be independently adjusted. The permeability of these arrays relative to packed beds results in faster flow and hence better efficiency. Since inter-pillar gap is expected to be important in determining both resistance to mass transfer in the mobile phase as well as flow rate, which influences that mass transfer effect as well, we study herein the effect of reducing inter pillar gaps on flow and band dispersion. Atomic layer deposition is used to narrow the gap between the pillars for photo-lithographically defined and reactive ion etch prepared pillar arrays. The gap-adjusted arrays are both modeled and experimentally evaluated. The modeled data indicates that the smallest inter-pillar gap distance will yield a minimized plate height whereas the experimental data concludes that the larger inter-pillar gap and the smaller diameter pillar scenarios cause diminished plate height.

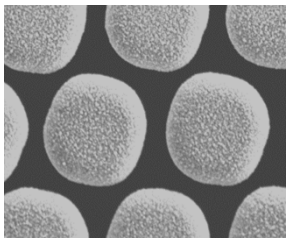
Stages of Depositions on Pillar Arrays



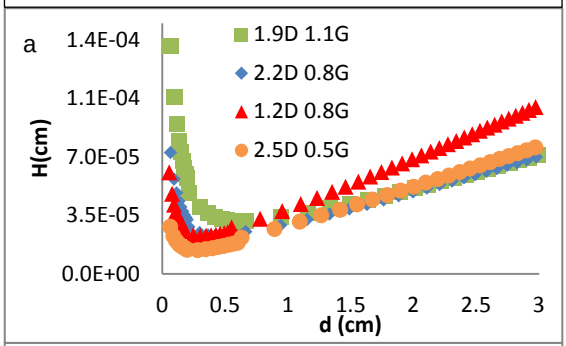
1.1µm Gaps Pillar Array

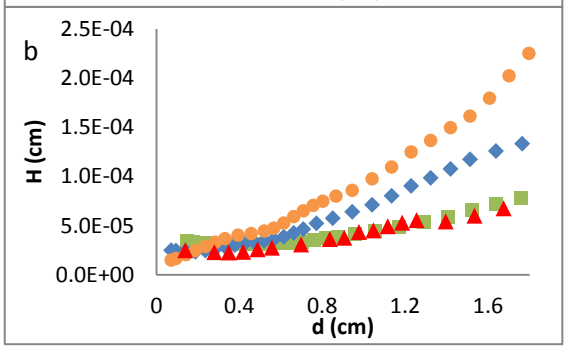


0.5µm Gaps Magnified



Modeled (a) and Experimental (b) van Deemter Curves for Acetonitrile





Plasmonic Behavior and Optical Transmission of Silver-Cobalt Thin Film Hole Arrays

A. E. Farah[1], R. Davidson[2], B. Lawrie[2], R. Pooser[2], R. Kalyanaraman[1]
[1]University of Tennessee; [2]Oak Ridge National Laboratory

Metallic nanostructures with subwavelength hole arrays made from plasmonic metals like silver (Ag) exhibit useful extraordinary optical transmission (EOT) that can be used for chemical sensing and biodetection. However, the degradation of Ag due to oxidation and diffusion limits its use in actual devices. We fabricated various multilayered EOT films consisting of Ag with ultrathin cobalt (Co) layers and characterized their morphology and broadband optical behaviors over extended time periods. Devices made with Ag/Co showed significantly enhanced optical stability over pure Ag devices. The likely mechanisms for this performance improvement will be discussed in the context of oxidation suppression and reduced atomic mobility. The reduced oxidation rate will enable more accessible, long term use of Ag-based films for sensing, which are desirable for their large plasmonic response in the visible and NIR regions, leading to higher sensitivities.

Engineered Exciton Localization in Colloidal Cadmium Chalcogenide Quantum Well Heterostructures

Qiuyang Li, Kaifeng Wu, Tianquan Lian

Abstract

CdSe/CdS or CdSe/CdTe core/crown (CC) NSs, where CdSe NSs are extended laterally by CdS(CdTe) crowns with exactly the same amount of monolayers, represent a type of heterostructure where exciton localization can be engineered. Due to its type-I (CdSe/CdS) and type-II (CdSe/CdTe) band alignment, electron and hole excited states are confined and then emit in the CdSe core (type-I) or the interface between core and crown (type-II). Compared with 1D CdSe/CdS heteronanorods, 2D core/crown NSs have the zinc blend NSs are terminated by Cadmium atoms which might eliminate hole trapping states. Moreover, due to absence of energetic disorder, exciton transport might be fast enough to compete with, if there are, exciton trapping processes. Therefore, investigating the efficiency and rates of exciton localization process in CC NSs is the prerequisite for implementing these materials into light-driven solar concentrator.

An iron oxide based transparent amorphous semiconductor with extraordinary electronic conductivity and mobility

A. Malasi,[1] H.Taz,[2] A. Farah,[3] M. Patel,[3] B. Lawrie,[4] R. Pooser,[4] A. Baddorf,[5,6] G. Duscher,[3,6] and R. Kalyanaraman[1,2,3]

[1]Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee, 37996, USA
[2]Bredesen Center, University of Tennessee, Knoxville, Tennessee 37996, USA

[3]Department of Material Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA
[4]Quantum Information Science Group, Computational Sciences and Engineering Divison, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[5]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[6]Material Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Iron oxide is one of the most abundant naturally occurring minerals on earth and hematite (α-Fe_2O_3), has been extensively investigated for semiconductor applications. But it is an extremely poor electrical conductor and despite several advances, including epitaxial film growth, the highest reported Hall mobility of hematite is still very low, at $\leq$ 0.6 cm^2/V-s for Ti-doped material. Here we report *amorphous* films made by pulsed laser deposition at room temperature and containing primarily iron oxide along with a novel combination of heavy metal dopants show extraordinary room temperature conductivity > 5×10^4 S/m, regular Hall mobility > 30 cm^2/V-s and extremely high optical transparency (>90%). This emerging new oxide material has potential for applications as a transparent conducting oxide, and/or as a thin film transistor material for solar cells, touch screens, flat panel displays and flexible electronics.

Crowding α-Hemolysin in a Functional Model Membrane

Bill McClintic,[1] Pat Collier[2]
[1]*University of Tennessee;* [2]*Oak Ridge National Laboratory*

Organization is crucial for cellular processes. The cell crowds, confines, and clusters molecules so that order can be established and function can be achieved. One phenomenon shown to give organization to cells is membrane domains: a piece of the cell membrane with differing geometry and structure that aids the cell in performing a task. Higher levels of membrane packing can control protein function by changing the environment. In fact, we want to study pore-forming protein, α-hemolysin, interacting with bilayer domains in a DOPC/DPhPC/cholesterol lipid mixture. The goal is to investigate if the proteins are motivated to leave the membrane, insert into the membrane, change structure, combine with one another, or alter the rate of blocking from the blocker molecule β-cyclodextrin. All-the-while, the activity of the system can be monitored with electrical measurements and with total internal reflection microscopy (TIRFM). A model membrane system called a droplet on hydrogel bilayer (DHB) will be used.

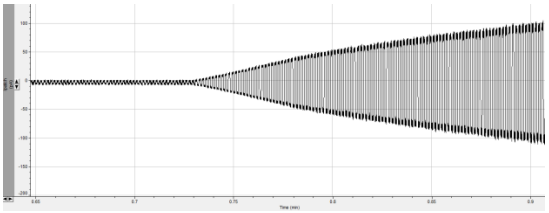


Figure 1 Capacitive Currents Reveal Information about the Bilayer.
In order to detect the presence of a bilayer, the bilayer is assumed to have electrical properties like that of a capacitor. A waveform is sent to the lipid bilayer and a response waveform is recorded. In the figure we see the response of the lipid bilayer to a ten hertz, ten millivolt triangle wave. The bilayer transforms this signal into a square wave as seen in the figure. This square wave tells us a bilayer is present.

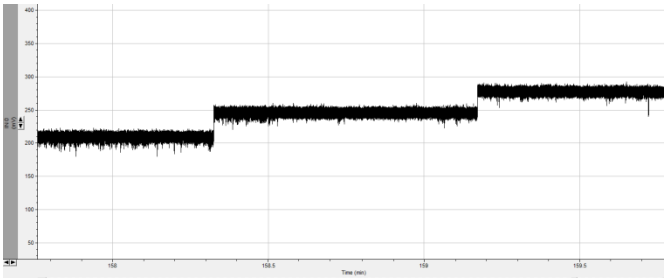


Figure 2 α-Hemolysin Signature Step-up in Overall Current Over the Lipid Bilayer.
When the pore-forming protein α-hemolysin encounters a lipid bilayer, the protein can achieve a lower energetic state by inserting itself into the bilayer. Insertion forms a pore, allowing increased conductivity of the bilayer. Individual α-hemolysin insertion events are seen in the figure as stair steps when examining current over the whole bilayer. A total of three α-hemolysin protein insertion events are shown in the figure.

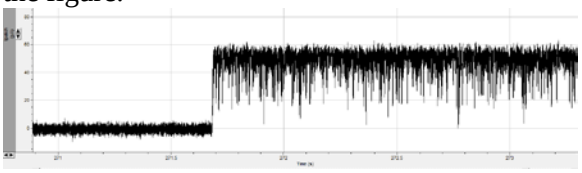


Figure 1 α-hemolysin and β-cyclodextrin Binding Kinetics.
The quick spikes downward indicate the quick block of α-hemolysin by β-cyclodextrin.

Diffusional Response of Layer-by-Layer Assembled Polyelectrolyte Chains to Salt Annealing

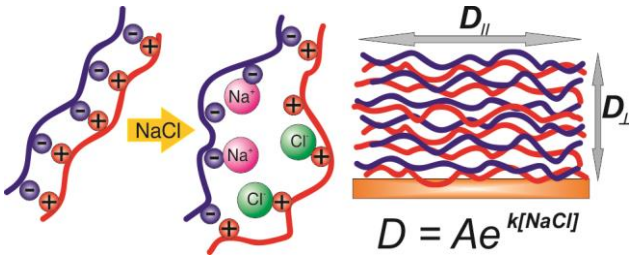
Victor Selin[1], John F. Ankner[2], Svetlana A. Sukhishvili[1]

[1]*Department of Materials Science & Engineering, Texas A&M University, College Station, TX 77843, USA*

[2]*Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

Abstract

We report on the effect of salt on diffusion of polyelectrolyte (PE) chains within electrostatically assembled polyelectrolyte multilayers. Layer-by-layer (LbL) films were assembled using poly(methacrylic acid) (PMAA) as a polyanion and quaternized poly-2-(dimethylamino)ethyl methacrylate as a polycation. Fluorescence recovery after photobleaching and neutron reflectometry were used to monitor the center-of-mass diffusion of PMAA chains in directions parallel and perpendicular to the substrate ($D_{//}$ and $D_{\perp}$, respectively). Film intermixing and polymer chain diffusion in the direction perpendicular to the substrate exhibits an unusual dependence on the PMAA molecular weight, with dramatically stronger diffusional response to salt annealing for the films formed by PMAA with the lowest molecular weight of 7 kDa. Films assembled with this lowest-molecular weight PMAA reveal that both diffusion coefficients of PMAA chains ($D_{//}$ and $D_{\perp}$) depend exponentially on the concentration of salt in the annealing solutions, with much faster diffusion in the direction parallel to the substrate.

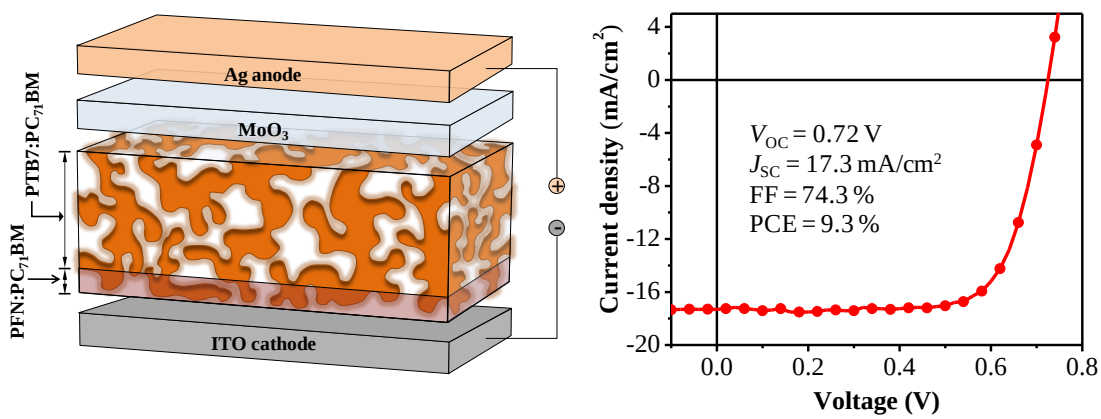


Correlating High Power Conversion Efficiency of Inverted Organic Solar Cells to Nanoscale Structure

Sanjib Das,[a] Jong Keum,[*b,c] James Browning,[c] Gong Gu,[a] Bin Yang,[b] Ondrej Dyck,[d] Changwoo Do,[c] Jihua Chen,[b] Ilia N. Ivanov,[b] Kunlun Hong,[b] Adam J. Rondinone,[b] Pooran C. Joshi,[e] David B. Geohegan,[b] Gerd Duscher,[d] Kai Xiao[*b] *; E-mail: keumjk@ornl.gov and xiaok@ornl.gov

[a]Department of Electrical Engineering and Computer Science, University of Tennessee. [b]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory (ORNL). [c]Neutron Sciences Directorate, ORNL. [d]Department of Materials Science and Engineering, University of Tennessee. [e]Materials Science and Technology Division, ORNL.

Advances in materials design and device engineering led to inverted organic solar cells (i-OSCs) with superior power conversion efficiencies (PCEs) to their "conventional" counterparts, in addition to the well-known better ambient stability. Here, we report an in-depth morphology study of the i-OSC active and cathode modifying layers, employing a model system with the well-established bulk-heterojunction, PTB7:$PC_{71}BM$ as the active layer and poly-[(9,9-bis(3′-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) as the cathode surface modifying layer. We have also identified the role of a processing additive, 1,8-diiodooctane (DIO), used in the spin-casting of the active layer to increase PCE. Using various characterization techniques such as transmission electron microscopy, neutron reflectometry and grazing incidence wide-angle scattering, we demonstrate that the high PCEs of i-OSCs are due to the diffusion of electron-accepting $PC_{71}BM$ into the PFN layer, resulting in improved electron transport. The diffusion occurs when residual solvent molecules in the spun-cast film act as a plasticizer. Addition of DIO to the casting solution results in more $PC_{71}BM$ diffusion and therefore more efficient electron transport. This work provides important insight and guidance to further enhancement of i-OSC performance by materials and interface engineering.[1]



[This research was 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, U.S. Department of Energy]

1. **S. Das** *et al.*, Correlating High Power Conversion Efficiency of PTB7:$PC_{71}BM$ Inverted Organic Solar Cells to Nanoscale Structure, *Nanoscale* 2015, Accepted.

Intermetallic Alloys Facing Functional Oxides: An Emerging Opportunity for Multiferroics

Zhiqi Liu

CNMS

Multiferroic heterostructures consisting of magnetic intermetallic alloys and functional oxides emerge as highly promising candidates for giant magnetoelectric coupling and low energy-consuming information storage devices. In this talk, I would introduce the epitaxial integration of intermetallic alloys on functional oxides, electrical and magnetic property studies of intermetallic films and especially the electric control of magnetic phase in such multiferroic heterostructures, which has enabled us to achieve a giant electroresistance effect in the metallic alloy, potential for non-volatile resistor memory devices.

Biosensing and Optical Modulation on a Silicon Platform

K. J. Miller, G. A. Rodriguez, Y. Zhao, P. Markov, S. Hu, R. E. Marvel, R. F. Haglund, & S. M. Weiss, Vanderbilt University

The realization of novel photonic structures has been possible via the combination of world-class fabrication capabilities at the CNMS and unique materials systems developed by the Weiss Group at Vanderbilt. These include (i) porous silicon (PSi) structures for biosensing and (ii) silicon – vanadium dioxide (VO_2) hybrid structures for on-chip optical modulation.

I. Biosensing using Porous Silicon (PSi)

PSi is a promising materials platform for biosensing due to its large internal surface area that can accommodate the infiltration of biological and chemical molecules and therefore enable significant interaction between molecules and the electromagnetic field inside the pores. Here, we present two PSi structures: a PSi ring resonator and a flow-through PSi membrane. For a PSi ring resonator of 25 µm radius, we measure a Q-factor of nearly 10,000, bulk detection sensitivity near 380 nm/RIU, and surface sensitivity near 4 pm/nM for nucleic acid detection. Additionally, biosensing experiments with streptavidin demonstrate that the response time of our flow-through PSi membrane sensor is reduced six times as compared to a conventional flow-over PSi sensor.

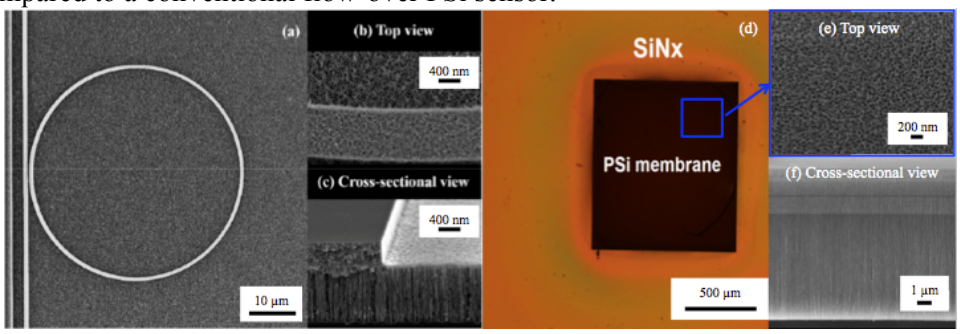


Figure 1. SEM and optical microscope images. (a) PSi ring resonator [1]. (b) Top view porosity profile of the waveguide (small pores) and cladding (large pores) layers. (c) Cross section of the waveguide. (d) Top view of PSi flow-through membrane. (e) Top view porosity profile. (f) Cross section of the membrane showing the PSi microcavity.

II. Silicon – Vanadium Dioxide (VO_2) Electrooptic Modulator

Small footprint devices that can consume lower power and achieve light modulation on THz speeds are necessary for the advancement of on-chip photonics. We present small footprint electrooptic modulators using a hybrid Si-VO_2 materials system. In a linear geometry, we have observed 5 dB modulation in response to a 100 ns electrical pulse and 1 dB modulation in response to a 10 ns electrical pulse. Currently, we are exploring resonator geometries to improve modulation depths so that faster switching speeds can be explored using this hybrid materials system.

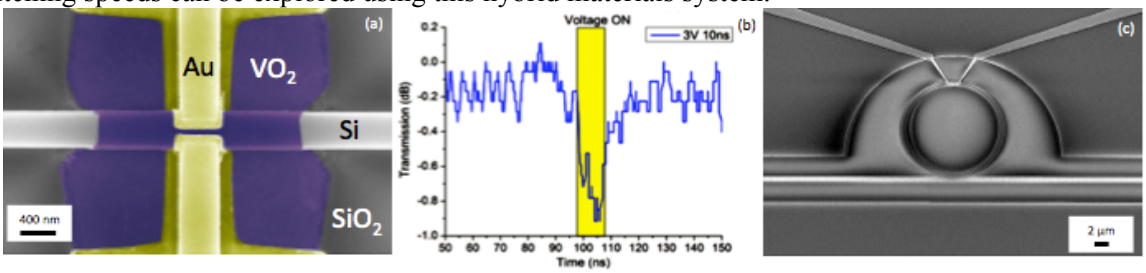


Figure 2. (a) False color SEM image of Si-VO_2 linear absorption modulator. (b) Optical transmission of linear absorption modulator in response to a 10 ns electrical pulse. (c) SEM image of fully fabricated Si-VO_2 ring resonator modulator with electrical contacts.

[1] G.A. Rodriguez, S. Hu, S.M. Weiss, Optics Express, 23 (2015) 7111-7119.

Multimodal PEDOT:PSS/QCM-Based Humidity and Pressure Sensor Using Artificial Neural Network

Eric Muckley[1, 2], James Lynch[2] and Ilia Ivanov[2]

[1]Bredesen Center, University of Tennessee, Knoxville, TN 37996
[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

The growing ubiquity of environmental sensing has increased demand for low cost gas/vapor sensors with low power requirements[1–3]. Quartz crystal microbal- ance (QCM)-based gas sensors have been studied extensively[4–7], but these devices generally lack the ability to deconvolve analyte response from quartz piezoelectric pressure response. Deconvolution of sensor response is critical for the improvement of selectivity in relative humidity (RH) sensors, as commercial RH sensors often show response to multiple gases, pressure, and temperature changes[8–10]. A room-temperature multimodal sensor composed of PEDOT:PSS solution deposited on a quartz crystal microbalance (QCM) crystal has been fabricated. We demonstrate the possibility of using an artificial neural network (ANN) for deconvolution of the PEDOT:PSS/QCM resistive humidity response from the frequency-based pressure response, which allows the single sensor to act both as a relative humidity (RH) sensor and a pressure sensor. The sensor has a resolution of <20% RH between 0 and 100% RH and generates numerical estimates of both RH and ambient pressure using only two electrodes. It is expected that upon further optimization of the ANN training set and neuron configuration the sensor accuracy and resolution will be improved. The multimodal sensor shows promise for use in low cost environmental sensing applications which require small size and low power consumption.

Acknowledgement:
This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. JL acknowledges financial support from the Science Undergraduate Laboratory Internship (SULI). The samples were provided by Siddharth Pradhan (University of Tennessee, Knoxville).

1 H. Farahani, R. Wagiran, and M. N. Hamidon, “Humidity sensors principle, mechanism, and fabrication technologies: A comprehensive review,” Sensors 14, 7881–7939 (2014).
2 Z. Chen and C. Lu, “Humidity sensors: a review of materials and mechanisms,” Sensor letters 3, 274–295 (2005).
3 O. K. Varghese and C. A. Grimes, “Metal oxide nanoarchitectures for environmental sensing,” Journal of Nanoscience and Nanotechnology 3, 277–293 (2003).
4 F. Pascal-Delannoy, B. Sorli, and A. Boyer, “Quartz crystal microbalance (QCM) used as humidity sensor,” Sensors and Actuators A: Physical 84, 285–291 (2000).
5 N. Horzum, D. Tascioglu, C. Ozbek, S. Okur, and M. M. Demir, “VOC sensors based on a metal oxide nanofibrous membrane/QCM system prepared by electrospinning," New Journal of Chemistry 38, 5761{5768 (2014).
6. B. Ding, J. Kim, Y. Miyazaki, and S. Shiratori, Electrospun nanofibrous membranes coated quartz crystal microbalance as gas sensor for NH3 detection," Sensors and Actuators B: Chemical 101, 373{380 (2004).
7.J. Hu, F. Zhu, J. Zhang, and H. Gong, A room temperature indium tin oxide/quartz crystal microbalance gas sensor for nitric oxide," Sensors and Actuators B: Chemical 93, 175{180 (2003).
8.N. Han, Y. Tian, X. Wu, and Y. Chen, Improving humidity selectivity in formaldehyde gas sensing by a two-sensor array made of Ga-doped ZnO," Sensors and Actuators B: Chemical 138, 228 235 (2009).
9.H. Shurmer, J. Gardner, and H. Chan, “The application of discrimination technique to alcohols and tobaccos using tin-oxide sensors," Sensors and Actuators 18, 361{371 (1989).
10.H. Inc.,” A Comparison of Relative Humidity Sensing Technologies”, Applications Note 2004-2 (2004).

Helium Ion Induced Patterning of sub-10 nm Structures in Liquid Cell

Nathan Philip[3], Vighter Iberi[1,2], Ray Unocic[1,4], Adam J. Rondinone[1], David C. Joy[1,2], Alex Belianinov[1,4], Olga S. Ovchinnikova[1,4]

[1.] Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA, [2.] Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA, [3.] Bredesen Center, University of Tennessee, Knoxville, TN 37996, USA, [4.] The Institute for Functional Imaging of Materials and the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TM 37831, USA.

The reduction in nanostructure size while maintaining high veracity is essential for progression in many areas of nanofabrication research such as the development of semiconductors. While electron-beam lithography is capable of sub-10nm direct write resolution on solid resists in two dimensions, fundamental interactions such as transport limitations of solvated electrons and ionic species, as well as contamination confine patterning in liquids to the micron scale. However, a helium ion beam – with an opposite charge and shorter mean free path than an electron beam – provides appropriate conditions to reduce the volume of the reaction environment, allowing for direct write of structures in liquids on a single digit nanometer scale while maintaining structure purity. We demonstrate *in situ* helium ion induced patterning in a platinum chloride solution with sub-10nm resolution. The essential characteristics of the induced platinum growth are analytically extracted from the *in situ* platinum growth movies using in-house developed software, available to CNMS users. We investigate suggested mechanisms for beam induced growth and reduction of the interaction zone by relating the optimal beam parameters to structure synthesis. Tuning parameters are discussed in an effort to define the implications of direct writing in minute domains and opportunities to further decrease structure size, as well as provide an avenue toward three dimensional nanofabrication.

Acknowledgements

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

Nanoscale Characterization of Zinc Electrodeposition using in situ electrochemical STEM

Reed M. Wittman[1,2], Raymond R. Unocic[3], Thomas A. Zawodzinski[2,4]

[1]Bredesen Center, Energy Science and Engineering Department, University of Tennessee – Knoxville, TN; [2]Physical Chemistry of Materials Group, Oak Ridge National Laboratory, Oak Ridge; [3]Microscopy Group,CNMS, Oak Ridge National Laboratory, Oak Ridge; [4] Chemical and Biomolecular Engineering Department, University of Tennessee – Knoxville, TN

Secondary zinc-air batteries are a promising technology for portable and large scale energy storage systems. Their major advantage over standard Li-ion batteries is that Zn-air batteries have a much higher energy density making them ideal for transportation applications. The formation of dendrites on the Zn anode during electrochemical cycling, has been a major issue for their development which has been shown to result in loss of capacity, low columbic efficiency, and overall loss in device functionality when the cell short-circuits [1, 2]. Efforts to inhibit dendritic growth are hindered by a lack in understanding of why dendrites form during Zn deposition on a fundamental level [3]. In situ electrochemical STEM characterization can directly observe the physical phenomenon that occurs on the nanoscale level as the result of an electrochemical process while simultaneously gathering relevant electrochemical data to the phenomenon [4-8]. Here, in situ electrochemical STEM studies were conducted to directly observe and study the mechanisms of dendrite growth and formation during electrodeposition, figure 1 shows an example of Zn deposits produced using in situ electrochemical STEM. These studies were coupled with COMSOL modeling to better understand cell behavior such as global and local overpotential changes, solute concentration, and current distributions. Ex situ experiments corresponding to in situ experiments were done to confirm the results seen in situ. The results of this study have helped to further elucidate the growth mechanisms of Zn during deposition and created a framework for future studies on nucleation and growth of Zn in aqueous solutions.

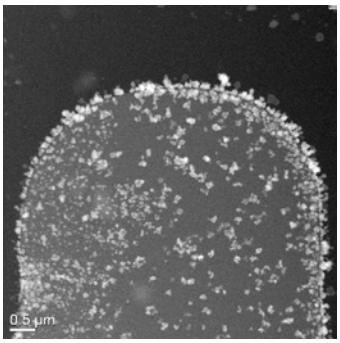


Figure 1: Zn deposited onto a Ti working electrode during an in situ electrochemical STEM experiment

References:

1. Rahman, M.A., X.J. Wang, and C.E. Wen, *High Energy Density Metal-Air Batteries: A Review.* Journal of the Electrochemical Society, 2013. **160**(10): p. A1759-A1771.
2. Lee, J.S., et al., *Metal-Air Batteries with High Energy Density: Li-Air versus Zn-Air.* Advanced Energy Materials, 2011. **1**(1): p. 34-50.
3. Li, Y. and H. Dai, *Recent advances in zinc-air batteries.* Chem Soc Rev, 2014. **43**(15): p. 5257-75.
4. Radisic, A., et al., *The morphology and nucleation kinetics of copper islands during electrodeposition.* Surface Science, 2006. **600**(9): p. 1817-1826.
5. Radisic, A., F.M. Ross, and P.C. Searson, *In situ study of the growth kinetics of individual island electrodeposition of copper.* J Phys Chem B, 2006. **110**(15): p. 7862-8.
6. Unocic, R.R., et al., *Quantitative electrochemical measurements using in situ ec-S/TEM devices.* Microsc Microanal, 2014. **20**(2): p. 452-61.
7. White, E.R., et al., *In situ transmission electron microscopy of lead dendrites and lead ions in aqueous solution.* ACS Nano, 2012. **6**(7): p. 6308-17.
8. Sun, M., et al., *Structural and morphological evolution of lead dendrites during electrochemical migration.* Sci Rep, 2013. **3**: p. 3227.

Exploring a Simple Synthetic Route to Metal Oxide Nanowires with the Spinel Crystal Structure

Lei Yu,[1] Amita Patel,[1] Yan Zhang,[1] Bethany M. Hudak,[1] Damon K.Wallace,[1] Doo Young Kim,[1] and Beth S. Guiton*[1,2]

[1]Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, USA.

[2]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA.

Oxides with the spinel crystal structure are of interest for a wide range of applications such as catalysts for oxidation and reduction reactions, and battery materials, due to the versatility of the spinel-type crystal structure with its many interstices, and for its ability to accommodate transition metal cations which display multiple oxidation states. Nano-sized spinels are especially desirable since they have large surface-to-volume ratios advantageous for catalytic properties, and can display size and shape confinement of properties such as magnetism. Though some reports exist on the synthesis of spinels with nanoparticle morphology, synthesizing these compounds as an anisotropic nanorod or nanowire is still challenging for many compositions. Here, we report a simple and versatile route to synthesize single-crystalline spinel nanowires with a range of compositions including Mg_2MnO_4, $CuMn_2O_4$, and several Fe and Mg oxide stoichiometries, *via* the solid-state reaction of M'OOH nanowire precursors with metal oxides or hydroxides. These wires are of interest both for their electrochemical catalytic activity, and for their magnetic properties. Particularly remarkable is the retention of nanowire morphology during this reaction, given the structural difference between the M'OOH nanowire precursors, and the resulting spinel. To further understand the reaction mechanism, we performed *in situ* heating experiments in the transmission electron microscope (TEM), in which we place metal hydroxide powders and M'OOH reactant crystals in contact with each other on a TEM heating substrate, and observe the solid-state reaction directly as it progresses. As the temperature is ramped, a single-crystalline to polycrystalline to single-crystalline structural progression is observed within an individual γ-MnOOH nanowire, and the wire is seen to develop a measureable magnesium content *via* contemporaneous spectroscopic measurements. We speculate that magnesium diffusion into, and subsequent reaction with, the γ-MnOOH wire may be aided by the transient nanocrystalline grain boundary formation. Further investigations of the reaction using this *in situ* approach, as well as electrochemical catalytic and magnetic characterization are ongoing.

Direct Observation of Phase Transformations in Individual Hafnia Nanorods

B. M. Hudak,[1] S. W. Depner,[2] G. Waetzig,[3] S. Banerjee[3], B. S. Guiton,[1,4]

[1]*Department of Chemistry, University of Kentucky, Lexington, KY 40506*
[2]*DEMIEN LLC, Amhurst, NY 14228*
[3]*Department of Chemistry, Texas A&M University, College Station, TX 77842*
[4]*Materials Science and Technology Division, Oak Ridge National Lab, Oak Ridge, TN 37831*

Hafnia is a wide band-gap and high dielectric constant material that is thermally stable on Si substrates, making it an attractive candidate to replace SiO_2 as a gate dielectric material. The tetragonal phase of hafnia, occurring at 1720°C, is desired for device application due to its larger band gap and high permittivity in comparison to the monoclinic phase. However, in bulk, the tetragonal phase of HfO_2 cannot be quenched to room temperature. It has been shown that below a critical size of about 15-30 nm, the tetragonal phase of ZnO_2 – an isomorph of HfO_2 – can be stabilized with respect to the monoclinic phase. It is estimated, though, that the critical size for stabilization of the HfO_2 tetragonal phase is sub-10 nm, and it is therefore much more difficult to stabilize than the tetragonal phase of ZnO_2. Since the tetragonal phase of HfO_2 is more important for technological applications than the monoclinic phase, finding a way to induce the stable, tetragonal phase of HfO_2 at low temperature is of utmost importance. In this research, we utilize *in situ* heating to observe phase transformation on the atomic scale to gain insight into factors crucial to stabilizing a low-temperature, tetragonal phase of hafnia.

High aspect ratio, monoclinic HfO_2 nanorods are grown *via* a nonhydrolytic sol-gel synthesis with tri-n-octylphosphine oxide (TOPO) as the coordinating solvent and passivating ligand. When heated *in situ* in a scanning transmission electron microscope (STEM) we can observe atomic-scale transformation from the monoclinic phase to the tetragonal phase, and upon slow cooling we observe reduction of the HfO_2 nanorods to hafnium metal nanorods. This later transformation is likely due to the low oxygen environment of the STEM column. Using these *in situ* techniques, we are able to study this transformation mechanism in real time and with single-atom resolution, providing fundamental insight into the atomic pathways of classical Martensitic processes. This is the first step to stabilizing tetragonal HfO_2 nanocrystals.

Characterization of Dynamic Materials Interfaces in Electrochemical Energy Systems

Matthew T. McDowell
Assistant Professor
Georgia Tech

The chemical, structural, and mechanical characteristics of interfaces play a major role in determining the behavior of electrochemical systems. In novel materials for electrochemical energy storage and conversion, dynamic processes at internal solid-solid interfaces, as well as at the solid-electrolyte interface, must be understood and controlled for optimal performance. In this presentation, our work on understanding interfaces will be presented in the context two different systems, batteries and solar fuels devices. New materials for lithium- and sodium-ion batteries offer improved charge storage capacity, but cycle life is often limited because of reaction-induced volume changes and mechanical degradation. Here, *in situ* transmission electron microscopy (TEM) of the reaction of lithium with single battery nanostructures reveals nanoscale transformation pathways and kinetics in next-generation materials, including silicon and metal sulfides. The results show that mechanical stresses evolved during the electrochemical transformation can have a controlling effect on the kinetics of the reaction, and that interparticle interactions can significantly influence cycling behavior. Next, in photoelectrochemical systems for converting sunlight into fuels, the solid/electrolyte interface at a semiconductor electrode is highly susceptible to photocorrosion, which often prevents long-term operation. Metal oxide overlayers of varying thickness and with controlled electronic properties are shown to effectively protect a number of moderate band gap semiconductors from photocorrosion while also allowing for facile carrier transport, thus enabling stable and efficient photo-driven water oxidation. Pathways towards characterizing and understanding these stabilizing interfaces during operation will be presented. Together, these results demonstrate the importance of understanding and controlling interfaces in energy systems, and they are a step towards improved electrochemical devices.

Perovskite Solar Cells with Near 100% Internal Quantum Efficiency Based on Large Single Crystalline Grains and Vertical Bulk Heterojunctions

Bin Yang,[1] Ondrej Dyck,[2] Jonathan Poplawsky,[1] Jong Keum,[1] Alexander Puretzky,[1]

Sanjib Das,[3] Ilia Ivanov,[1] Christopher Rouleau,[1] Gerd Duscher,[2]

David Geohegan,[1] Kai Xiao[1]

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

2 Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN, 37996, USA.

3 Department of Electrical Engineering and Computer Science, University of Tennessee, Knoxville, TN, 37996, USA.

Grain boundary (GB) losses have plagued polycrystalline solar cells for several decades, where defects, traps as well as energetic disorder cause significant non-radiative recombination energy loss and strongly limit achievable device power conversion efficiencies (PCEs). This challenge now faces the new hybrid organic-inorganic halide-perovskite solar cells. To address this challenge, we developed a simple layer-by-layer fabrication process based on air-exposure followed by thermal annealing to grow a new type of microstructured thin film architecture containing large, vertically-oriented single-crystalline grains of perovskite and vertical GBs that extend through the entire thickness of the film. Cross-section transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) mapping clearly show that the hole-transport medium Spiro-OMeTAD organic material is then infiltrated into the GBs to form vertically-aligned bulk heterojunctions. Through state-of-the-art electron beam induced current (EBIC) imaging, we show the Spiro-OMeTAD channels activate the grain boundaries as efficient channels for carriers (holes), and also appear to aid in exciton dissociation and charge separation via space-charge fields. Active-GB solar cells yielded internal quantum efficiency of near 100%. The devices showed average PCE of 16.3 ± 0.9%, comparable to the best solution-processed perovskite devices, establishing them as important alternatives to growing ideal single crystal films in the pursuit toward theoretical maximum PCE with industrially realistic processing techniques.

[1] B. Yang et al., "Perovskite Solar Cells with Near 100% Internal Quantum Efficiency Based on Large Single Crystalline Grains and Vertical Bulk Heterojunctions." Journal of the American Chemical Society. accepted (2015).

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

Polymer Membranes for Large-Scale Energy Conversion and Storage

Michael A. Hickner
Center for Nanophase Materials Sciences
Oak Ridge National Laboratory

New polymer membranes are needed to advance energy storage and conversion technologies for distributed and grid-scale applications. We have recently demonstrated new ion-conducting polymer membranes that have achieved excellent performance and long-lifetime stability in vanadium redox flow batteries, a leading technology candidate for deployment in renewable power networks and grid-scale energy storage systems with sizes ranging from 10s to 100s of megawatts. By tuning the nanoscopic self-assembly of the ionic domains in the polymers, we are able to increase the cycle life of the device by impeding vanadium ion transport through the membrane while facilitating high conductivity in the electrolyte to maintain the battery current density. For instance, by decreasing the vanadium permeability of the membrane by a factor of two, we have been able to double the lifetime of the device, which provides significant life-cycle cost savings. We have also demonstrated membranes with nearly zero vanadium permeability that show 100 % coulombic efficiency in flow battery charge-discharge cycling tests. Currently, we are working on demonstrating these membranes over 100s of charge-discharge cycles.

We have also been involved in the search for fuel cell membranes that conduct protons with minimal amounts of added water. To achieve high proton conductivities, we have investigated superacidic polymers that contain perfluorinated sulfonic acid side chains attached to aromatic backbones. Superacids appear to be a key feature of high-performance proton exchange membranes and provide a pathway for scalable new materials based on random copolymers. This poster will show how polymers with new chemical structures can be applied to different types of electrochemical devices. Common design principles and considerations for fabricating new ion exchange membranes for energy processes will be demonstrated.

Charge transport and hydrogen-bonding in imidazole/carboxylic acid mixtures

Tyler Cosby,[1] Adam Holt,[2] Phillip Griffin,[3] Yangyang Wang[4], and Joshua Sangoro[1]

[1]University of Tennessee, Department of Chemical and Biomolecular Engineering, Knoxville, TN 37902
[2]University of Tennessee, Department of Physics and Astronomy, Knoxville, TN 37902
[3]University of Pennsylvania, Department of Material Science, Philadelphia, PA 19104
[4]Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Deep eutectic mixtures are receiving increased attention as potential materials for applications in chemical separation processes, drug delivery, solar cell electrolytes, supercapacitors, chemical sensors, and solvents for chemical synthesis.[1,3] These mixtures are formed by simple mixing of two chemicals capable of forming intermolecular hydrogen-bonds, which serve to disrupt the crystalline structure present in the parent materials. The full realization of the great potential of these materials requires a better understanding of the relationship between molecular structure, intermolecular interactions and mixture properties. As a step toward accomplishing this goal we have investigated mixtures formed between 2-ethyl-4-methylimidazole and levulinic acid over wide temperature and composition ranges by broadband dielectric spectroscopy, differential scanning calorimetry, rheology and dynamic light scattering. The influence of levulinic acid on the ionic conductivity, viscosity, charge transport and structural relaxation rates present in pure 2-ethyl-4-methylimidazole provides a better understanding of the origin of the unique properties of imidazole + acid-based deep eutectic mixtures.[2]

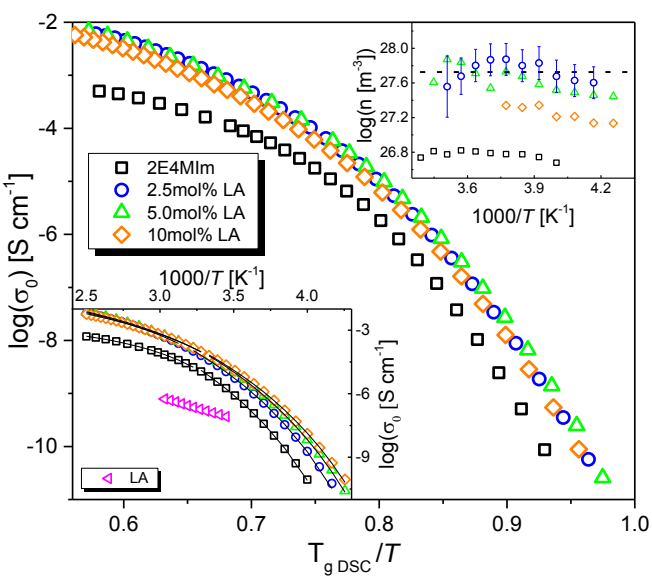


FIG. 1: DC conductivity of pure 2-ethyl-4-methylimidazole, 2.5mol%, 5.0mol%, and 10mol% LA mixtures plotted versus temperature normalized by the calorimetric glass transition temperature, T_g. The conductivity increases upon addition of very small amounts of acid and the offset of these DC conductivities when scaled by T_g indicates an increase in the effective number density of charge carriers upon addition of levulinic acid.

Inset Bottom: Temperature dependence of DC conductivity for 2E4MIm, levulinic acid, the 2.5mol% LA mixture, and the 5.0mol% LA mixture.

Inset Top: Estimate of the effective number density of charge carriers plotted versus 1000/*T*.

References:

(1) Ruß, C.; König, B., Low Melting Mixtures in Organic Synthesis – An Alternative to Ionic Liquids? *Green Chemistry* **2012,** *14* (11), 13.

(2) Griffin, P. J.; Cosby, T.; Holt, A. P.; Benson, R. S.; Sangoro, J. R., Charge Transport and Structural Dynamics in Carboxylic-Acid-Based Deep Eutectic Mixtures. *The Journal of Physical Chemistry. B* **2014,** *118* (31), 9378-85.

(3) Yasuda, T.; Watanabe, M., Protic Ionic Liquids: Fuel Cell Applications. *MRS Bulletin* **2013**, *38* (7), 6.

Charge transport and structural dynamics in ammonium based polymerized ionic liquids and their monomeric analogues

Maximilian Heres
University of Tennessee

Ionic conduction and structural dynamics in a series of ammonium based polymerized ionic liquids, and their monomeric analogues are investigated using broadband dielectric spectroscopy, temperature modulated differential scanning calorimetry and Rheology. The dielectric spectra are dominated in the low frequency regime by electrode polarization while hopping conduction is the underlying mechanism at higher frequencies in both polymerized and monomeric samples. In contrast to monomeric ionic liquids, polymerized ionic liquids show a strong decoupling of ionic conduction from structural relaxation [1]. At their respective calorimetric glass transition temperatures, the DC conductivity of polymerized ionic liquids exceed that of the monomeric ionic liquid by over five orders of magnitude. Furthermore, the polymerized ionic liquids show a strong correlation between the pendant group length and ionic conductivity [2]. These results are discussed within the recent approaches proposed to explain the decoupling of charge transport from structural dynamics.

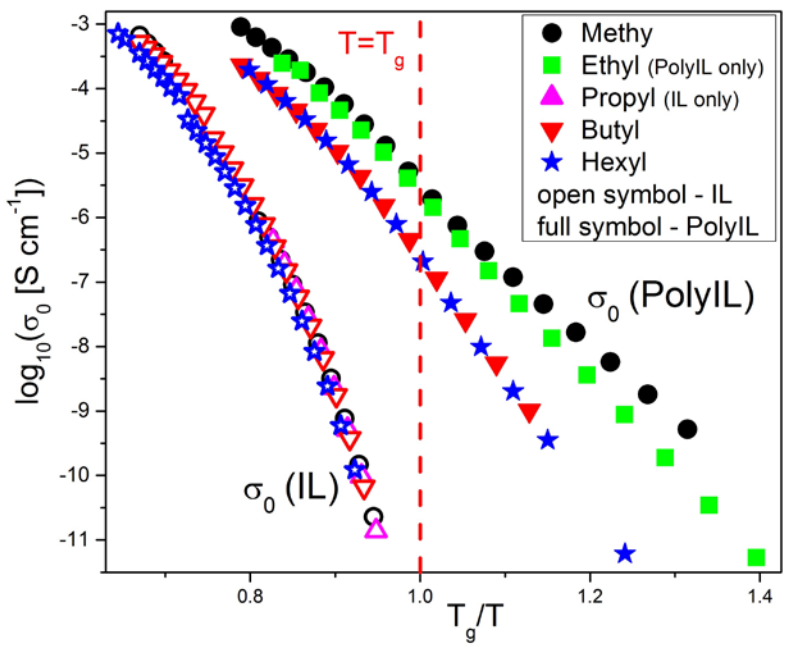


Figure 1: DC conductivity of a series of ammonium based monomeric and polymerized ionic liquids with respect to inverse temperature, normalized by the calorimetric glass transition (T_g).

1. (Mecerreyes 2011)Mecerreyes, D. (2011). "Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes." Progress in Polymer Science **36**(12): 1629-1648.
2. Sangoro, J. R., et al. (2014). "Decoupling of ionic conductivity from structural dynamics in polymerized ionic liquids." Soft Matter **10**(20): 3536-3540.

DESIGN OF A POLYMER THERMOELECTRIC GENERATOR USING RADIAL ARCHITECTURE

Akanksha K. Menon
G.W.W. School of Mechanical Engineering
Georgia institute of Technology
Atlanta, GA, USA
akm4@gatech.edu

Shannon K. Yee
G.W.W. School of Mechanical Engineering
Georgia institute of Technology
Atlanta, GA, USA
shannon.yee@me.gatech.edu

Thermoelectric generators (TEGs) are solid-state heat engines consisting of p-type and n-type semiconductors that convert heat into electricity via the Seebeck effect. The efficiency of these devices is dictated by the material figure-of-merit (zT) which requires a high electrical conductivity and thermopower, and a low thermal conductivity. The technology has been limited to niche applications owing to low efficiencies of conventional inorganic TE materials. Herein, we examine another class of materials, namely electrically conducting and metal-coordinated polymers for low-cost, large-scale applications. Polymers have several intrinsic advantages over their inorganic counterparts since they are abundant and flexible, can be solution processed thereby reducing manufacturing costs, and have an inherently low thermal conductivity. Furthermore, the transport properties in polymers can be tuned via doping strategies that are inaccessible to inorganic TEs. Inclusion of inorganic nanowires in a conducting polymer matrix further enhances the performance, as investigated in this work. Current examples of polymer TE devices have been limited to traditional flat-plate geometries with power densities on the $\mu W/cm^2$ scale, where their potential is not fully realized. Herein, we report a novel radial architecture and evaluate the improved performance of a polymer-based TEG. Our radial architecture accommodates a fluid as the heat source and can utilize natural convection alone (due to heat spreading) thereby forgoing heat exchanger costs. Analytical heat transfer models are presented that optimize the device to obtain high power densities of 1-3 mW/cm^2 using state-of-the-art polymer TEs (PEDOT:PSS and Poly[K_x(Ni-ett)]) subjected to a temperature difference of 100 K. This has implications beyond waste-heat recovery, towards wearable electronics (body heat-powered watch) and self-powered medical sensors.

Carbon Nanotube Based Dosimetry of Neutron and Gamma Radiation

Tony Nelson-PhD Candidate, Engineering Mechanics, Virginia Tech

Neutron and gamma dosimetry is important for a number of critical applications including reactor instrumentation, nuclear non-proliferation, and radiation safety for hazards associated with nuclear reactors, space travel, and neutron sources used in science and medicine. These fields could benefit greatly from an effective, robust, real-time dosimeter such as the one demonstrated in this project. Carbon nanotubes have unique electrical properties that are highly influenced by changes in their microstructure, such as those caused by neutron and gamma radiation exposure. It is this sensitivity that makes them so attractive for dosimetry applications. In addition to developing a novel radiation dosimeter, the effects of neutron bombardment on the microstructure and electrical properties of carbon nanotubes (CNTs) were examined in detail, contributing to a particularly under-investigated field. Furthermore, the effect of dopants such as water were investigated.

The device consists of a thin layer of randomly oriented high purity CNTs (fig. 1a) spanning the gap between copper electrodes on a fused silica substrate (fig. 1b). The electrical impedance was measured before and after exposure to gamma and neutron radiation in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Lab (ORNL). The resulting changes in the microstructure of the CNTs were investigated via micro Raman spectroscopy at the Center for Nanophase Materials Sciences (CNMS) at ORNL. The adsorption of water by the CNT networks, and the effects on the electrical properties, were examined in the environmental control chamber at CNMS.

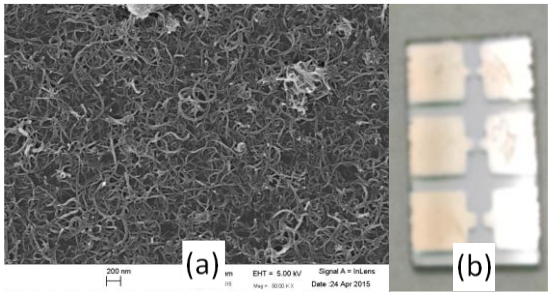


Figure 1: Random CNT network (a), and electrode pattern (b)

The devices showed a generally linear increase in electrical resistivity with increasing radiation dose (fig. 2a), indicating great promise for radiation dosimetry. Raman spectroscopy revealed that increasing radiation dose caused an increase in the D/G ratio (fig. 2b), which is a qualitative indicator of the extent of damage to the CNTs. This demonstrates that the increase in resistivity is the result of radiation induced damage to the microstructure of the nanotubes.

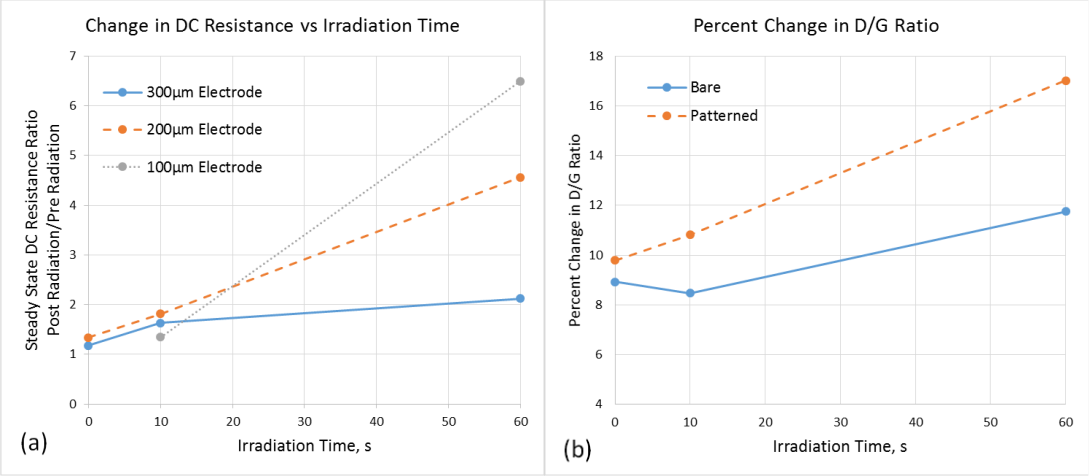


Figure 1: Effect of irradiation on electrical resistivity (a) and microstructure (b) of CNT networks

The results of this research indicate that 2D randomly oriented CNT networks show great potential for dosimetry applications. In light of these results, improved devices will be irradiated on August 10 at HFIR, the results of which will be included in this poster presentation.

Electrical characteristics of InSe-WSe_2 van der Waals heterojunctions

Akinola Oyedele[1,2], Ming-Wei Lin[2], Kai Wang[2], David B. Geohegan[2], Kai Xiao[2]

[1]Bredesen Center for Interdisciplinary and Graduate Education, University of Tennessee, Knoxville, TN, 37996, USA. [2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA.

Abstract

In the past decade, the emergence of graphene has brought an increased interest on two-dimensional (2D) materials owing to their superior electronic transport and mechanical properties. However, the absence of a band-gap has limited its application in field-effect switching devices which are integral components of modern electronic devices. This has led to the search of other layered, two-dimensional materials with semiconducting properties. An important class of these new materials is the layered transition metal dischalcogenides, represented as MX_2, where M is a transition metal and X is a chalcogen. The individual 2D material provides a large range of exciting properties, which when combined into heterostructures offer ever greater functionality and scope, and the opportunity to study the interfacial phenomenon in these heterojunctions. In this work, a novel van der Waals heterostructure based on n-type indium selenide and p-type tungsten diselenide was built by a mechanic exfoliation and determined dry transfer process. The electrical properties of this junction displayed a pronounced rectification behavior similar to that of p-n junction diodes. And interestingly displays a photovoltaic (PV) effect under light which can be extended to thin solar cell applications.

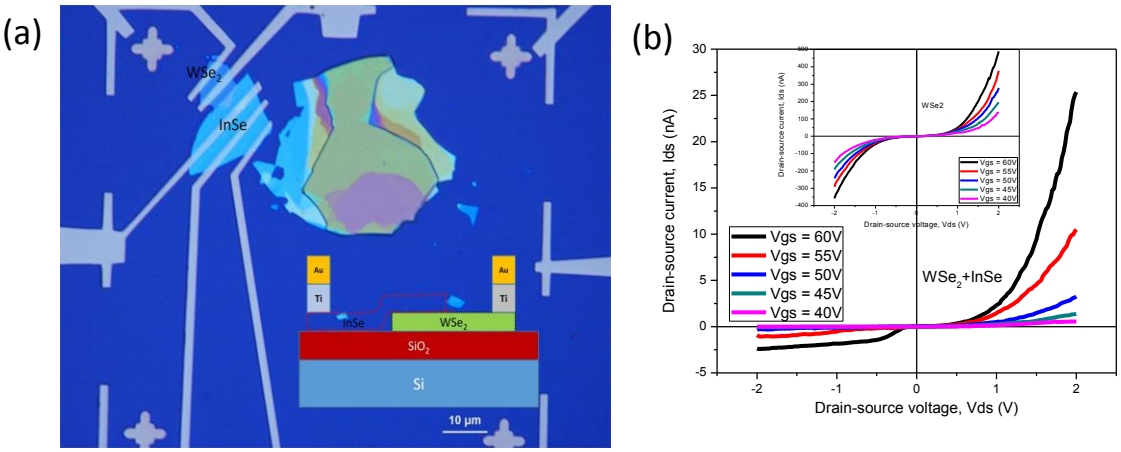


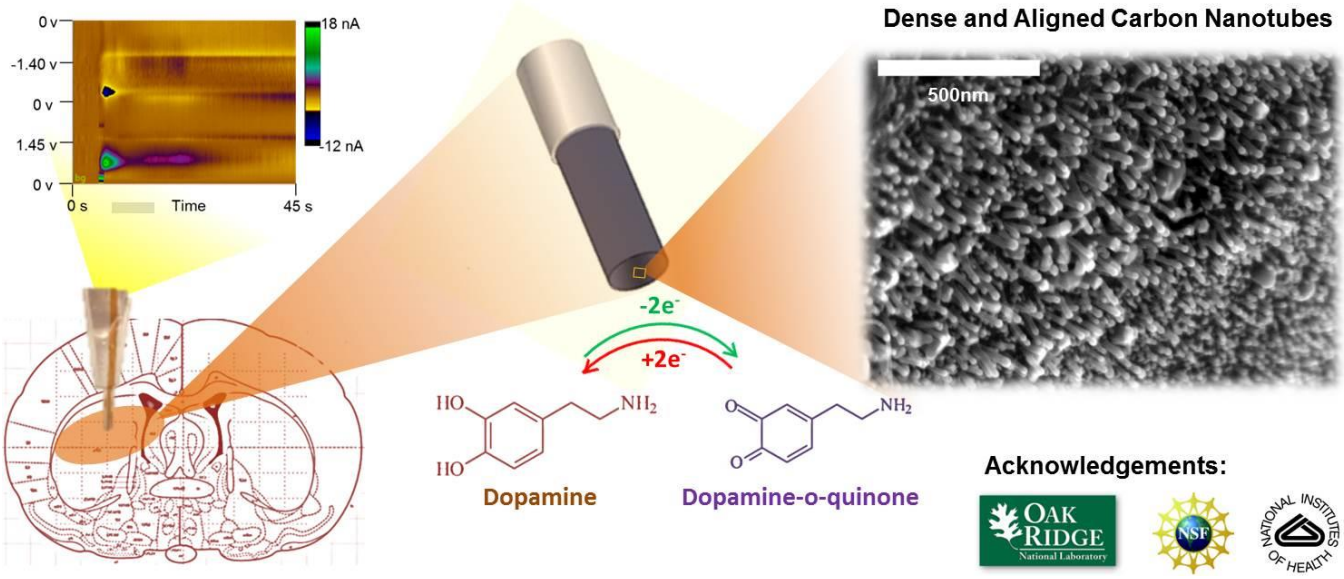
Figure: (a) Optical microscopy image of mechanically exfoliated few-layer InSe (9 nm) and WSe_2 (7 nm) on 290 nm SiO_2/Si, with Ti/Au (5nm/30nm) contacts. Inset: Schematic diagram illustrating the arrangements of the field effect transistor. (b) Electrical output characteristics of few-layer InSe-WSe_2 field effect transistor at different gate bias showing rectifying behavior. Inset: Output characteristics of few-layer WSe_2 with no rectifying behavior.

This research was conducted at the Center for Nanophase Materials Sciences (CNMS), which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, U.S. Department of Energy.

Carbon Nanotubes Grown on Metal Microelectrodes for the Detection of Dopamine

Cheng Yang,† Christopher B. Jacobs,† Mallikarjunarao Ganesana,† Michael D. Nguyen,† Alexander G. Zestos,† Ilia N. Ivanov, ‡ Alex A. Puretzky,‡ Christopher M. Rouleau,‡ David B. Geohegan,‡ B. Jill Venton*†

†Department of Chemistry, University of Virginia, McCormick Road, Box 400319, Charlottesville, Virginia 22904-4319, United States.
‡Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, 1 Bethel Valley Road Bld. 8610, Rm. M166, Oak Ridge, Tennessee 37831, United States



Microelectrodes modified with CNTs are useful for detection of neurotransmitters because the CNTs enhance sensitivity and have electrocatalytic effects. CNTs can be grown on carbon fiber microelectrodes but the low conductivity of carbon fibers may lead to slow electron transfer kinetics and the intrinsic electrochemical activity of carbon fibers makes evaluating the effect of CNT enhancement difficult. Metal wires have high conductivity and have no intrinsic electrochemical activity for dopamine so we investigated CNTs grown on metal wires as microelectrodes for neurotransmitter detection. Scanning electron microscopy shows that aligned CNTs can be grown on metal wires, particularly tantalum and niobium wires. Using fast-scan cyclic voltammetry, CNT-coated niobium (CNT-Nb) microelectrodes have higher sensitivity and lower ΔE_p values compared to CNTs grown on carbon fibers or other metal wires. The limit of detection for dopamine at CNT-Nb microelectrodes is 11±1 nM, which is approximately five fold lower than CNT grown carbon-fiber microelectrodes (CFMEs) and two fold lower than CFMEs. Adsorption processes were modeled with a Langmuir isotherm and it revealed dopamine oxidation is more reversible at CNT-grown microelectrodes than at CFMEs. CNT-Nb microelectrodes were used to monitor stimulated dopamine release in anesthetized rats. Detection of other neurochemicals was also characterized, including ascorbic acid, DOPAC, serotonin, adenosine, and histamine. The enhancement for dopamine was greater than ascorbic acid at CNT-Nb electrodes. This study demonstrates that CNT-grown metal microelectrodes, especially CNTs grown on niobium, are useful for monitoring neurotransmitters.

Influence of Submicron Agro Waste Silica Particles and Vinyl Acetate on Mechanical, Diffusivity and Thermal Properties of High Density Polyethylene Matrix Composites

Oluyemi O. Daramola [a,Ψ], Isiaka O. Oladele [b], Benjamin O. Adewuyi [c],
Rotimi Sadiku [d], and Stephen C. Agwuncha [e]
[a, b, c] Department of Metallurgical and Materials Engineering, Federal University of Technology, PMB 704, Akure, Ondo State, Nigeria;
[a]E-mail: ojaythompsoms@yahoo.com; [b]E-mail: wolesuccess2000@yahoo.com;
[c]E-mail: tayo_adewuyi@yahoo.com
[d, e] Division of Polymer Technology, Department of Chemical, Metallurgical, and Material Engineering, Tshwane University of Technology, Bag X680, Pretoria 0001, South Africa;
[d]E-mail: sadikur@tut.ac.za; [e]E-mail: acsjanil22@gmail.com

ABSTRACT

Development of polymeric composites has invoked much interest in recent years. These fillers have great effect on the mechanical and thermal properties of polymers. The present study aims to develop High Density Polyethylene (HDPE) matrix composite reinforced with silica particles extracted from rice husk ash (RHA). The silica powder particles with average particle size of 489 nm was produced by Sol-Gel process. HDPE based composites were prepared by melt compounding with 2, 4, 6, 8 and 10 wt. % of silica particles with a Rapra single screw extruder and was produced by compression moulding. Mechanical behaviour, thermal behaviour, water absorption properties and microstructure of the developed composites were studied. It was observed that the mechanical properties increased with an optimum value of 4wt. % of silica particles in HDPE while the maximum thermal-degradation analysis of the siliceous composites increase with increase in SiO_2 weight fraction. The results of the thermal-degradation analysis of the neat HDPE, EVA, and HDPE/SiO_2/TiO_2 composites shows that HDPE/ SiO_2/TiO_2 composites with 10 wt.% SiO_2 has the best maximum thermal degradation temperature of 382.38 ^oC. The results of the water absorption test showed that the amount of water absorbed by the composites increases with the increase in the silica particles content, less absorption took place in SiO_2/TiO_2/HDPE composite with 2wt.% SiO_2 weight fraction with an average value of 0.16% followed by composite with 4wt.% SiO_2 content with a value of 0.17%.

Gelation of anisotropic silica nanoparticles with thermoreversible short-range interactions

POSTER 29

Ryan Murphy, *University of Delaware*

Anisotropic particles such as proteins, cellulose nanocrystals, clays, and mineral crystals are important components in various pharmaceuticals, consumer products, paints, and coatings. The rheological and thermodynamic properties of anisotropic particle suspensions are significantly influenced by particle shape, for example, by introducing orientation-ordered phases, enhanced shear-thinning behavior, or elasticity at lower volume fractions. However, the combined effects of particle shape and interaction strength on dynamic arrest transitions, such as gel and glass formation, are not understood for anisotropic particle suspensions. To explore the gelation and phase behavior of anisotropic particle suspensions, we have developed a model system of adhesive hard rods (AHR) with thermoreversible, short-range interactions having tunable dimensions (300-3000 nm) and low polydispersity (10-20%). The model thermoreversible gel consists of rod-shaped silica particles coated with an octadecyl-brush suspended within tetradecane, which enables control over the particle aspect ratio, volume fraction, and temperature-sensitive particle interactions. With this model system, we aim to quantify the fundamental effect of particle shape on the gelation mechanism and to map the first state diagram for anisotropic particles. Preliminary rheological measurements revealed that the gel transition temperature significantly increased and broadened with increasing aspect ratio. Ongoing work aims to reduce the silica rod diameter (< 100 nm) to limit gravitational effects and gel network collapse at low volume fractions. Furthermore, linking the microscopic structure determined from scattering methods with the macroscopic rheological properties will greatly benefit particle technology design, suspension formulation, and manufacturing processes that employ anisotropic particle suspensions.

Mechanical Behavior of All-Acrylic Multigraft Copolymers Based on Side Chain Molecular Weight and Volume Fraction

Andrew Goodwin[1], Weiyu Wang[1], Nam-Goo Kang[1], Yangyang Wang[2], Kunlun Hong[2], Jimmy Mays[1, 3]

[1]Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996
[2]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
[3]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
Email: Goodwin@ion.chem.utk.edu; Jimmymays@utk.edu

All-acrylic multigraft copolymers composed of glassy poly(methyl methacrylate) side chains randomly attached to a rubbery poly(*n*-butyl acrylate) backbone were synthesized using a 'grafting-through' approach and characterized for their use as thermoplastic elastomers (TPEs). The synthetic procedure, which employed both anionic and reversible addition-fragmentation chain-transfer radical polymerization techniques, produced high molecular weight (>100 kg/mol) materials with both tunable volume fractions of each component and average number of branch point junctions per chain. The mechanical properties were investigated using rheology, dynamic mechanical analysis, and tensile testing to compare the results of the branched material to their linear MAM triblock copolymer counterparts. Additionally, the effects of structure, composition, and side chain molecular weight of the multigraft samples on the observed bulk physical properties were explored in order to gain insight into the structure-property relationship and optimize the elastomeric properties of these all-acrylic materials.

Accessing Next-Generation Polyolefins and Gas Separation Membranes via Coordination-Insertion Polymerization

Brian K. Long
University of Tennessee

Coordination-insertion polymerizations are responsible for more than 50% of all commercial polymers produced globally. This staggering number is largely comprised of a class of polymers known as polyolefins. Polyolefins are the most widely produced and utilized polymers in the world, owing much of their success to their low-cost, excellent mechanical properties, and heavy utilization for a wide range of commodity applications. As global demand for these polyolefin-based materials steadily increases, researchers are continually pushed to develop new and innovative catalysts that can produce polyolefins with enhanced and/or tailored physical and mechanical properties. To address this challenge, we have 1) developed a class of thermally robust Ni(II) α-diimine catalysts that display near perfect thermal stability at temperatures as high as 90 °C, and 2) have discovered a unique feature of commonly employed catalysts that has enabled us to readily tailor polyolefin branching content via redox chemistry.

The second project that will be presented is the development of next-generation gas separation membranes. In 2012, carbon dioxide (CO2) accounted for approximately 82% of all U.S greenhouse gas emissions. These excessive CO2 levels have been attributed to climate change and potentially have a wide range of negative effects on human health and well-being. On June 18th 2014, the EPA published a new plan to incentivize power plants across the country to heavily reduce their carbon emissions into the atmosphere known as the Clean Power Plan. To address this grand challenge, our research has focused on the development of thin-film polymeric membranes capable of separating gases in a passive manner. We approach the synthesis of those membranes using coordination-insertion polymerization techniques, and target highly rigid polynorbornene-based materials.

Improved Carbon nanotube yarns through crosslinking

Xinyi Lu
University of Tennessee

Abstract: Due to difficulties in dispersing pristine carbon nanotube(CNT) in composites, attention is being increasingly drawn to direct assembly of CNTs into macroscopic fibers or sheets. The high tensile strength of an individual CNT has not been translated into useful macro assembly, mainly due to weak intertube attractions and slippage. Applying crosslinks between the tubes has been proved to enhance the tensile strength of CNT fiber by simulations and experiments on a bundle scale. In this work, a potentially scalable method of crosslinking CNT macro structures has been designed. Polymer crosslinkers of different lengths involving benzocyclobutene (BCB) moieties have been synthesized by anionic polymerization. The polymer was mixed with multi-walled carbon nanotube (MWCNT) powder or infiltrated into CNT yarn. Crosslinking with MWCNT and CNT fiber have been confirmed by x-ray photoelectron spectroscopy (XPS), thermo gravimetric analysis (TGA), scanning electron microscope (SEM) and transmission electron microscopy (TEM). Mechanical test of crosslinked CNT yarns proved that this process increases tensile modulus by 4 fold and tensile strength by 50%. An average of 20% wt. of polymer was grafted on to CNTs after the crosslinking reaction.

Title: Development of Passive Polymer Membranes for Carbon Dioxide Separation

Tao Hong, Sabornie Chatterjee, Shannon Mahurin, De-en Jiang, Brian Long, Jimmy Mays, Alexei Sokolov, Tomonori Saito

Chemical Sciences Division
Oak Ridge National Laboratory
Bethel Valley Road
PO BOX 2008 MS6210
OAK RIDGE TN 37831-6210

Abstract:
The vast majority of the world's energy is presently derived from the burning of fossil fuels, which releases vast quantities of carbon dioxide (CO_2) into the environment and results in undesirable climate change. Practical and cost efficient methods of CO_2 separation and capture would thus solve one of the most challenging problems facing humanity today. This presentation summarizes our effort on the development of novel polymer membranes for CO_2 separation and the investigation of the fundamental understanding in its molecular transport through the polymer membranes. Our strategy focuses on tuning solubility selectivity in addition to diffusion selectivity for achieving high permeability membranes combined with good selectivity. Various synthetic techniques including ROMP and post functionalization were used and the careful design permits to prepare well-defined novel high permeable polymers containing CO_2-philic groups. The structure-property relationships including CO_2 uptake, CO_2 and N_2 permeability, CO_2/N_2 selectivity to the polymer structure will be discussed.

Organic-organic amorphous nanocomposites

Chau D Tran,[1] Tony Bova,[1] Jihua Chen,[2] Jong K Keum,[2,3] and Amit K Naskar[1]
[1]Materials Science and Technology Division, [2]Center for Nanophase Materials Science and [3]Neutron Science Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37831,
naskarak@ornl.gov

Here, we report the synthesis of nanocomposite based on controlled interaction between two amorphous polymeric materials. A diene based soft matrix is chemically interacting with a hard phenolic compound to produce a wide variety of materials. Matrix-dispersed morphology with domain sizes above 10 microns is changing to a nanostructured network with domain sizes below 100 nm by incorporating polar functional group to the diene matrix. The compounds composed of phenolic material with styrene butadiene or butadiene rubbers exhibit a glassy behavior and negligible mechanical properties due to large phase domain sizes. Upon switching to acrylonitrile containing butadiene rubber, a significant reduction in domain sizes of hard phenolic compound as well as excellent mechanical property is achieved. This behavior is due to combined effects of increased compatibility and interfacial reaction. By changing acrylonitrile content from 33 % to 50% in the butadiene rubber, tensile strength increases from 14 MPa to 40 MPa while domain sizes are significantly reduced to below 100 nm as seen under transmission electron microscopy (TEM) (Fig. 1). Small angle X-ray scattering (SAXS) further confirms the existence of these nano domain sizes which are acting as a hard domain to reinforce the soft matrix. The ultrahigh mechanical properties of these compounds emphasize the excellent replacement of polymeric materials for typically used carbon nanoparticles as reinforcement in nanocomposite. Furthermore, the use of bio-renewable material (such as lignin), instead of petroleum derived phenolic resins, offers equivalent properties, a tremendous economic and societal impact and open a new path for increased biomass use.

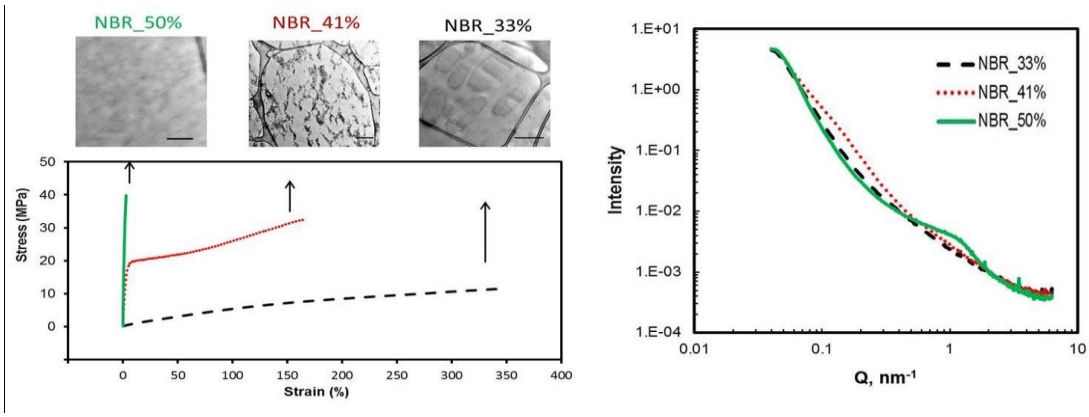


Figure 1- Tensile property and corresponding TEM images (left) and SAXS (right) of compounds composed of lignin with acrylonitrile butadiene rubber containing 33% (NBR_33%), 41% (NBR_41%), and 50% (NBR_50%) mole % of acrylonitrile. In NBR_33%, lignin appears as dispersed particles with domain sizes of 0.2 to 1 micron. Lignin is further exfoliated into a network of less than 100 nm (dark color, stained with ruthenium tetroxide) when NBR_41% is used. Further increasing acrylonitrile content to 50% (NBR_50%) results in a homogenous mixture with hardly observable contrast between two phases. The scale bars are 200 nm in TEM images.

Cellular Organizations in *Escherichia coli* Mechanically Probed by a Novel Microfluidic Device

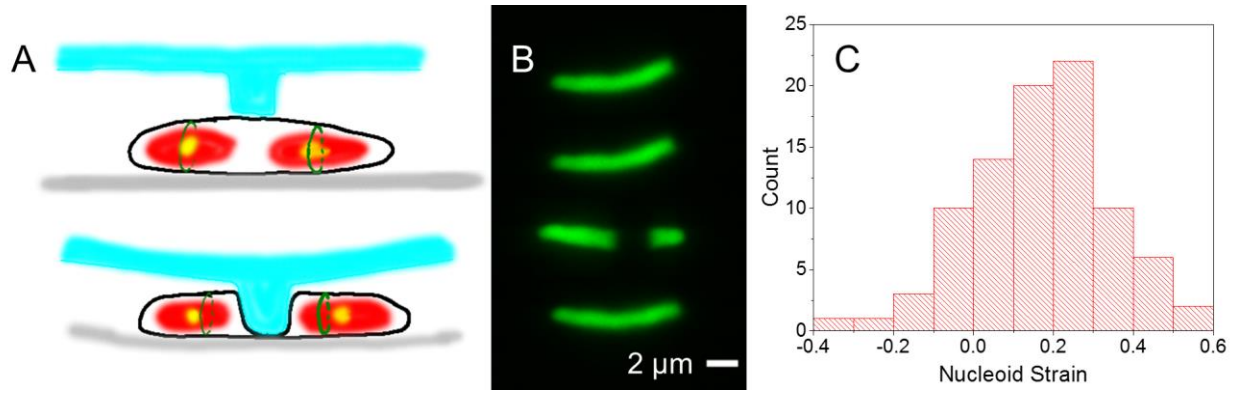
Da Yang, Branndon Jones, Scott Retterer, Jaan Männik

Escherichia coli is the main model organism in cell biology. The common approach to understand how cellular organizations are maintained is by perturbing that organization, then observing the response from the cells. Those perturbations have traditionally been carried out using chemical agents. Here, we present mechanical perturbations to cellular organizations in microfluidic chips.

Our experimental design is based on pressure actuated microfluidic valves. An *Escherichia coli* bacterium is placed under a microfluidic valve, which is constructed by a pair of flow and control channels perpendicular to each other. Valve closing by an actuating pressure deforms the bacterium and perturbs its internal organization. We implement that design in PDMS based multilayer microfluidic chips. Those chips enable us to monitor bacteria and their cellular structures undergoing mechanical deformations in real time.

Our previous measurements show that considerable deformations of bacteria and displacements of their chromosomes are achievable in those devices. However, bacteria tend to displace frequently when pressure is applied to a control channel or when culture media is flown. Moreover, the ceiling of a given flow channel tends to enclose the bacterium. Here, we describe the findings obtained using Valve Post Chips. In that design, we “trim off” part of the material in the ceilings of the flow channels to ensure that the ceiling surfaces are under tension just before contacting bacteria. That modification overcome aforementioned drawbacks. Similar to our previous experiments, by switching the control pressure off (top of *Fig. A*) and on (bottom of *Fig. A*), we mechanically perturb the bacterium and its internal organization. With fluorescence microscopy, we observe the bacterium responding to those perturbations.

First, we find that, while a control pressure is applied to the device, a cell envelope elongates and the cytoplasm appears to be shorter (*Fig. B*); further, an “indentation” of the cytoplasm sometimes occur, and often away from the post. Second, gaps between nucleoids remains during the application of control pressure (squeezing), and nucleoids are condensed (*Fig. C*); those gaps undergo different dynamics after squeezing. Third, during squeezing, the colocalized pairs of Z-rings (the cell division apparatus) and the Ter-regions (the portion of bacterial chromosome being replicated last) are dissociated. Z-rings displace less than that of the Ter-regions. The colocalization of Z-rings and Ter-regions reforms shortly, but not immediately, after squeezing. In addition, we also present fabrication procedures of the Si wafers based molds for molding PDMS elastomer, which includes a chip mark aligned electron beam lithography step.



Big data techniques for investigation of the tip-induced ferroelectric switching

A.V. Ievlev and S.V. Kalinin
[1] The Center for Nanophase Materials Sciences, Oak Ridge National Laboratory,
Oak Ridge, TN 37831

Ferroelectric materials are currently considered as a perspective platform for a wide range of practical application, such as such as sensors, microactuators, infrared detectors, microwave phase filters, data storage and processing devices. Scanning probe microscopy (SPM) has become a standard tool for complex study of the various ferroelectric materials. It allows both visualization and modification of the domain structures with the nanometer spatial resolution.

In this work we considered the variety of domain morphologies produced by the scanning probe microscope tip on the polar and non-polar cuts of ferroelectric single-crystals. We performed analysis of their parameters based on the principal component analysis (PCA). It allowed gaining insights into the highly nontrivial process of the polarization reversal limited by the screening dynamics and provided descriptors of the domain shape. These descriptors can be used as inputs of the neural network for recognition of a wide range of the domain properties(e.g. shape of the switching pulse used during switching). Suggested approach potentially enables a novel approach to the multilevel information storage, when data is decoded via the shape of ferroelectric domain through the used sequence of electric pulses applied to the tip.

Similarly, the considered approach can be used for determination of the thermodynamic properties of the sample encoded in the features of the domain shape.

A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Extraction and analysis of dynamic information in SPM

Alexei Belianinov, Suhas Somnath, Sergei Kalinin, Stephen Jesse

Institute for Functional Imaging of Materials and the Center for Nanophase Materials Science, Oak Ridge National Laboratory,
Oak Ridge, TN 37831

In the last three decades, Scanning Probe Microscopy (SPM) have emerged as primary tools for exploring and controlling the nanoworld. A critical part of SPM measurements is the information transfer from the tip-surface junction to a macroscopic measurement system. This process reduces the many degrees of freedom of a vibrating cantilever to relatively few parameters recorded as images. Hence, the amount of information available to the external observer is severely limited, and its selection is biased by the chosen data processing method. We report a new approach to SPM imaging using information based analysis of the data stream from the detector. This approach allows full exploration of complex probe-surface interactions, spatial mapping of multidimensional variability of material properties and their mutual interactions, and data collection at the information channel capacity limit. Extension of the technique to spectroscopic and higher dimensional imaging modes will also be discussed. Challenges and opportunities in transitioning to a high performance computing environment, and the outlook for expanding this technique into other microscopy fields will be presented.

Acknowledgements

Research for all authors 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. Research was supported by the US Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division.

Rama Vasudeven

Oak Ridge National Laboratory

Abstract not yet available

Advanced Understanding of Bias-Induced Dynamic Phenomena in SPM

Nina Balke, Qian Li, Stephen Jesse, Petro Maksymovych, Sergei Kalinin
Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Email: balken@ornl.gov

Nanoscale bias-induced phenomena have been studied using scanning probe microscopy (SPM) for over a decade Common electromechanical phenomena studied using SPM include ferroelectricity, ionic transport, phase transitions, etc. While SPM instruments become more and more available, there is a rapid development of measurement techniques featuring dynamic electromechanical testing, utilization of contact resonance dynamics and multi-frequency approaches creating a plethora of information and large data sets. While it is crucial to extract physical mechanisms from the experimental data using big data approaches, it is just as crucial to understand the effects happening under a biased SPM-tip. In reality, many different effects can contribute to the induced electromechanical sample response and it is important to be able to determine and separate them in order to interpret the experimental data correctly. This is a difficult task and many contributing effects have been ignored. This poster aims at starting the discussion about electromechanical phenomena happening under a biased SPM tip and discusses different sample system to characterize the different phenomena.

Electron Energy Loss Spectrum Analysis for Van der Waals Heterostructures

Nicholas Cross[1], Lei Liu[2], Ali Mohsin[2] Gong Gu[2], Gerd Duscher[1,3]

[1.] Department of Materials Science and Engineering, the University of Tennessee, Knoxville, TN 37996, United States
[2.] Department of Electrical Engineering and Computer Science, the University of Tennessee, Knoxville, TN 37996, United States
[3.] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

Van der Waals (vdW) heterostructures of two-dimensional (2d) materials have attracted considerable research interest. This works investigates 2d materials boron nitride (BN) and graphene with electron energy loss spectroscopy (EELS) and density functional theory (DFT). Samples for the study were grown using atmospheric-pressure chemical vapor deposition. BN precursor charge is significantly increased to create areas of BN double layers and BN/graphene vdW heterostructures. Atomic-resolution imaging and EELS was performed using the state-of-the-art UltraSTEM 100, at an accelerating voltage of 60 kV. Computational results were obtained using time-dependent DFT, to account for interband, intraband and plasmonic excitations in the calculation. Experimental and theoretical findings show to have a good agreement and indicate there is an in-plane plasmon (dipole) interaction that result in a blue shift of the $\sigma+\pi$ plasmon.

Proton Conduction Mechanisms in Yttrium-doped Barium Zirconate

Jilai Ding, Evgheni Strelcov, Gabriel Veith, Craig Bridges, Janakiraman Balachandran, Panchapakesan Ganesh, Sergei Kalinin, Nazanin Bassiri-Gharb and Raymond Unocic

Ionic dynamics underpin the performance and efficiency of a broad spectrum of techniques ranging from energy storage and conversion devices to sensors and actuators. Doped barium zirconate (BZO) has attracted significant scientific attention, due to its relatively high proton conductivity while maintaining chemical stability at intermediate temperatures (400-700 °C), which is thought to be one of the most promising candidates as electrolyte in proton-conducting solid oxide fuel cells (SOFCs). However, due to the refractory nature, the reported proton conductivity of doped BZO often suffers from inconsistency, and the role of defects such as oxygen vacancies on the proton transport at nanoscale is still not well understood. This underscores the challenges of BZO in practical applications and the need for further fundamental studies.

In this study, the ionic dynamics in yttrium doped BZO (Y-BZO) is investigated using energy discovery platforms, which is a synergy of nanofabricated device and time resolved Kelvin probe force microscopy (tr-KPFM) under controllable external stimuli. Y-BZO films were prepared by pulsed laser deposition (PLD) on <100> oriented single crystal MgO substrates. Through tr-KPFM, the surface potential variation as a function of temperature and humidity is obtained in a sub-micron resolution, and 10 ms to 10 s temporal resolution. Polarization and relaxation are observed at above 100 °C, and such phenomena are mainly a result of Grotthuss mechanisms of proton transport in Y-BZO. Finite element analysis is performed to correlate the observed surface potential profile with proton generation and migration, and the physical parameters including mobility and diffusivity is also obtained.

ELUCIDATION OF RARE PATHWAYS SAMPLED DURING BIOMOLECULAR BINDING EVENTS

Ahmad Haider[1], Daniel Potter[1], Todd Sulchek[1]
1. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta

Introduction

The binding and unbinding of ligands to proteins is an essential biochemical process, yet there are few experimental techniques that can directly measure the energetic depth and physical extent of biomolecular bonds. We have recently developed a technique using atomic force microscopy to directly map the intermolecular energy landscape curve of a biotin-avidin interaction. The method utilizes Brownian fluctuations of a sensitive microcantilever probe in close proximity to the interaction energy potential of biotin and avidin that are decorated on the tip and substrate surfaces, respectively. By recording subtle deviations from the harmonic cantilever vibrations, we can reconstruct entire energy landscapes of biotin-avidin interactions, including rare, meta-stable states.

Materials and Methods

Silicon nitride MSCT cantilevers (Bruker, California) were functionalized with biotinylated bovine serum albumin (Sigma Aldrich). A monolayer of avidin (Fluka) was physically adsorbed to freshly cleaved mica (Gruber-Ebner protocol). Cantilever D, with a resonance frequency, f_0, between 10 and 13 kHz in liquid, was used to obtain force-distance curves at a data rate of 50 kHz, four times f_0, satisfying the Nyquist sampling theorem. To obtain large data sets, the force curve z-piezo translation velocity was 100 pm/s. The cantilever drift was less than 6 Å/min.

Results

The mapping of interaction energy landscapes via Brownian fluctuations is based upon previously reported methods [1-2]. Data processing was performed by routines written in MATLAB (Mathworks Inc.). Figure 1 below shows the energy landscape reconstruction approach.

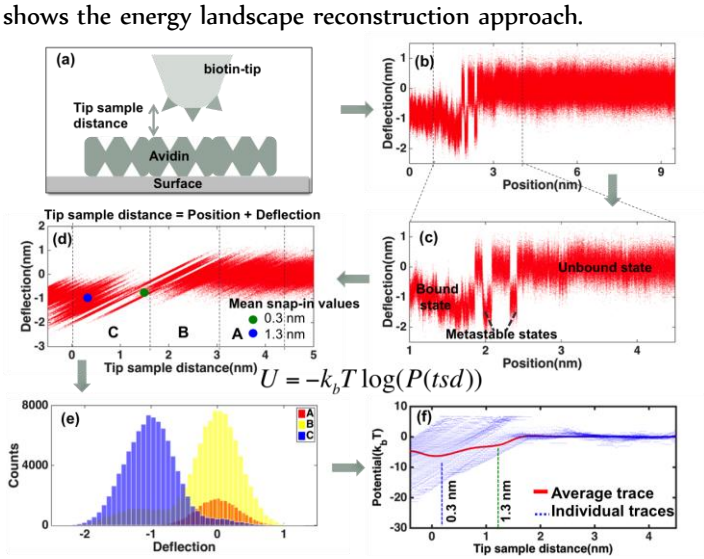


Figure 1: (a) Schematic of a cantilever tip decorated with biotin over an avidin coated substrate (b) Overall approach curve including Brownian fluctuations (c) Zoomed in section of the approach curve showing presence of metastable states (d) Transformation of position to tip-sample-distance(tsd) to account for cantilever fluctuations at each position (e) Histogram of the cantilever positions during fluctuations at different window locations (f) Energy of each window (U),computed by Boltzmann eqn. [U=-k_bT log(probability(tsd))], T=300K. Tip-sample interaction energy computed after subtracting the cantilever harmonic potential. Both individual (blue) and average(red) binding energy pathways are plotted

The interaction pathways, as well as the average pathway, are important in fully understanding the complexity of molecular binding along the energy landscape. The individual traces depict the entire energy landscape of biotin-avidin interactions determined by the probability of the cantilever position at each tip-sample distance. These methods can identify energy landscapes during rare binding pathways for metastable events which are sampled infrequently. In contrast, the average trace determines overall trends such as presence of multiple wells corresponding to alterations in molecular positioning or multiple binding events. The average is computed by a weighted average cantilever residence at each position [2]. Energies for rare binding pathways cannot be readily deduced by examination of the average force-distance trace. We see that while the method can detect rare biotin-avidin interactions with a maximum binding energy of 29 k_bT, it estimates the energy landscape of biotin avidin interactions as having two binding pockets with average energies of $3k_bT$ and $6k_bT$.

References: [1] Ashby P.D., Lieber C. L., J Am. Chem. Soc., 126:16973-16980, 2004. [2] Willemsen, O.H., Kuipers , L. et al., J Langmuir, 16:4339-4347, 2000

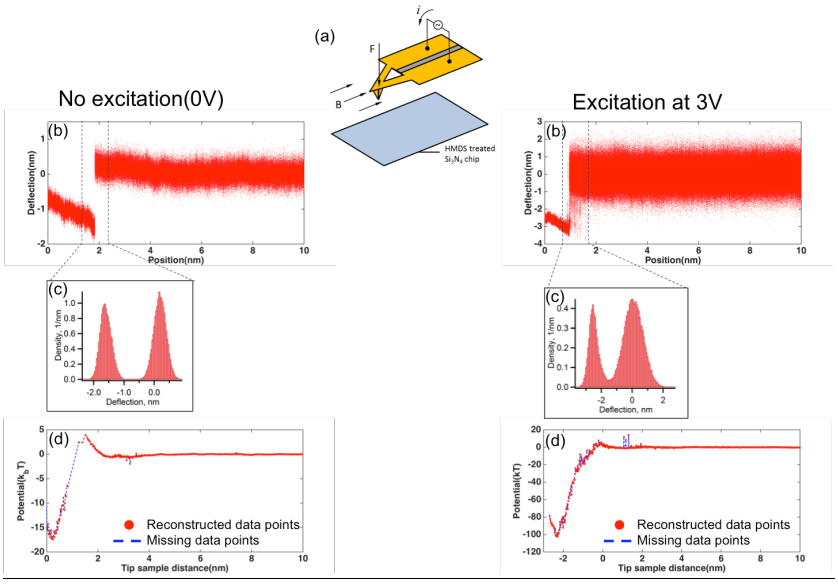
ENHANCED THERMAL EXCITATION OF AFM CANTILEVERS TO IMPROVE SAMPLING OF RARE STATES DURING ENERGY LANDSCAPE RECONSTRUCTION

Daniel Potter[1], Ahmad Haider[1], Todd Sulchek[1]
1. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta

Introduction Free energy landscapes underpin the interactions of surfaces and biomolecules. The direct measurement of the free energy landscape between two charged surfaces has been accomplished through the use of atomic force microscopy and the analysis of thermal fluctuations using the Boltzmann distribution [1,2]. However, it is difficult to fully sample high energy interactions between charged surfaces. A soft cantilever will snap-to-contact, while a stiff one will fail to sample the full energy landscape. We overcome this challenge by utilizing white noise excitation of a cantilever to enhance sampling of rare metastable binding states. By elucidating the energy landscape with the Boltzmann distribution, we show that increased excitation leads to increased energy landscape resolution

Materials and Methods Silicon nitride iDrive-compatible cantilevers (BL-TR400PB, Asylum Research, California) were cleaned and placed in an iDrive cantilever holder. Clenaed 1 mm x 3 mm silicon nitride chips surface are treated by evaporating 30 uL of hexadimethyl silazane from it's surface at 70°C. In the AFM, 50 uL of 100 mM NaCl is placed on the chip, the cantilever is immersed in the fluid and equilibrated to less than 5 Å/min. Cantilever 1, with a resonance frequency, f_0, between 29 and 33 kHz in liquid, was used to obtain force distance curves at velocities of 100 nm/s. To increase tip-sample interaction time, we scanned at 0.005 Hz

Results



(a) Schematic for an idrive cantilever on a HMDS treated Si_3N_4 chip (b) Approach curves collected for no excitation (left) and 3V white noise excitation (right) applied to the cantilever holder (c) Histograms of the contact regions (d) Reconstructions of tip sample interaction energy from the histogram distributions via Boltzmann distribution approach. 3V excitation allows us finer resolution of the interaction potential during jump to contact

While weak springs are good for sampling strong tip sample interactions because of their high sensitivity to applied forces, they tend to get trapped in steep energy wells because of low restoring forces. On the other hand, stiff cantilevers have low deflection sensitivity and may not be able to fully sample steep energy wells. Utilizing a soft cantilever and supplying it additional energy through external excitation allows us to fully sample steep potential wells by jumping in and out of them multiple times. We reconstruct the potential energy landscapes of charged interactions of an excited cantilever versus a passive cantilever as it approaches the surface. From the negligible point density between histogram peaks for 0V, it is clear that a passive cantilever is able to sample one state at a time as compared to the active lever. The corresponding energy reconstructions of 0 V has lower resolution during snap to contact that is evident through a larger proportion of missing data points as compared to number of reconstructed data points. The excited cantilever can sample stronger interactions corresponding to deeper potential wells.

References: [1] Willemsen, O.H., Kuipers, L. et al., J Langmuir, 16:4339-4347, 2000 [2] Koralek, D.O., Heinz, W.F. et al., Applied Physics Letters, 76:2952-2954, 2000

Formation Mechanism of Mn Containing Precipitates during Homogenization in 6xxx Series Aluminum Alloys

Gongwang Zhang[a], Yi Han[b], Yi Xu[b], Hiromi Nagaumi[b], Sha Gang[c], Chad M. Parish[d], Donovan Leonard[d], Tongguang Zhai[a]

[a] Department of Chemical and Materials Engineering, University of Kentucky, 177 F. Paul Anderson Tower, Lexington, KY 40506, USA
[b] Suzhou Research Institute for Nonferrous Metals, Shenhu Road 200, Suzhou Industrial Park, Suzhou, China
[c] School of Materials Science and Engineering, Nanjing University of Science and Technology, No. 200 Xiaolingwei, Nanjing, Jiangsu, 210094, China
[d] Microscopy Group, Materials Science & Technology Division, Oak Ridge National Laboratory, 1 Bethel Valley Rd., Building 4515, Rm. 191, Oak Ridge, TN 37831-6064, USA

A 6xxx series Al alloy with addition of Mn, Cr and Cu was homogenized at temperatures ranging from 350 °C to 550 °C after casting. α-Al(MnCrFe)Si dispersoids were formed in the alloy, significantly retarding recrystallization by pinning dislocations and grain boundary during downstream thermomechanical processing (Fig. 1). It was found that the dispersoids were formed at the expense of a lathe-shaped Q-AlMgSiCu phase which formed at a lower temperature, i.e., Q phase was the precursor phase for the formation of α-dispersoids. 3-D Atom probe tomography (APT) experiments revealed that Mn atoms segregated at the interface of Q phase and the matrix (Fig. 2), before Q phase was discomposed with Cu atoms diffusing into the matrix first, followed by Mg and Si (Fig. 3). After segregation of Mn at the Q phase interface, Si subsequently participated followed by Cr and Fe to form α-dispersoids, while the Q phase being discomposed.

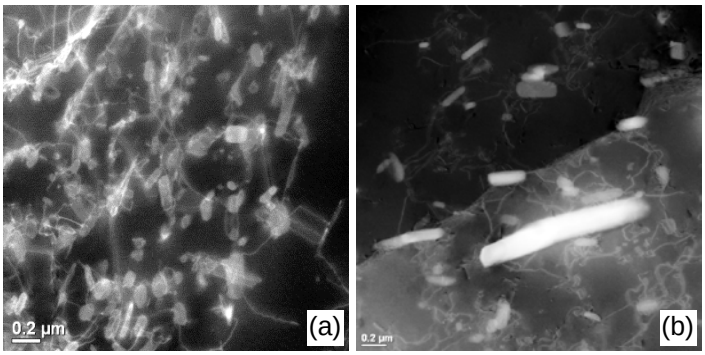


Fig. 1. STEM micrographs showing pinning effect of α-dispersoids in the 6xxx series Al alloy hot forged (80% forging ratio) on (a) Dislocations; (b) Grain boundary.

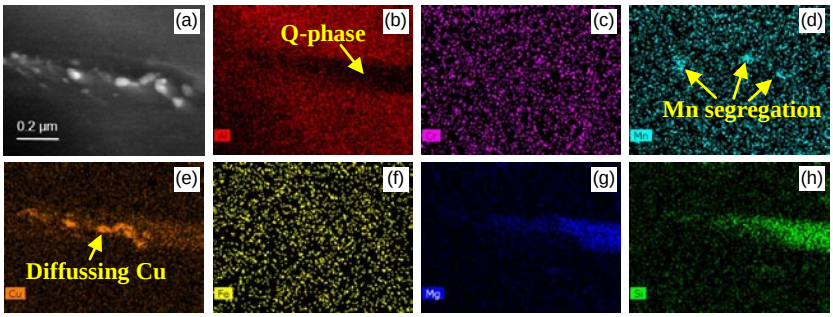


Fig. 3. (a) STEM micrograph of a decomposing Q-phase; (b-h) EDS elemental maps of Al, Cr, Mn, Cu, Fe, Mg, and Si, respectively, in the same area as in (a) in early stage of homogenization (slow heating to 400 °C, then quench).

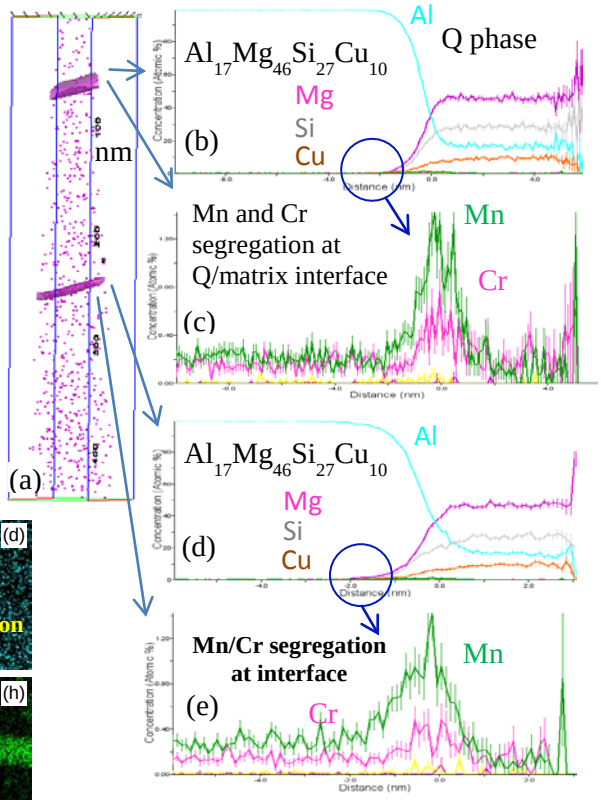


Fig. 2. (a) Atom-probe micrograph of Q-phase; (a) and (d) elemental distributions of the Q-phase particles across the Q phase interface; (c) and (e) segregation of Mn and Cr at the Q-phase and matrix interface (slow heating to 350°C, then quench).

Scalable Analysis of Multidimensional Imaging and Spectral Data in Material Science

A. Belianinov,[1,2] E. J. Lingerfelt,[3] S. Jesse,[1,2] E. Endeve,[3] O. Ovchinnikov,[5] M. B. Okatan,[1,2] C. T. Symons,[4] M. Shankar,[4] R. K. Archibald[3]

[1] The Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

[2] Institute for Functional Imaging of Materials, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

[3] Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

[4] Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Abstract

Advances in imaging technology in the beginning of the twenty-first century have opened the floodgates on the availability of high-quality information on structure and functionality. Largely, this progress was enabled by computer-assisted methods operation, data acquisition, and analysis. From the microscope hardware perspective, high-resolution methods routinely resolve atomic positions with approximately picometer precision, allowing for quantitative measurements of individual bond lengths and angles. Similarly, functional imaging often leads to multidimensional data sets containing partial or full imaging and spectral information on the properties of interest, acquired as a function of multiple parameters (time, temperature, or other external stimuli). We present a new computational infrastructure for advanced analysis of multi-dimensional spectral and imaging materials data – the Bellerophon Environment for Analysis of Materials (BEAM). BEAM software system will, for the first time, enable scientists and users at ORNL's Center for Nanophase Materials Sciences to leverage the integrated computational power of ORNL's Compute And Data Environment for Science platform with HPC resources at the Oak Ridge Leadership Computing Facility to perform near real-time, scalable data analysis of multi-dimensional experimental data through a web-deliverable Java application. At the core of BEAM system is a web and data server, enabling multiple concurrent users to securely access and upload data, execute materials science workflows, and interactively engage analysis artifacts. Furthermore, BEAM offers long-term data management services utilizing CADES large-scale storage system allowing users the ability to easily manipulate remote directories and uploaded data in their private data storage area as if they were browsing locally.

Acknowledgements

This work has been supported by the Laboratory Directed Research and Development (LDRD) program at Oak Ridge National Laboratory. ORNL is managed by UT-Battelle, LLC for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725. We would also like to acknowledge ORNL's John Quigley and Ken Barker for their assistance with standing up the BEAM infrastructure on CADES.

Statistical Thermodynamics with Point Defects in 2-Dimensional Materials

Nicholas Cross[1], Lei Liu[2], Ali Mohsin[2], Wolfgang Windl[3], Gong Gu[2], Gerd Duscher[1,4]

[1.] Department of Materials Science and Engineering, the University of Tennessee, Knoxville, TN 37996, United States
[2.] Department of Electrical Engineering and Computer Science, the University of Tennessee, Knoxville, TN 37996, United States
[3.] Department of Materials Science Engineering, Ohio State University, Columbus, Ohio 43210, United States
[4.] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

This work employs a novel, direct observation technique to determine the point defect concentration in monolayer boron nitride (BN) films. Using this technique the stoichiometry of the BN samples will be determined. The results; along with, density function theory (DFT) will be used to determined changes in the band structure, based on the stoichiometry and relative concentration of point defects. BN films were grown through a chemical vapor deposition (CVD) process and to achieve large, contamination free areas were transferred onto microscopy grids using a direct transfer method. Atomic-resolution images were obtained using the state-of-the-art UltraSTEM 100 at 60 kV acceleration voltage, with fifth-order aberration correcting capabilities. This gives the ability to accurately distinguish between boron and nitrogen atoms. A python program was created to assist in analyzing the images. The key features of the program are to count atomic pairs, identify potential vacancies and anti-sites and keep track of these metrics. Preliminary data and their comparison with DFT results suggests that the BN films in consideration are stoichiometric with their Fermi level lying in the range of 3.3 to 3.5 eV, relatively close to the conduction band.

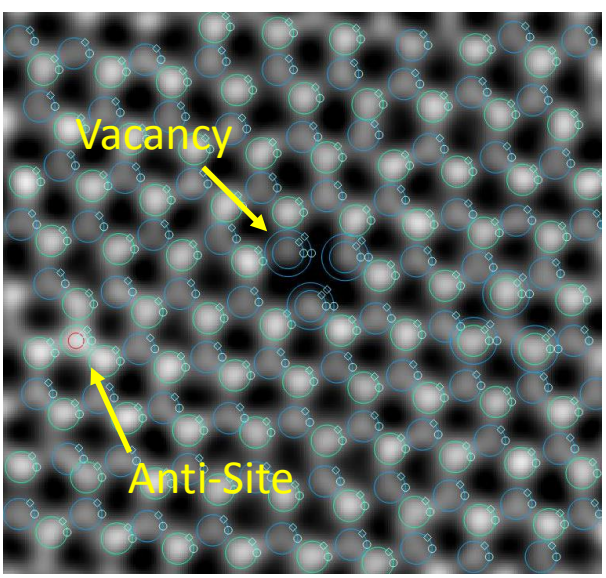


Figure 1: Monolayer BN lattice analyzed using the computer assisted atom counting (CAAC) program. Image has been processed using a Lucy-Richardson deconvolution using a 0.16 nm probe diameter. Green circles indicate atoms identified as nitrogen by the program and blue being boron. A nitrogen anti-site present has been detected and labeled with a red marker while the under-coordinated boron atoms surrounding a nitrogen vacancy are easily visible by the larger concentric blue circles around them. Atoms and defects are then saved to the image.

A Novel Spectroscopy Technique for Ultrafast Polarization Switching in Ferroelectrics

Suhas Somnath, Alexei Belianinov, Sergei V. Kalinin, Stephen Jesse

Institute for Functional Imaging of Materials, Center for Nanophase Materials Sciences, Physical Sciences Directorate, Oak Ridge National laboratory, Oak Ridge, TN 37831-6131

Polarization switching in ferroelectric and multiferroic materials forms the basis for the next generation of electronic devices such as race-track memories, field effect transistors, and tunneling devices. In these materials, the switching mechanisms are highly sensitive to the local defects and structural imperfections at the micro and nanometer scale which have undesirable effects on ferroelectric domains. These considerations necessitated the development of Piezoresponse Force Microscopy (PFM) techniques to measure and manipulate local polarization states. However, the current state-of-art PFM spectroscopy techniques suffer from serious compromises in the measurement rate, voltage and spatial resolutions since they require the combination of a slow (~ 1 sec) switching signal and a fast (~ 1 – 10 msec) measurement signal. Furthermore, transients in the cantilever response at higher vibrational modes and harmonics are lost since the signal from only a single, or a narrow band of frequencies is typically acquired. We report on a fundamentally new approach that combines the complete acquisition of the cantilever response signal with intelligent signal filtering techniques to directly measure material strain in response to the probing bias. Our technique enables precise spectroscopic imaging of the polarization switching phenomena 3,500 times faster than currently reported methods. The improved measurement speed enables dense 2D maps of material response with minimal drift in the tip position.

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.

DIRECT MEASUREMENT OF BIOLOGICAL ENERGY LANDSCAPES USING BOLTZMANN'S EQUATION

Todd Sulchek[1], Ahmad Haider[1], Daniel Potter[1],
1. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta

Introduction

Atomic force microscopy offers an unprecedented ability to determine adhesion forces between individual biological molecules due to its highly sensitive ability to measure and apply forces. However the direct mapping of biomolecular energy potentials between two molecules and under equilibrium conditions is more challenging. We have recently developed a technique using atomic force microscopy to directly map the intermolecular energy landscape of a biotin-avidin interaction. The method utilizes Brownian fluctuations of a sensitive microcantilever probe in close proximity to the interaction energy potential of biotin and avidin that are decorated on the tip and substrate surfaces, respectively. By recording subtle deviations from the harmonic cantilever vibrations, we can reconstruct entire energy landscapes of biotin-avidin interactions, including rare, meta-stable states.

Materials and Methods

Silicon nitride cantilevers (MSCT, Bruker, California) were functionalized with short-chained PEG-27-biotin, and a monolayer of avidin was physically adsorbed to freshly cleaved mica (Gruber-Ebner protocol). Cantilever D, with a resonance frequency, f_0, between 10 and 13 kHz in liquid, was used to obtain force-distance curves, which were collected at 40 to 50 kHz, four times f_0, satisfying the Nyquist sampling theorem. To obtain large data sets, the force curves were collected at scanning at 0.02 Hz (100 nm force distance, 2 nm/s z-piezo translation rate) and the cantilever was equilibriated to ensure drift was less than 7 Å/min.

Results

The mapping of interaction energy landscapes via variation of Brownian fluctuations is based upon previously reported methods examining chemical interactions [1-2]. Data processing was performed by routines written in MATLAB (Mathworks Inc.). Figure 1 below shows the energy landscape reconstruction approach.

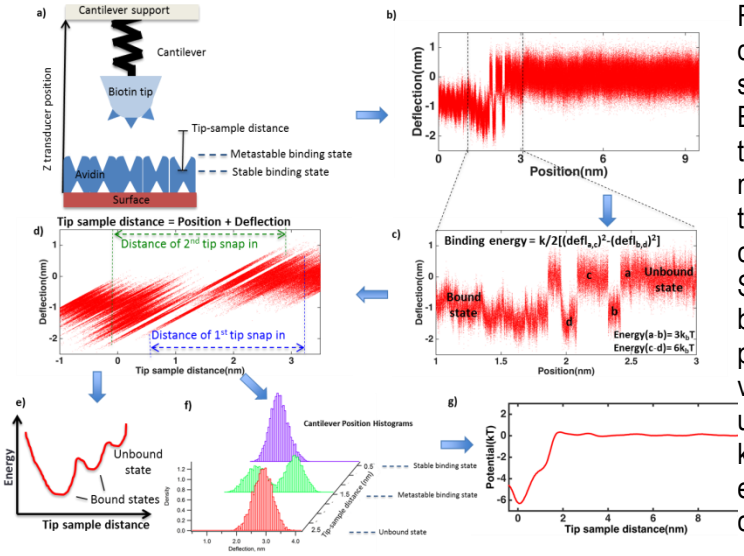


Figure 1: (a) Schematic of a cantilever tip decorated with biotin over an avidin coated substrate (b) Overall approach curve including Brownian fluctuations (c) Zoomed in section of the approach curve showing presence of metastable states (d) Transformation of position to tip-sample-distance (tsd) to account for cantilever fluctuations at each position (e) Schematic of energy landscape of multiple bound states. (f) Histogram of the cantilever positions during fluctuations at different tsd values. (g) Computed energy landscape (U), using Boltzmann's equation [U= -k_bTlog(probability(tsd))]. Tip-sample interaction energy computed after subtracting the cantilever harmonic potential.

The interaction landscape is needed to fully understand the complexity of molecular binding, yet rare binding states are easily missed during atomic force microscopy binding. These methods can identify energy landscapes during rare binding pathways through metastable events which are sampled infrequently. In contrast, the analysis of the conventional force-distance curve typically records only the bound and unbound state of interactions, with little ability to observe meta-stable states.

References: [1] Ashby P.D., Lieber C. L., J Am. Chem. Soc., 126:16973-16980, 2004. [2] Willemsen, O.H., Kuipers, L. et al., J Langmuir, 16:4339-4347, 2000.

Van der Waals Epitaxial Growth of Two-Dimensional Single-Crystalline GaSe Domains on Graphene

*Xufan Li,[1] Leonardo Basile,[1,2] Bing Huang,[1] Cheng Ma,[1] Jaekwang Lee,[1] Ivan V. Vlassiouk,[3] Alexander A. Puretzky,[1] Ming-Wei Lin,[1] Mina Yoon,[1] Miaofang Chi,[1] Juan C. Idrobo,[1] Christopher M. Rouleau,[1] Bobby G. Sumpter,[1] David B. Geohegan,[1] Kai Xiao[1]**

[1]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

[2]Departamento de Física, Escuela Politécnica Nacional, Quito, Ecuador.

[3]Energy & Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

*To whom correspondence should be addressed: E-mail: xiaok@ornl.gov

Two-dimensional (2D) van der Waals (vdW) heterostructures are a family of artificially-structured materials that promise tunable optoelectronic properties for devices with enhanced functionalities. Compared to transferring, direct epitaxy of vdW heterostructures is ideal for clean interlayer interfaces and scalable device fabrication. Here, we report the synthesis and preferred orientations of 2D GaSe atomic layers on graphene (Gr) by vdW epitaxy. GaSe crystals are found to nucleate predominantly on random wrinkles or grain boundaries of graphene, share a preferred lattice orientation with underlying graphene, and grow into large (tens of microns) irregularly-shaped, single-crystalline domains. The domains are found to propagate with triangular edges that merge into the large single crystals during growth. Electron diffraction reveal that approximately 50% of the GaSe domains are oriented with a 10.9° interlayer rotation with the underlying graphene. Theoretical investigations of interlayer energetics reveal that this interlayer rotation is the most energetically preferred vdW heterostructure. In addition, strong charge transfer in these GaSe/Gr vdW heterostructures is predicted, which agrees with the observed enhancement in the Raman E^2_{1g} band of monolayer GaSe and highly-quenched photoluminescence compared to GaSe/SiO_2. Despite the very large lattice mismatch of GaSe/Gr through vdW epitaxy, the predominant orientation control and convergent formation of large single-crystal flakes demonstrated here is promising for the scalable synthesis of large-area vdW heterostructures for the development of new optical and optoelectronic devices.

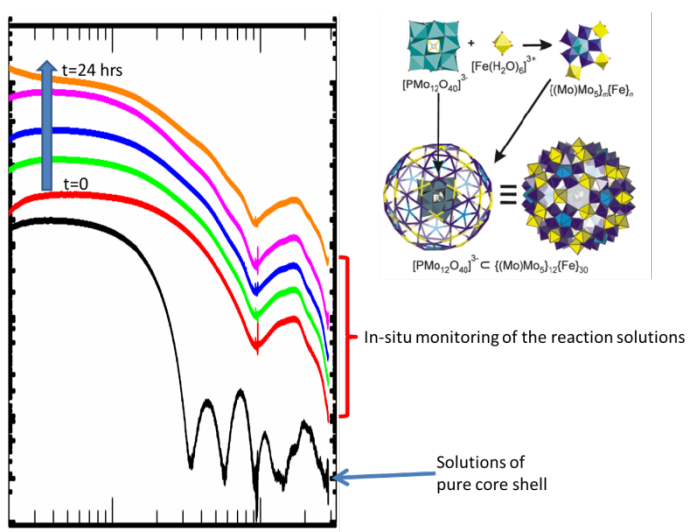
Synthesis science and theoretical studies sponsored by the Materials Science and Engineering Division, Office of Basic Energy Sciences, U.S. Department of Energy. Materials characterization conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. L.B. acknowledges the financial support of the National Secretariat of Higher Education, Science, Technology and Innovation of Ecuador (SENESCYT). J.L. acknowledges support from ORNL Laboratory Directed Research and Development. This research used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the US DOE (contract no. DE-AC02-05CH11231).

Uncover the Template Effect in the Synthesis of Gigantic Molecular Clusters

Panchao Yin
Oak Ridge National Laboratory

Due to their redox properties, large sizes, high negative charges, and nucleophilicity, polyoxometalates (POMs), a large group of metal oxide clusters with well-defined molecular structures, have been attracting more and more interest for their wide applications as catalysts, photo-electronic/magnetic materials, and medicines.[1] Although these nano-scaled molecular clusters are of varied topologies and morphology, they are usually starting from the self-assembly of simple small organic ligands or metal-oxo anions (e.g. MoO_4^{2-}). Interestingly, a tiny variance of the solution parameters (e.g. pH, ionic strength, or temperature) could lead to the obtaining of completely different molecular clusters, which are still beyond of our knowledge on physical and inorganic chemistry.[2] Only the robust molecular clusters, which can survive during the crystallization process, can be observed and reported to the science community since single-crystal X-ray diffraction was the only way to characterize the clusters till today. However, lots of information of the clusters is actually missed because: 1) not all the clusters can be crystallized; 2) the clusters might decompose to form other species during the crystallization process.

On the other hand, POM scientist proposed that there is a so-called chemical evolution in the solutions of polyoxometalates.[3] Some gigantic spherical and wheel type POMs are considered to derivative from some simple small POM ions by inheriting their symmetries. It is assumed that the small POMs serve as template and the building units grow around them to form the large POMs.[3-5] However, no direct evidence has been provided. Additionally, there is no explanation on the possible mechanism of the template effect. The authors have succeeded in applying Small-angle X-ray scattering (SAXS) technology in CNMS and Argonne National Laboratory to monitor the reaction solutons. Carefully fitting with built models, the monitoring results show the continuous growth of large POMs shell around the 'template'. Combined with neutron scattering study, the drive force for such template-based synthesis is confirmed to be water bridged hydrogen bonding.



(1) Hill, C. L. *Chem. Rev.* **1998**, *98*, 1.

(2) Long, D.-L.; Burkholder, E.; Cronin, L. *Chem. Soc. Rev.* **2007**, *36*, 105.

(3) Miras, H. N.; Cooper, G. J. T.; Long, D.-L.; Bögge, H.; Müller, A.; Streb, C.; Cronin, L. *Science* **2010**, *327*, 72.

(4) Qiu, J.; Ling, J.; Sui, A.; Szymanowski, J. E. S.; Simonetti, A.; Burns, P. C. *J. Am. Chem. Soc.* **2011**, *134*, 1810.

(5) Todea, A. M.; Szakács, J.; Konar, S.; Bögge, H.; Crans, D. C.; Glaser, T.; Rousselière, H.; Thouvenot, R.; Gouzerh, P.; Müller, A. *Chem. Eur. J.* **2011**, *17*, 6635.

First Principle Study of Thermal Transport at Graphene and Hexagonal Boron Nitride Interfaces

Zhequan Yan[1], Liang Chen[1], Mina Yoon[2] and Satish Kumar[1]

[1]*G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, United States*

[2]*Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA*

Hexagonal boron nitride (h-BN) is a promising substrate for the graphene based nano-electronic devices owing to its planar hexagonal lattice structure and atomically smooth surface which has a small lattice mismatch with the graphene. Graphene sandwiched between h-BN layers could remove the equivalence of two carbon atoms in the unit cell to open a band gap and change the electronic properties of graphene. Therefore, h-BN has the potential to lead to breakthrough in the applications of graphene based devices. In this study, we investigate phonon transport at the interface of graphene and h-BN using first principle density functional theory (DFT) and atomistic Green's function (AGF) simulations considering the influence of different lattice stackings. The h-BN/graphene/h-BN sandwiched structures are first optimized using DFT simulations, and then the phonon dispersion relations and phonon density of states of graphene and h-BN are calculated using this optimized structure in order to explore the phonon coupling mechanism at the interfaces. We perform atomistic Green's function (AGF) simulations to predict the phonon transmission and thermal boundary conductance (TBC) across graphene/h-BN interfaces considering different lattice stackings. In addition, the contributions of different phonon modes to the TBC in different h-BN/graphene/h-BN sandwiched structures are investigated by computing frequency and wave-vector dependent transmission function. We find that the in-plane acoustic modes have the dominant contributions to the TBC for the interfaces with the carbon atom located directly on top of the boron atom (C-B matched) because of the low interfacial gap. As the interfacial gap increases, the in-plane modes' contribution decreases leading to increase in relative contribution of the out-of-plane acoustic modes, e.g., in the structures with the carbon atom directly on top of the nitrogen atom (C-N matched). We find that the C-B matched interfaces have stronger phonon-phonon coupling than the C-N matched interfaces, even though C-N atoms have more intense force interactions. The TBC can be enhanced by more than 50% by changing the lattice stacking arrangements from C-N matched to C-B matched. The findings in this study will provide insights to understand the phonon transport mechanism at h-BN/graphene/h-BN interfaces, and to engineer these interfaces to enhance heat dissipation in graphene based electronic devices.

Role of Disorder in Proton Conduction in Oxide Materials

Janakiraman Balachandran[1], Craig Bridges[3], Yongqiang Cheng[2], Ganesh Panchapakesan[1]

Solid-oxide electrolytes with high proton conductivity can help to decrease the operating temperature -- in turn greatly improving the safety and performance of solid oxide fuel cells. In this work, we describe our computational study to understand how material structure, especially disorder in local material structure influences the proton adsorption and transport in solid oxide materials. In particular we focus on two important class of oxides namely – Perovskites ($BaZrO_3$) & disordered Fluorites ($La_{5.4}WO_{11.1}$). A combination of theoretical methods, such as density functional theory (DFT) based molecular dynamics, nudged-elastic-bands and cluster-expansion calculations were employed to enable us understand how the disorder in atomic structure influences the transport properties. The results obtained from the computational study correlates well with the experimental studies performed with neutron scattering. A systematic understanding of the structure-property relationship would enable us to design better electrolyte materials with improved safety and performance.

[1]Center for Nanophase Material Sciences, ORNL.
[2]Spallation Neutron Source, ORNL
[3]Materials Chemistry Group, ORNL

Theoretical predication of two-dimensional electrides

Wenmei Ming and Mina Yoon

CNMS, ORNL

Electride, a new type of ionic compound with excess electrons at empty space of material, has received increasing research interest in recent years due to its promising applications for electron emitters, surface catalyses and high mobility electronic devices. Already-existing two-dimensional (2D) electride candidates, however, are very limited to be only a few among layered Alkaline-Earth Nitrides/Carbides. Here, we have extended the possibility of 2D electrides in both structure and stoichiometry by design, using density functional theory calculation combined with particle swarm optimization algorithm. Systems of M_xN_y (M = group IA, IIA and IIIB element, N = VA, VIA, VIIA elements) having imbalanced oxidation numbers were investigated. We have found that (1) strong dependence of structural stability on local cation-anion bonding symmetry, which is sensitively affected by the relative size of cation/anion and crystal structure; (2) The spatial localization of states around Fermi-energy shows controllable variation as a function of atomic configuration of the sandwiching atomic layers. It is originated from the tunable potential profile of the empty space by the sandwiching atomic layers; (3) the stabilization of excess electrons at the empty space can be tuned by the thickness of electride film. Our results will shed new light on searching for better electrides and understanding on design physics of electrides for practical applications.

Predictive Power of Density Functional Theory in Finite-Temperature Hydrogen Adsorption/Desorption Thermodynamics with Corrective Energies and Potential Surfaces

Changwon Park, Bobby Sumpter, Mina Yoon

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

For the past few decades, density functional theory (DFT) has been widely employed to study the gas adsorption properties of surface-based/nanoscale structures. However, recent indications are sufficient to raise questions about the trustworthiness of the literature values, especially in terms of the DFT exchange-correlation (XC) functional. Using hydrogen adsorption on metalloporphyrin-incorporated graphenes (MPIG) as an example, we performed a benchmark study on the XC functional dependence of their thermodynamic properties of hydrogen adsorption, explicitly including entropic as well as energetic contributions [1]. We find that thermodynamic properties are strongly XC functional dependent, with high dependence not only for the energetic but also for the entropic contributions. Using chemical potential as a descriptor we identify required calculational accuracy with which DFT can serve as a predictive tool for experimental guidance.

This work was supported by theme research 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.

References

[1] "Finite-Temperature Hydrogen Adsorption and Desorption Thermodynamics Driven by Soft Vibration Modes", S. J. Woo, E. S. Lee, M. Yoon, and Y. H. Kim, Phys. Rev. Lett. **111,** 066102 (2013).

Tailoring the Growth of Organic Thin Films by Selective Orbital Coupling

Sean R. Wagner[1], Bing Huang[2], Changwon Park[2], Jiagui Feng[1], Mina Yoon[2], and Pengpeng Zhang[1]

[1] Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824-2320, USA
[2] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

Control of highly ordered organic molecular thin films with extended π systems is currently of intense interest for integrating molecules into modern electronics due to their tunable nature. Selection of molecules and substrates can lead to desired transport properties such as charge transfer, charge injection, exciton diffusion, etc., at the hetero-interface, which is crucial to the development of organic and molecular electronics. However, achieving large-scale molecular ordering remains a significant challenge that requires a thorough understanding of the growth mechanism.[1,2] Combing scanning tunneling microscopy and density functional theory, we show that by controlling the degree of orbital hybridization from negligible to strong coupling between phthalocyanine molecules and the deactivated Si surface via the selective *p-d* orbital coupling, we can tune the molecular ordering and orientation at the hetero-interface.[3] This offers the possibility of driving the critical interactions to an ideal balance, leading to ordered molecular thin films on a technologically relevant substrate for silicon-based devices.

1. S. R. Wagner, R. R. Lunt and P. P. Zhang, *Phys. Rev. Lett.* **110**, 086107 (2013).
2. S. R. Wagner and P. P. Zhang, *J. Phys. Chem. C* **118**, 2194 (2014).
3. S. R. Wagner, B. Huang, C. Park, J. Feng, M. Yoon, and P. P. Zhang, *under review in Phys. Rev. Lett.* (2015).

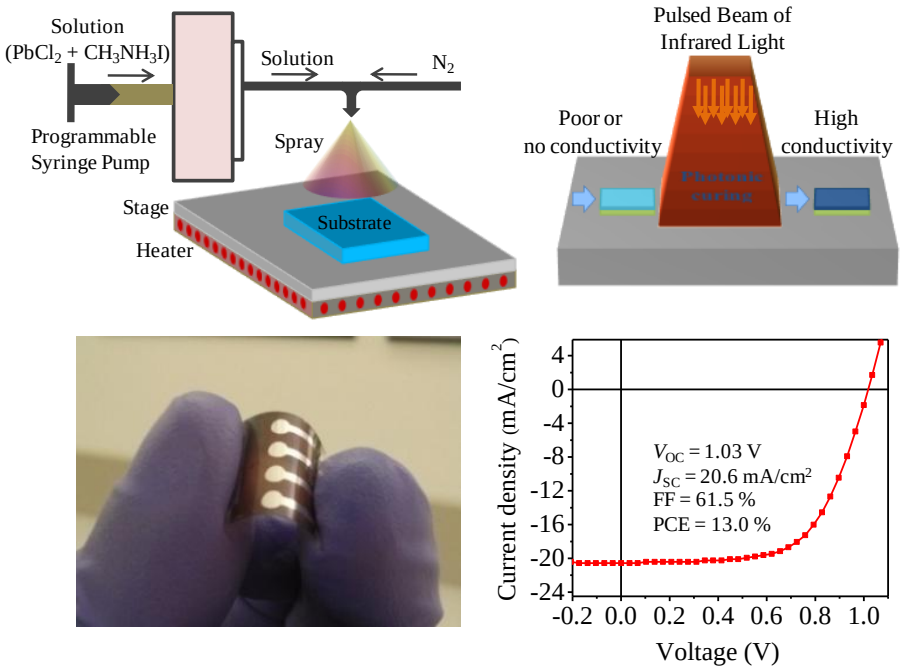
Experimental work (S. R. W., J. F., and P. P. Z.) is funded by the U. S. Department of Energy (DOE) Office of Science Early Career Research Program (DE-SC0006400) through the Office of Basic Energy Sciences. Theory work (B. H., C. P. and M. Y.) conducted at Oak Ridge National Laboratory is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. DOE.

High-Performance Flexible Perovskite Solar Cells by Using a Combination of Ultrasonic Spray-Coating and Photonic Curing

Sanjib Das,[†] Bin Yang,[‡] Gong Gu,[†] Pooran C. Joshi,[§] Ilia N. Ivanov,[‡] Christopher M. Rouleau,[‡] Tolga Aytug,[⊥] David B. Geohegan,[‡] and Kai Xiao[*,‡]

[†]Department of Electrical Engineering and Computer Science, University of Tennessee. [‡]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory (ORNL). [§]Materials Science and Technology Division, ORNL. [⊥]Chemical Sciences Division, ORNL. [*]E-mail: xiaok@ornl.gov

Realizing the commercialization of high-performance and robust perovskite solar cells urgently requires the development of economically scalable processing techniques. Here we report a high-throughput ultrasonic spray-coating (USC) process capable of fabricating perovskite film-based solar cells on glass substrates with power conversion efficiency (PCE) as high as 13%. Perovskite films with high uniformity, crystallinity, and surface coverage are obtained in a single step. Moreover, we report USC processing on TiO_2/ITO-coated polyethylene terephthalate (PET) substrates to realize flexible perovskite solar cells with PCE as high as 8.1% that are robust under mechanical stress. In this case, a photonic curing technique was used to achieve a highly-conductive TiO_2 layer on flexible PET substrates for the first time. The high device performance and reliability obtained by this combination of USC processing with optical curing appears very promising for roll-to-roll manufacturing of high-efficiency, flexible perovskite solar cells.[1]



[This research was conducted at the Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility. S. D., P. J., and T. A. acknowledge support provided by a Laboratory Directed Research and Development award from Oak Ridge National Laboratory]

1. **S. Das** *et al.*, High-Performance Flexible Perovskite Solar Cells by Using a Combination of Ultrasonic Spray-Coating and Low Thermal Budget Photonic Curing, *ACS Photonics* 2015, 2, 680.

Quantum Model of Plasmon-Quantum Emitter Interaction in the Strong-Coupling Regime

Roderick B Davidson II[1,2], Pavel Lougovski[1], Ben J. Lawrie[1]
1Quantum Information Science Group, Oak Ridge National Laboratory, Oak Ridge, TN, 37830-8050
2 Department of Physics and Astronomy, Vanderbilt University, Nashville, TN, 37235-1807
roderick.b.davidson@vanderbilt.edu

Strong coupling (SC) between atoms or quantum dots and photons in optical cavities enables the optical transduction of atomic nonlinearities at the single photon level in traditional cavity-quantum-electrodynamics. The concept that a plasmonic resonator could strongly couple to a single quantum dot or a dye molecule as an analogue to an optical cavity could enable similar nonlinear optics over broadly tunable plasmonic resonances under ambient conditions. We will present an experimental-design-driven quantum model of quantum emitter-plasmon interactions in the presence of decoherence that allows us to quantitatively describe observed experimental results and guide our experimental effort towards achieving strong plasmonic coupling to an individual quantum emitter.

The time evolution of the density matrix of the combined emitter-plasmon system $\boldsymbol{\rho_{EP}}$ is then described in the quantum master equation by,

$$\frac{d}{dt}\boldsymbol{\varrho_{EP}} = -\frac{i}{\hbar}[\boldsymbol{H_{0E}} + \boldsymbol{H_{0P}} + \boldsymbol{H_{EPint}}, \boldsymbol{\rho_{EP}}] + \frac{\Gamma_0+\Gamma_{pl}}{2}\boldsymbol{\mathcal{L}_1\rho_{EP}} + \frac{\kappa}{2}\boldsymbol{\mathcal{L}_2\rho_{EP}}, \quad (1)$$

where $H_{0E} = \hbar\omega_{ab}\sigma^\dagger\sigma$ is the Hamiltonian describing a two level quantum emitter with the transition frequency ω_{ab} and $H_{0P} = \hbar\sum_k \omega_k\, a_k^\dagger a_k$ is the Hamiltonian for the free modes supported by the plasmonic nanostructure enumerated by the index k. The interaction Hamiltonian $\boldsymbol{H_{EPint}} = \hbar\sum_{\boldsymbol{k}} g_{\boldsymbol{k}}\,(a_{\boldsymbol{k}}^\dagger\sigma + a_{\boldsymbol{k}}\sigma^\dagger)$ describes the dipole interaction between the emitter and plasmons in the rotating wave approximation and $g_{\boldsymbol{k}}$ are correspondent coupling constants. The Lindblad operators $\mathcal{L}_1$ and $\mathcal{L}_2$ describe the decoherence channels due to spontaneous emission *(Γ_0)*, and non-radiative decay *(Γ_{pl})* of the quantum emitter ($\mathcal{L}_1$) and plasmon mode decay *(κ)* due to thermal effects ($\mathcal{L}_2$).

Eq. (1) can be solved numerically given the set of parameters $(\mathbf{g_k}, \boldsymbol{\Gamma_0}, \boldsymbol{\Gamma_{pl}}, \boldsymbol{\kappa})$. We are particularly interested in the plasmon dynamics in the SC regime (i.e. when $\mathbf{g_k}^2/\boldsymbol{\kappa}(\boldsymbol{\Gamma_0} + \boldsymbol{\Gamma_{pl}}) \gg \mathbf{1}$). Therefore, our primary goal is to optimize the experimental design of the plasmonic nanostructure such that it yields the highest coupling strength possible. The geometry of plasmonic nanostructures can be tuned for optimal mode-volume and electric-field intensities and the related parameter space can be explored numerically using finite-difference time-domain (FDTD) simulations. We note that the decay parameters $\boldsymbol{\Gamma_{pl}}$ and $\boldsymbol{\kappa}$ also depend both on the choice of the plasmonic nanostructure and the emitter.

Here we treat three experimental plasmonic geometries for coupling to quantum emitters using this quantum model. Fig. 1 (a-c) shows SEM images of split-ring resonators (SRR), bow-tie antennas, and a nanohole array. Each of the plasmonic geometries were designed to be resonant at the transition energies of quantum dots which can be deterministically placed within the electric-field 'hotspots' that they create. However, the energy of the plasmon is broadly tunable over the optical frequency range.

By modelling these plasmonic structures using experimentally and numerically determined parameters in Eq. 1, we will be able to fabricate and optimize nanostructures exhibiting strong plasmonic coupling to individual quantum emitters. This work will therefore provide a realistic framework for the deterministic generation of optical nonlinearities at the single photon level and the preparation of plasmons exhibiting quantum statistics.

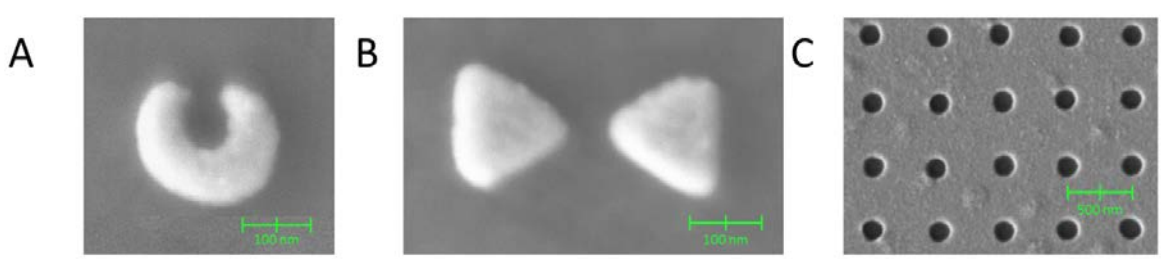


Figure 1: Three plasmonic geometries made with electron beam lithography for probing coupling mechanisms between plasmons and quantum emitters. A - Spilt ring resonator. B – Bow-tie antenna. C – Nanohole array.

All-Optical-Field-Induced Second-Harmonic Generation

Roderick B Davidson II[1,2], Anna Yanchenko[3], Jed Ziegler[1], Sergey M. Avanesyan[1], Richard F. Haglund Jr.[1]
1 Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235-1807
2 Oak Ridge National Laboratory, Oak Ridge, TN, 37830-8050
3 Department of Physics, University of Virginia, Charlottesville, VA, 22904-4714
roderick.b.davidson@vanderbilt.edu

Efficient frequency modulation techniques are crucial to the development of plasmonic metasurfaces for information processing and energy conversion. Nanoscale electric-field confinement in optically pumped plasmonic structures enables stronger nonlinear susceptibilities than are attainable in bulk materials. The interaction of three distinct electric fields in $\chi^{(2)}$ optical processes allows for all-optical modulation of nonlinear signals. Here we demonstrate efficient second harmonic generation (SHG) in a serrated nanogap plasmonic geometry that generates steep electric field gradients within a dielectric material. We utilize an ultrafast optical pump to control the plasmonically induced electric-fields and to generate bandwidth-limited second-harmonic pulses driven by the control pulses. All-optical control of these designer plasmonic metasurfaces enables ultrafast switching technologies for on-chip nonlinear processes.

In our all-optical-field-induced SHG experiment, a serrated nanogap (SNG) structure, is illuminated with two orthogonal pulses controlled by a spatial light modulator, Figure 1a. When the gap is filled with a dielectric medium, Figure 1B, the plasmonic excitation polarizes the material and decreases the inversion symmetry of its electronic structure. This creates a larger $\chi^{(2)}$ within the dielectric and enhances the second-harmonic signal from the dielectric.

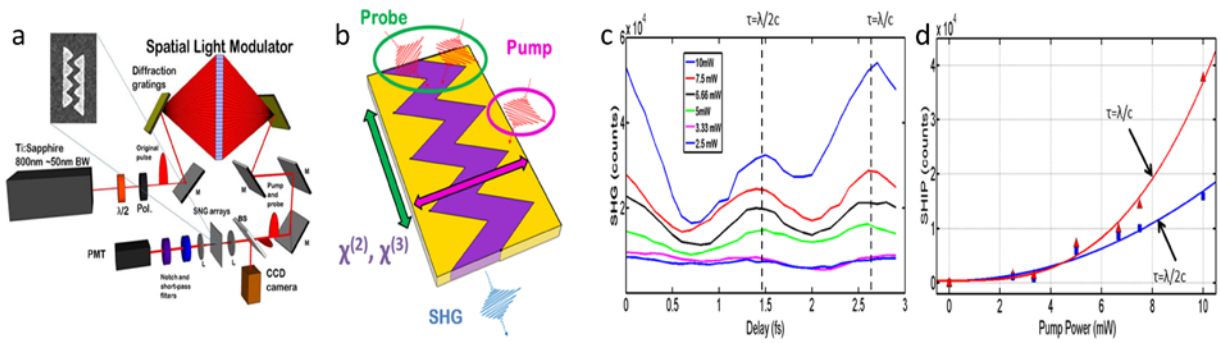


Figure **1**: A – SEM images of the SNG nanoparticles. B – FDTD simulation of a horizontally excited SNG plasmon. C – All-optical-field-induced SHG from a plasmonically polarized dielectric. The pump polarization axis is shown by the black arrows.

In this experiment, the nanogap is filled with poly(methyl methacrylate) (PMMA) and probed using second-harmonic interferometric pump-probe spectroscopy (SHIP). Two degenerate pulses were created with orthogonal polarizations using a spatial light modulator (SLM). One of these pulses was horizontally polarized (perpendicular to the gap) and used as a pump while the other was vertically polarized (parallel to the gap) and used to probe the plasmon. The SHG signal was monitored while scanning the delay between the pump and the probe pulses introduced by the SLM. The excitation sources used for both the pump and the probe were 30 fs pulses from a Ti:Sapphire laser tuned to 800nm.

In figure 1c the SHIP signal for single optical cycle shows a high-contrast interference pattern with a period half that of the fundamental frequency. These SHG peaks result from interference between the probe and the plasmonic oscillations that are the driving external electric field. The period of the SHIP signal is half that of the fundamental because the hotspots experience peak electric-field strengths when the delay is at the λ and $\lambda/2$ points. In order to view the dependence of the SHIP signal on the pump pulse power and demonstrate the dependence of $\chi^{(2)}$ on the plasmon strength, the probe pulse was kept at a constant 10mW while the pump pulse power was varied, Figure 1d. These results have demonstrated a means of generating switchable nonlinear light pulses using entirely optical power sources.

Na-ion Conducting Membranes for Non-Aqueous Redox Flow Batteries: Vibrational Spectroscopy Studies

Jagjit Nanda, Rose Ruther and Frank Delnick

Materials Science and Technology Division

Oak Ridge National Laboratory, Oak Ridge TN USA

Recently we proposed a new concept for high energy density redox flow batteries that utilize two highly soluble polyaromatic hydrocarbons to mediate reversible redox reactions on the surface of high capacity solid anode materials located in flow reactor reservoirs. Among other things, the success of this technology depends on the development of a membrane separator that has high Na^+ or Li^+ ion conductivity with minimal cross-over effect. In addition the membrane should also be chemically stable with respect to highly reactive anion radical in this case, biphenyl. In an attempt towards achieving such goals, we first improve the Na^+ ion conductivity of polyethylene oxide (PEO) membrane by using tetraethyleneglycol Dimethylether (TEGDME) as a plasticizer with sodium triflate (NaTFS) as salt. Our results show 3 orders of magnitude higher conductivity compared to NaTFS-PEO films. In general films with more plasticizer showed less trans-granular impedance at low temperature, and higher amorphous conduction at higher temperatures. In this study we report Raman-microscopy combined with FT-IR spectroscopy to characterize the changes in the chemical structure & coordination effect of PEO when blended with the plasticizer and salt. Micro-Raman imaging/mapping also provides spatial information about homogeneity (or lack of) for each phase when they are mixed. This could provide more insights into the chemical stability and ion-transport mechanism in such polymer composites.

This work is supported by Dr. Imre Gyuk, Manager, Energy Storage Program, Office of Electricity Delivery and Reliability, Department of Energy.

The Development of Lanthanum Phosphate Based Magnetic-Luminescent Nanocomposites

Austin Plymill

University of Tennessee

By combining magnetic and optical properties into a single material, a great increase in functionality can be achieved, as this allows for a luminescent material to possess the manipulability of magnetic nanoparticles. Hence, these multifunctional materials have become of significant interest in a wide variety of applications. We have successfully developed nanocomposites composed of superparamagnetic Fe_3O_4 and luminescent $LaPO_4$: X (X = Tb^{3+}, Eu^{3+}, Ce^{3+}, and Pr^{3+}). A coprecipitation process was utilized to create the Fe_3O_4 nanoparticles and a direct precipitation method was used to form the composite particles.

Probing Synaptic Activity through Graphene Optoelectronic Platforms

Rui Wang[1], Bryson M. Brewer[2], Mingjian Shi[3], Deyu Li[2], Donna J. Webb[3,4] and Ya-Qiong Xu[1,5]

[1]*Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, USA*
[2]*Department of Mechanical Engineering, Vanderbilt University, Nashville, TN 37235, USA*
[3]*Department of Biological Sciences and Vanderbilt Kennedy Center for Research on Human Development, Vanderbilt University, Nashville, TN 37235, USA*
[4]*Department of Cancer Biology, Vanderbilt University, Nashville, TN 37235, USA*
[5]*Department of Electrical Engineering, Vanderbilt University, Nashville, TN 37235, USA*

Abstract:

The human brain is built on billions of neurons, which communicate through trillions of highly specialized synaptic junctions that are structurally composed of pre- and postsynaptic terminals. Intriguingly, recent data indicate that individual spines and synapses are unique and can exhibit different properties and activities, leading to sophisticated neuronal networks that enable the extraordinary functionality of our brain. However, the functional significance and underlying molecular mechanisms for distinct synapses are not well understood, pointing to an urgent need to investigate the activities of individual synapses in neuronal networks. Here, we integrated graphene transistors with a neuron-glia co-culture microfluidic platform to study electrical activities of individual synapses through scanning photocurrent measurements. Remarkable photocurrent signals were observed at spots where spines and synapses were located. We also compared our photocurrent measurements with traditional fluorescence imaging approaches to underscore the validity of our approach.

Transduction of Entangled Images by Localized Surface Plasmons

A. M. Marino[1], M. Holtfrerich[1], R.C. Pooser[2], B.J. Lawrie[2], and R. Davidson[2]

1. Homer L. Dodge Department of Physics and Astronomy, The University of Oklahoma, Norman, Oklahoma 73019, USA

2. Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

1. Introduction

The field of quantum plasmonics has attracted broad interest in recent years, motivated by both nanoimaging and sub-wavelength photonic circuits. However, to enable quantum plasmonic imaging or multi-spatial mode parallel quantum information processing, different entanglement sources and nanostructures which exhibit localized surface plasmons (LSP) are required. It was previously shown that quantum noise reduction can be efficiently transmitted by LSPs for a range of wavevectors, but up to now the interface between multi-mode, continuous variable entangled light and localized surface plasmons –a necessary ingredient for continuous variable quantum plasmonic information processing– has not been investigated. Here, we study the interface between continuous-variable (CV) entangled images and localized surface plasmons (LSPs). We show that the transfer of entanglement and quantum information in multispatial mode photons to LSPs and back to photons is a coherent process that preserves the entanglement properties and spatial structure of the light. Finally, we have demonstrated that distant plasmons on two different substrates have been entangled together by transferring this property from individual light fields into each plasmon independently.

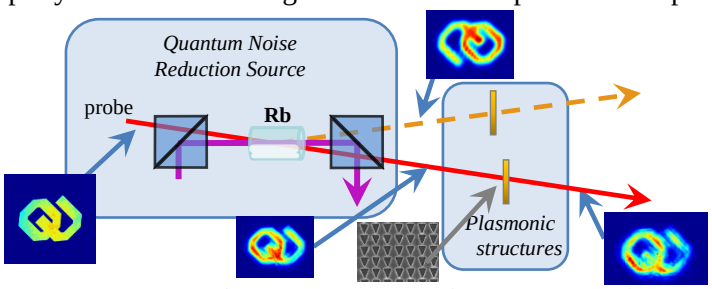


Fig. 1. Experimental setup for the characterization of the transduction of entangled images through a plasmonic structure.

The experimental setup to study the transduction of quantum states of light through a plasmonic structure is shown in Fig. 1. The quantum states are generated through the use of four-wave mixing (FWM) in Rb atoms. We have previously shown that this process can generate highly multi-spatial mode CV entangled beams which we call probe and conjugate. This makes it possible to generate highly entangled images.

We seed the FWM process with an image of the "OU logo" to generate entangled images. The beams are then sent through plasmonic structures which consist of arrays of triangular nanoholes in a silver metal film, after which their entanglement is characterized.

As can be seen in Fig. 1, the plasmoinc structure based on LSPs preserves the spatial properties of the entangled images. The continuous-variable (CV) entanglement between the probe and the conjugate can be characterized thought the inseparability criterion proposed by Duan *et al.*, $I = \langle \Delta \hat{X}_-^2 \rangle + \langle \Delta \hat{Y}_+^2 \rangle < 2$, where $\langle \Delta \hat{X}_-^2 \rangle$ and $\langle \Delta \hat{Y}_+^2 \rangle$ are the amplitude difference and phase sum noises, respectively. According to this criterion, the presence of squeezing in both the amplitude difference and the phase sum is a sufficient condition for CV entanglement.

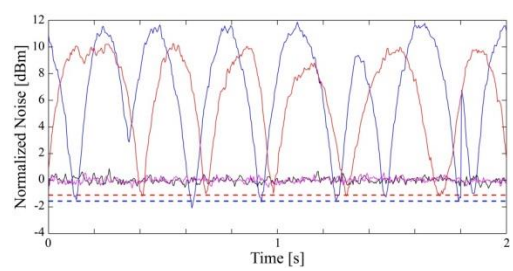


Fig. 2. Entanglement measurements. Intensity difference squeezing (a) before the plasmonic structure (blue trace) and (b) after the plasmonic structure (red trace).

We characterized the entanglement properties before and after transduction through the plasmonic structures, as shown in Fig. 2. The intensity difference noise of the source is only slightly degraded after transduction through the plasmonic structure from 1.5 dB of squeezing (blue trace) to 1.0 dB of squeezing (green trace), which means the entanglement level of the entangled images, $\boldsymbol{I = 1.4}$, is only slightly degraded to $\boldsymbol{I = 1.6}$ by the plasmonic structures. These results show that both the entanglement and spatial properties of the entangled images are preserved after transduction through the plasmonic structures. Given the coherent transfer of quantum information between photons and plasmons, the entanglement is transferred between the probe and the conjugate to entanglement between the two independent plasmonic structures for a short period of time.

Molecular dynamics simulations of Leidenfrost droplets on a vibrating nano-ratchet

Kumar Abhishek[1], Nickolay V. Lavrik[2], Miguel Fuentes-Cabrera[2]
[1]Computer Science and Mathematics Division, Oak Ridge National Laboratory
[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Asymmetrically nanostructured surfaces can function as Brownian ratchets, that is, create a bias in mass or energy flows in response to thermal noise or in a more general case, isotropic excitations. Recently, experimental studies at CNMS have shown that it is possible to induce directional movement of water droplets deposited on a vertically vibrating hydrophobic substrate made of inclined nanopillars. Here we show that classical molecular dynamics, MD, simulations on high-performance computers at ORNL can efficiently be used to simulate this phenomenon. Further, with MD we are able to reveal new phenomena and provide insights into how control the movement further. In particular, it was found that at certain critical amplitude and frequency, the motion of the droplet transits from circular to linear to oscillatory. Current efforts are underway at CNMS to verify whether there is a correlation between these predictions and behaviors of experimentally accessible systems.