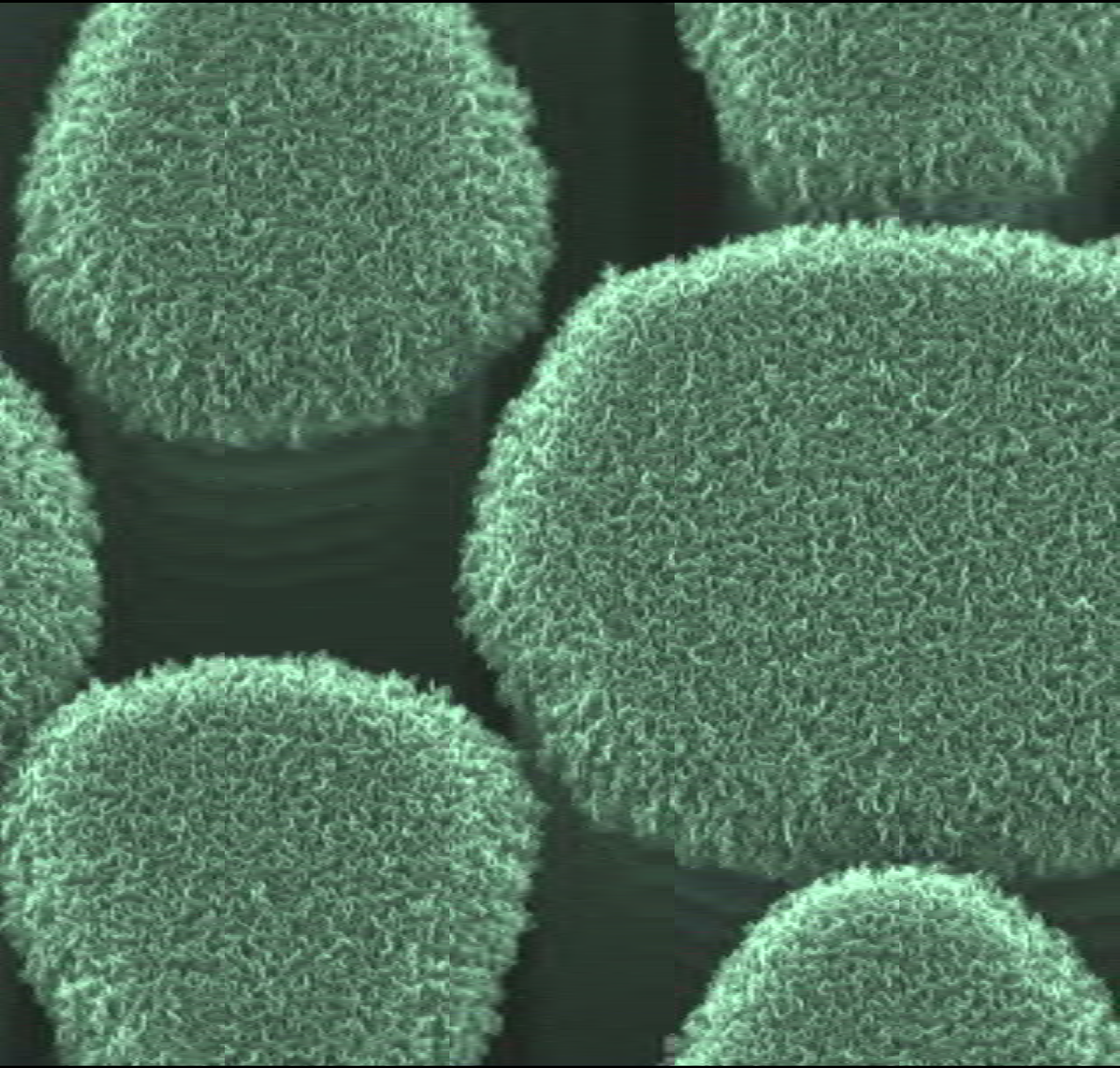
Center for Nanophase Materials Sciences



2012 User Meeting
Agenda and Abstracts

Table of Contents

Cover Image

Conformal coatings of PECVD-grown petal-like carbon on high-aspect ratio Si pillars for separation studies.

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

Agenda

2012 CNMS User Meeting
Oak Ridge National Laboratory
Oak Ridge, Tennessee

Thursday, September 13 at 4pm: Poster Session and Networking (light refreshments) Spallation Neutron Source Auditorium: The 7th edition of *RidgeDance NanoScience Film Festival* will follow at 5:00.

Friday, September 14, 2012

	PLENARY SESSION *Iran Thomas Auditorium, SNS* **Chair**: Sean Smith, CNMS Director	
7:45	Registration and continental breakfast - Posters available for viewing	
8:30	**Welcome and Announcements** (including DOE, ORNL welcomes)	
8:50	"Crystal Design for Organic Semiconductors," **John Anthony,** *U. Kentucky*	
9:30	"Structured Epitaxial Graphene," **- Walter de Heer**, *Georgia Tech*	
10:10	**Break**	
	Track A (Auditorium) **Chair:** Tony Hmelo, Vanderbilt U.	**Track B (CLO, C-156)** **Chair:** Vivek Prabhu, NIST
10:40	**INVITED USER:** "Recent Advances in Focused Electron-Beam Induced Processing using Bulk Liquid Reactants," **J. Todd Hastings** (U. Kentucky)	**INVITED USER:** "Investigating Polyelectrolyte Dendrimer Solutions using Neutron Scattering and Simulations," **Wei-Ren Chen** (Oak Ridge National Laboratory)
11:10	"In Situ Laser Processing in a Scanning Electron Microscope," **Gregory A. Magel** (Oxford Instruments Nanoanalysis)	"Nanopatterned Supported Lipid Bilayer Surfaces as Tools for the Study of Receptor Signaling," **Daniel Stabley** (Emory U.)
11:25	"Surface Chemistry Controlled Defect Engineering in Silicon Nanowires," **Michael A. Filler** (Georgia Tech)	"Conjugated Bottle-Brush Polymers Incoporating P3HT as Brush Side-Chains," **Suk-kyun Ahn** (CNMS)
11:40	**Lunch & Poster Session**	
	Track A (Auditorium) ***continued*** **Chair:** Ichiro Takeuchi, U. Maryland	**Track B (CLO, C-156)** ***continued*** **Chair:** Marco Buongiorno Nardelli, U. North Texas
13:00	**INVITED USER:** "Surfactant Assisted Growth of Smooth Oxides on GaN," **Jon-Paul Maria** (N.C. State)	**INVITED USER:** "Polypeptoids: Synthesis, Characterization and Materials Properties," **Donghui Zhang** (Louisiana State U.)
13:30	"Electronic Structure and Quantum Transport Properties of Layered Heterostructures," **Alejandro Lopez-Bezanilla** (CNMS)	"Scanning Angle Raman Microscopy: Measurements of Polymer Film Thickness and Composition," **Emily Smith** (Iowa State U.)
13:45	"Anomalous High Ionic Conductivity of Nanoporous ß-Li$_3$PS$_4$," **Zengcai Liu** (CNMS)	"Spontaneous Wrinkling-Type Patterns in Azlactone Based Functional Polymer Thin Films," **Muruganathan Ramanathan** (CNMS)
14:00	"Extrinsic Contributions to the Piezoelectric Response of Ferroelectric Nanostructures," **Nazanin Bassiri-Gharb** (Georgia Tech)	"Thermal Transport through Van Der Waals Interfaces between Individual Nanostructures," **Deyu Li** (Vanderbilt U.)
14:15	**INVITED USER:** "Nanoscale Materials Science Challenges for Spin-Torque-Transfer Random Access Memory," **William H. Butler** (U. Alabama)	**INVITED USER:** "Nanoscale Carbon Based Electronic Junction Control Devices," **Andrew G. Rinzler** (U. Florida)
14:45	**User Group Town Hall meeting (*Auditorium*)** **Posters available for viewing**	
16:00	**Adjourn**	

Center for Nanophase Materials Sciences
2012 User Meeting
Poster Session

Thursday, September 13, 2012
4:00 – 5:00p

Posters will also be available for viewing on Friday, September 14

01 **Pillar arrayed chips for planar separation and detection**

Teresa Kirchner,1 Nichole Crane,1 Chris Freye,2 Nickolay Lavrik,2 Michael Sepaniak1

1Department of Chemistry, University of Tennessee, Knoxville, 552 Buehler Hall 1420 Circle Dr , Knoxville TN 37996
2Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN, 37831

02 **Silicon nanopillars for field enhanced surface spectroscopy**

Jennifer Charlton,[1] Sabrina Wells,[1] Michael Kandziolka,[1] Igor Merkulov,[2] Ivan Kravchenko,[2] Nickolay Lavrik,[2] James Bradshaw,[3] and Michael Sepaniak[1]

[1]Department of Chemistry, University of Tennessee, Knoxville, 552 Buehler Hall 1420 Circle Dr , Knoxville TN 37996
[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN, 37831
[3]Y-12 National Security Complex

03 **Extraordinary optical transmission of multimode quantum correlations via localized surface plasmons**

Benjamin Lawrie, Philip Evans, Raphael Pooser

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

04 **Nanophotonics: From novel fabrication technologies to reconfigurable photonics**

Shuren Hu,[1] Judson D. Ryckman,[2] Yang Jiao,[2] Jeremy W. Mares,[2] and Sharon M. Weiss[1,2]

[1]Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235
[2]Department of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, Tennessee 37235

05 **Raman Plasmonic Enhancement based on Biomimetic Metal Nanostructures**

Héctor I. Areizaga,[1] Raymond A. Velez-Calder,[1] Marco A. De Jesús,[1] Michael J. Sepaniak,[2] Nickolay V. Lavrik,[3] Ivan I. Kravchenko[3]

[1]Department of Chemistry, University of Puerto Rico, Mayagüez, P.O. Box 9000, Mayagüez, PR 00681
[2]Department of Chemistry, University of Tennessee, Knoxville, 552 Buehler Hall 1420 Circle Dr , Knoxville TN 37996
[3]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN, 37831

06 **Single-molecule mobility in confined and crowded femtoliter chambers**

C. Patrick Collier

Center for Nanophase Materials Science, Oak Ridge National Laboratory

07 **Directed selfassemblage of soft matter nanostructures on inorganic surfaces**

S. Vespucci,[2] S. Retterer,[1] S. Baschieri,[3] C. Cantale,[3] M. Caruso,[2] C. Dalmastri,[3] C. Lico,[3] L. Mosiello,[3] P. Morales[3]

1Center for Nanoscale Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee
2The NAST Center, Tor Vergata University Unit Viale della Ricerca Scientifica 1, 00136 Roma, Italy
3ENEA, Centro Ricerche Casaccia and NAST Center Via Anguillarese 301 00123 Roma, Italy

08 Bio-inspired Assembly of Silica at the Nanoscale

Juan Pablo Hinestrosa,[1] Jonathan E. Sutton,[2] David P. Allison,[3,4] Mitchel J. Doktycz1,[3]Jamie M. Messman,[1] Scott T. Retterer,[1,3]
[1]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716
[3]Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[4]Department of Biochemistry & Cellular & Molecular Biology, University of Tennessee, Knoxville, TN 37996

09 Fracture Strength of Small Diameter Fibers with FIB and Nano-Tensile Testing

M. Kant and D. Penumadu
Civil and Environmental Engineering, University of Tennessee, Knoxville, TN USA

10 A triple beam microscope: Focused laser processing in a scanning ion/electron microscope

N. A. Roberts,[1,2] G. A. Magel,[1] C. D. Hartfield,[1] T. M. Moore,[1] J. D. Fowlkes[3] and P. D. Rack[2,3]
1 Omniprobe, Inc., an Oxford Instruments Company, 10410 Miller Rd., Dallas, Texas 75238
2 Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996
3 Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

11 Characterization of phase-separated, self-assembled, epitaxial Cu2O-TiO2 nano-pillar arrays for advanced photovoltaics

Daniela F. Bogorin,[1]Tolga Aytug,[1] Andrew R. Lupini,[1] Sergei Kalinin,[1] Evgheni Strelcov,[1] Ivan I. Kravchenko,[1] Adam J. Rondinone,[1]Ilia N. Ivanov,[1] Victor Maroni[2]
[1]Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Argonne National Laboratory, Argonne IL 60439

12 *Ab initio* based multi-scale modeling of segregation in solids

Hyunwook Kwak,[1] Yun-kyung Shin,[2] Adri C. T. van Duin,[2] and Alex V. Vasenkov[1]
[1]CFD Research Corporation, 215 Wynn Drive, Huntsville, AL 35805
[2]Pennsylvania State University, University Park, PA 16802

13 Phosphorous pentasulfide as a novel additive for high-performance lithium-sulfur batteries

Zhan Lin,[1] Zengcai Liu,[2] Wujun Fu,[2] Nancy J. Dudney,[1] and Chengdu Liang,[2*]
[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

14 Cr, N, -Codoped TiO_2 Mesoporous Microspheres for Li-ion Rechargeable Batteries

Zhonghe Bi,[1] Craig A. Bridges,[1] Bingkun Guo,[1] Xiao-Guang Sun,[1] Raymond R. Unocic,[1] Harry M Meyer III,[2] Sheng Dai,[1] and M. Parans Paranthaman[1]
[1]Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

15 TiO_2 Nanotube Arrays on Porous Ti Foam for Rechargeable Lithium and Sodium Ion Batteries

M. Parans Paranthaman,[1] Zhonghe Bi,[1] Paul A. Menchhofer,[2] Ryan R. Dehoff,[2] Craig A. Bridges,[1] Miaofang Chi,[2] Bingkun Guo,[1] Xiao-Guang Sun,[1] Sheng Dai[1]
[1]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

16 **Graphitic Mesoporous Carbons as the Supports of Promoted Rhodium and Molybdenum Carbide Catalysts for Alcohol Production from Synthesis Gas**

Song-Hai Chai,[1] Jane Y. Howe,[2] Viviane Schwartz,[3] Michelle Kidder,[1] Steven H. Overbury,[1,3] Sheng Dai,[1,3,4] De-en Jiang[1]

[1]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[3]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[4]Department of Chemistry, University of Tennessee, Knoxville, TN 37966

17 **Zeolite LTA-Polyimide Nanocomposite Membranes for Natural Gas Separations**

Megan Lydon,[1] Kinga Unocic,[2] Christopher Jones,[2,3] Sankar Nair,[3]

[1]School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, GA
[2]Oak Ridge National Laboratory, Oak Ridge, TN
[3]School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA

18 **Are the Surfaces of Oxide Nanocrystals With Defined Facets as Perfect as They Appear? – A Case Study of Nanoshaped Ceria Catalysts**

Zili Wu, Meijun Li, Steven H. Overbury

Chemical Science Division and Center for Nanophase Materials Sciences

18 **Solution-Based Lithium Incorporation and Delamination of Magnesium Diboride**

Daniel R. Sexton, Matthew T. Davidson, Christopher A. Barrett and Tina T. Salguero

Department of Chemistry, University of Georgia, Athens, Georgia 30602, USA

20 **In situ synthesis of oxynitrides**

Craig Bridges

Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

21 **Synthesis of Cadmium Selenide (CdSe) Quantum Dots via an Aerosol Route**

He Jing and Da-Ren Chen

Washington University in St. Louis, One Brookings Drive, St. Louis, Missouri, 63130

22 **SAXS studies of alkyl chain, temperature, and confinement effects on the structure of room temperature ionic liquids**

José Leo Bañuelos,[1] Song Li,[2] Guang Feng,[2] Pasquale F. Fulvio,[1] Nikolas Arend,[3] Gernot Rother,[1] Antonio Faraone,[4] Lawrence M. Anovitz,[2] Patrick Hillesheim,[1] Jianchang Guo,[1] Robert W. Shaw,[1] Sheng Dai,[1] Peter T. Cummings,[2,5] David J. Wesolowski[1]

[1]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee
[2] Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee
[3]Jülich Center for Neutron Science at the Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee
[4] NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland
[5]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee

23 **Enhanced Dispersion and Stability of Platinum on SiO_2 by Surface Modification with ZrO_2 and TiO_2 – Impact on CO Oxidation Performance**

Mi-Young Kim,[1] Jae-Soon Choi,[1] Todd J. Toops,[1] Viviane Schwartz,[1] Jihua Chen,[1] Eun-Suk Jeong,[2] Sang-Wook Han[1]

[1]Center for Nanophase Materials Science, Oak Ridge National Laboratory
[2]Chonbuk National University, South Korea

24 Effect of Solvent Quality on the Chain Conformation of Poly(3-Hexylthiophene) (P3HT) in Solution and the Crystalline Morphology of Solution-Casted Thin Film

Jong Kahk Keum,[1*] Kai Xiao,[2] Ilia N. Ivanov,[2] Kunlun Hong,[2] James F. Browning,[1*] Gregory S. Smith,[1] Ming Shao,[2] Kenneth C. Littrell,[1] Adam J. Rondinone,[2] Andrew E. Payzant[2]
[1]Neutron Scattering Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

25 End Functionalized Conjugated Polymers for Potential Self Assembly and Optoelectronic Applications

T. David,[1] S. Sun, [1] D. Pickel,[2] and K. Hong[2]
[1]Center for Materials Science (CMR), Norfolk State University
[2]Center for Nanophase Materials Science, Oak Ridge National Laboratory

26 Charge regulation and local dielectric function in planar polyelectrolyte brushes

Rajeev Kumar[1], Bobby G. Sumpter[2] and S. Michael Kilbey II[2,3]
[1] National Center for Computational Sciences, Oak Ridge National Laboratory, Oak Ridge, TN-37831
[2] Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN-37831
[3] Department of Chemistry, University of Tennessee, Knoxville, TN-37996

27 Temperature Gradient Interaction Chromatography: An inside look at polymer heterogeneity

Deanna L. Pickel, George C. Morar, David W. Uhrig, S. Michael Kilbey, II
Center for Nanophase Materials Science, Oak Ridge National Laboratory

28 Ab-initio calculations and molecular dynamics simulations of peptide adsorption onto metal oxide surfaces

C. Arcangeli,[1,2] I. Borriello,[1,2] M. Celino,[1,2] M. V. Falessi,[1] P. Morales,[1,3] N. Pellicciotta,[1] B. G. Sumpter,[4]
[1]NAST Centre, Nanoscience & Nanotechnology & Innovative Instrumentation, Università dgli Studi di Tor Vergata, Via della Ricerca Scientifica, 1 I-00133 Roma, Italy
[2]ENEA, UTTMAT-DIAG, Casaccia Research Center, Via Anguillarese 301, I-00123 Roma Italy
[3]ENEA, UTTMAT-SUP, Casaccia Research Center, Via Anguillarese 301, I-00123 Roma Italy
[4]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN USA

29 Applications of Scanning Probe Microscopy in Biology

V. Reukov,[1] A.S. Shaporev,[1] G.L. Thompson,[2] M. Nikiforov,[3] S.Jesse,[4] S. Kalinin,[4] A. Vertegel[1]
[1]Clemson University, Department of Bioengineering, Clemson, SC
[2]Air Force Research Laboratory, San Antonio, TX
[3]Argonne National Laboratory, Chicago, IL
[4]Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN

30 A search model for topological insulators with high-throughput robustness descriptors

Kesong Yang,[1] Wahyu Setyawan,[2] Shidong Wang,[1] Marco Buongiorno Nardelli,[3,4] and Stefano Curtarolo,[1,3,4]
[1]Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708
[2]Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352
[3]Department of Physics and Department of Chemistry, University of North Texas, Denton, TX 76203
[4]Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[5]Department of Physics, Duke University, Durham, North Carolina 27708

31 On The Information Content of Conductance Histograms: Transport Mechanisms, Cooperative Effects, and Junction Symmetries

Patrick D. Williams,[1,2] and Matthew G. Reuter[2,3]
[1]Oak Ridge High School, Oak Ridge, TN 37830
[2]Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[3]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

32 Electrochemical Nanowriting on CeO_2 Thin Films

Nan Yang,[1,3] Sandra Doria,[2] Amit Kumar,[3] Antonello Tebano,[1] Silvia Licoccia,[3] Sergei Kalinin,[4] and Giuseppe Balestrino[1]
[1]INFM-CNR SPIN and Department of Informatica Sistemi e Produzione, University of Rome, Tor Vergata, Via del Politecnico, 00133, Rome, Italy
[2]Departement of Physics, University of Rome, La Sapienza, Piazzale Aldo Moro 5, 00185, Rome, Italy
[3]Department of Chemical Science and Technologies & NAST Center, University of Rome, Tor Vergata, Via della Ricerca Scientifica, 00133, Rome, Italy
[4]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

33 Search for new materials - a computational approach

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

34 Epitaxial growth of highly conductive IrO2 thin films by pulsed laser deposition

Liang Qiao and Michael D. Biegalski
Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

35 Femtosecond Laser Micro-/Nano-machining of Holes and Lines in Fused Silica

B. K. Canfield, L. Costa, D. Rajput, A. Terekhov, W. H. Hofmeister, and L. M. Davis
Center for Laser Applications, University of Tennessee Space Institute, 411 B. H. Goethert Pkwy, MS 35, Tullahoma, TN 37388

36 The Role of Hydrogen During Si Nanowire Growth

Naechul Shin and Michael. A. Filler
Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA

37 Phonon Engineering of Si Nanowires by Controlled Chemical Doping

M.Babaeian,[1] M. Ontl,[2] T. Jayasekera,[1] A. Calzolari,[3] M. B. Nardelli[4,5]
[1]Department of Physics, Southern Illinois University, Carbondale, IL
[2]South Western Illinois College, REU Participant at Southern Illinois University, Carbondale, IL
[3]Theory@Elettra Group, DEMOCRITOS National Simulation Center CNR-IOM Istituto Officina dei Materiali, I-34014 Trieste, Italy
[4]Department of Physics and Department of Chemistry, University of North Texas, Denton, Texas 76203
[5]Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

38 Resonant Infrared Matrix-Assisted Pulsed Laser Evaporation of P3HT-based Bulk Heterojunctions: Small-Angle X-ray Scattering and Photovoltaic Device Characterization

Adrienne D. Stiff-Roberts and Ryan D. McCormick
Duke University, Department of Electrical and Computer Engineering, Box 90291 Durham, NC 27708

39 Novel Fullerene Acceptor Materials for Application in Advanced Organic Photovoltaics

Youjun He, Ming Shao, Kai Xiao, Sean C. Smith, Kunlun Hong
Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Center for Nanophase Materials Sciences

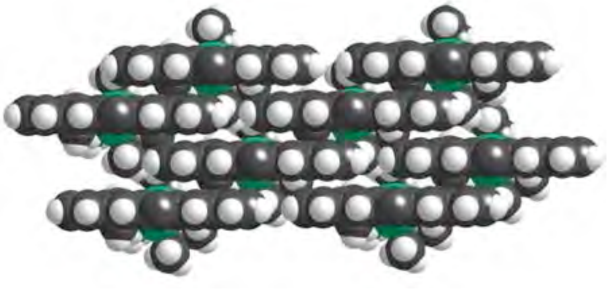
Plenary Session

2012 User Meeting

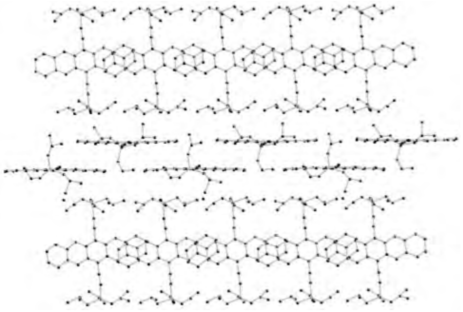
Crystal design for organic semiconductors

John E. Anthony, Center for Applied Energy Research and Department of Chemistry, University of Kentucky, Lexington KY 40511. anthony@uky.edu

The ease with which small-molecule organic semiconductors can be functionalized allows a single chromophore framework to be tuned for use in a myriad of electronic applications. Careful selection of substituents allows tuning of both solubility and crystal packing, which is important for the improvement of both film morphology and charge transport. Additional substituents on the chromophore can be added to improve stability, shift phase transitions, or change the dominant carrier type for the material. Using 4, 5 and 6 fused-ringed acenes and heteroacenes as the chromophore, our functionalization approach has created organic materials for use in high-performance organic transistors and organic solar cells. The crystal-packing arrangements for these two types of devices are dramatically different. This talk will examine how materials with two-dimensional, layered pi-stacking arrangements yield high-performance transistors, and how subtle tuning of the substituents can further improve performance. In the optimum case, hole mobility as high as 5 cm^2 / Vs was observed from a dip-cast film. Structure-property relationships in organic transistors are also explored in high-quality single crystals, showing how changes in crystalline order alter the intrinsic carrier properties of a homologous series of materials. In the case of bulk heterojunction organic solar cells, substitution of the acene chromophore with small electron-withdrawing groups yielded effective acceptors in blends with polythiophene donors. In this case, materials with strong pi-stacking interactions yielded the poorest-performing solar cells, while those with weak, 1-dimensional pi-stacking interactions yielded the best performance, with power conversion efficiencies greater than 1.5% in these fullerene-free blends. The details relating crystal packing to performance have now been determined, allowing us to develop new design rules for efficient photovoltaic acceptors.



Crystalline motif for transistors



Crystalline motif for OPV acceptors

STRUCTURED EPITAXIAL GRAPHENE

Walt A. de Heer
School of Physics,
Georgia Institute of Technology
Atlanta GA 30332

The original concept of graphene electronics focused on carbon nanotube properties. Carbon nanotubes were known to be high mobility ballistic, phase coherent conductors and quantum confinement effects produced significant bandgaps. However, it turns out to be very difficult to develop nanotube electronics platform for a variety of reasons including fundamental physical constraints related to the quantum mechanical properties of the metal-to-nanotube contacts. Graphene electronics can in principle overcome the major problems because graphene structures can be patterned using conventional lithography and dissipation at contacts can be controlled. However, these developments rely on the premise that narrow, ballistic graphene ribbons can be produced. Experiments on conventionally patterned graphene structures produced from graphene that is deposited on insulating substrates have been discouraging. The graphene ribbon mobilities are so low due to edge roughness effects, to render this direction to be impracticable. On the other hand, graphene produced on silicon carbide turns has been found to be more immune to edge scattering problems. This effect is explained in terms of a topologically protected edge state that are in fact expected in essentially all graphene ribbons with reasonably straight edges. Moreover, recent developments of template grown graphene structures on silicon carbide are promising. Very narrow ballistic graphene ribbons that demonstrate electronic phase coherent properties, have been produced with these methods which again brings the original concept of graphene based nanoelectronics back into play. Recent developments in the science and technological implications of epitaxial graphene nanostructures will be presented.

Oral Presentations

Track A

2012 User Meeting

Recent Advances in Focused Electron-Beam Induced Processing using Bulk Liquid Reactants

J. Todd Hastings, Electrical and Computer Engineering, University of Kentucky, Lexington, KY 40506

Focused electron-beam induced processing (FEBIP) enables the direct deposition and etching of functional materials with nanoscale resolution. The process has found application in integrated circuit mask repair, nanoscale rapid prototyping, and interconnection with chemically synthesized nanostructures. Our group is developing a new approach to FEBIP that replaces traditional gas-phase reactants with bulk liquids. The technique offers several advantages including higher deposit purity, access to new materials, faster deposition and etch rates, and the use of stable, low-cost, and low-toxicity reagents. Here we first summarize our efforts to deposit transition metals, including Cr, Co, Ni, Pd, Ag, Pt, and Au, from various aqueous solutions. In most cases, the solution is separated from the vacuum environment with an electron transparent membrane (polyimide or silicon nitride) as shown in Fig. 1(a). We have obtained resolutions as small as 15-nm half pitch for Ni and purities of at least 95at.% for Au. In these cases deposition proceeded on the membrane itself; however, preliminary studies of Pt and Ag show that deposition on separate substrates is possible as well.

In one potential application, we show that silver nanostructures deposited from silver nitrate solutions support localized surface-plasmon resonances (LSPR) at visible wavelengths. Both optical darkfield scattering spectra and energy dispersive x-ray spectroscopy suggest that the silver is deposited with sufficient purity to enable LSPR-based applications. We also present recent results evaluating the deposition of AuPt and AuAg bimetallic nanostructures from mixed solutions of $HAuCl_4$, H_2PtCl_6, and $AgNO_3$. These structures deposit as alloys, rather than core-shell structures, and the composition can be controlled by varying the composition of the precursor solution. Perhaps most interestingly, we find that alloy composition can be predicted based on solvated-electron reaction rates obtained from prior pulse-radiolysis studies. This suggests that the scientific community's vast accumulated knowledge concerning radiochemical reactions can inform FEBIP processes in liquids.

Along similar lines, we demonstrate the e-beam induced deposition of cadmium sulfide (CdS) nanowires as shown in Fig. 1(b). However, unlike the bimetallic deposition process, CdS deposits nearly stoichiometrically from solutions containing cadmium chloride ($CdCl_2$) and thiourea ($SC(NH_2)_2$). Finally, we discuss e-beam induced etching using a bulk liquid reactant. Specifically, we show that silicon-nitride membranes can be locally etched in dilute aqueous solutions of potassium hydroxide upon exposure to the electron beam. To date, 50-nm dense features have been etched, as shown in Fig. 1(c). For micron-scale features, the etch depth was found to be a highly linear function of dose, and the etch rate was at least 8 times faster than previously reported gas-phase etching processes.

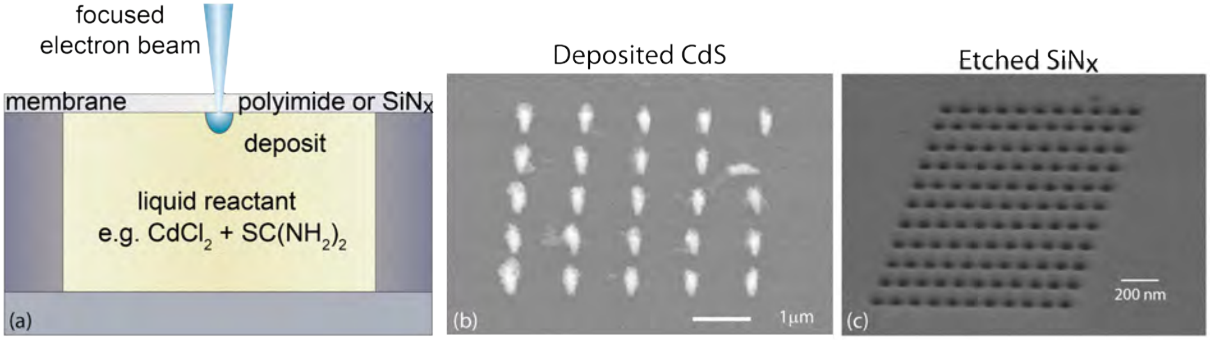


Fig. 1. (a) Schematic of e-beam induced deposition from a bulk liquid onto the electron-transparent membrane of a liquid cell. Both commercial (Quantomix, polyimide membrane) and custom (silicon nitride membrane) cells were used. Example reactants are listed for depositing CdS. (b) CdS nanowires deposited using a dose of 200 pC/wire on a polyimide membrane. (c) 50-nm half-pitch structures etched in a silicon nitride membrane using KOH (aq.) and a dose of 2 nC/dot. Both processes were carried out with a primary electron-beam energy of 20keV.

In situ laser processing in a scanning electron microscope

N. A. Roberts[1,2], G. A. Magel[1], C. D. Hartfield[1], T. M. Moore[1], J. D. Fowlkes[3] and P. D. Rack[2,3]

1 Oxford Instruments Nanoanalysis, Omniprobe Products, 10410 Miller Rd., Dallas, Texas 75238

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

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

A laser delivery system using multimode fiber optic delivery and bulk focusing optics has been constructed and used for laser processing within a scanning electron microscope (SEM). A prototype of this system has been installed on the FEI Nova 600 DualBeam SEM/FIB in the Nanofabrication Research Laboratory. A semiconductor diode laser with a pulsed current driver is used to produce 0–25 W of 915-nm wavelength light focused on a substrate surface for rapid, localized surface heating of a spot approximately 100 μm in diameter centered under the electron beam. Current modulation enables continuous or pulsed laser operation down to sub-microsecond durations.

The laser delivery system has initially been optimized to enable the laser assisted electron beam induced deposition (LAEBID) process, a nanoscale direct-write synthesis method that integrates an electron beam induced deposition (EBID) process with a synchronized pulsed laser step to induce thermal desorption of EBID reaction by-products. Localized, spatially overlapping and synchronized electron and photon pulses enhance desorption of reaction by-products while mitigating issues associated with bulk substrate heating, which can shorten the precursor residence time and distort pattern fidelity due to thermal drift. Using laser pulses synchronized to the e-beam writing cycle, we have achieved purification of platinum deposits (reduced carbon content by ~50%) and a significant reduction in deposit resistivity. Measured resistivities from platinum LAEBID structures (4×10^3 $\mu\Omega$-cm) are nearly four orders of magnitude lower than standard EBID platinum structures (2.2×10^7 $\mu\Omega$-cm) using the same precursor, and are better than the lowest reported EBID platinum resistivity using post-deposition annealing in a reactive atmosphere ($1.4\text{x}10^4$ $\mu\Omega$-cm). The LAEBID deposit is also ~25% smaller than comparable EBID deposits.

This apparatus can also be applied to other *in situ* processing or observations that can benefit from transient, localized, and/or surface heating, including other nano fabrication methods such as etching and ion-beam induced processes. In addition to LAEBID, the laser delivery system has so far been utilized for pulsed laser induced dewetting (PLiD) of thin metallic films during observation with the SEM, localized chemical vapor deposition and etching (local to the laser spot), and post-deposition laser annealing of EBID. This new capability will soon be offered to the CNMS User community to promote the transformative science programs being conducted at the CNMS.

Surface Chemistry Controlled Defect Engineering in Silicon Nanowires

Naechul Shin[1], Miaofang Chi[2], Jane Y. Howe[2], Michael. A. Filler[1]
[1] Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA
[2] Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN

Defect engineering offers a range of opportunities to control the physical properties of semiconductors. Despite the common occurrence of planar defects (e.g. twins and stacking faults) and polytypic domains in III-V nanowires synthesized via the vapor-liquid-solid (VLS) technique, these structural features are far less frequently observed in group IV materials. This difference is especially striking because such structures exhibit similar formation energetics in both systems and indicates that the governing phenomena are poorly understood. Here, we demonstrate how user-defined changes in sidewall chemistry near the triple-phase line can rationally introduce both twin boundaries (TBs) and stacking faults (SFs) during the growth of <111> oriented Si nanowires for the first time. We increase the concentration of hydrogen atoms bonded to the nanowire sidewall, thus initiating defects, by raising the partial pressure of Si_2H_6 and/or lowering temperature. SFs can begin at any of the {112} sidewalls and propagate across the nanowire at an angle relative to the growth direction. On the other hand, TBs are oriented perpendicular to the growth direction in a manner analogous to III-V nanowires. Statistical analysis of SF and TB position via electron microscopy confirms that only user-initiated process changes generate either type of defect. Furthermore, real-time *in-situ* infrared spectroscopy measurements definitively demonstrate that covalent Si-H bonds are the root source of these defects. We propose a simple model where SFs are initiated by local changes in hydrogen atom coverage. TBs result upon reaching a hydrogen coverage that favors {111} sidewall facets, as opposed to {112}, a transformation that stretches the triple-phase line and ultimately forces TB formation. Our findings suggest new routes to engineer the properties of this ubiquitous semiconductor and are an important step toward a fundamental understanding of the chemistry that underlies nanowire synthesis. [TEM work was performed through ORNL's Shared Research Equipment (ShaRE) User Program, which is sponsored by the Department of Energy's Office of Basic Energy Sciences.]

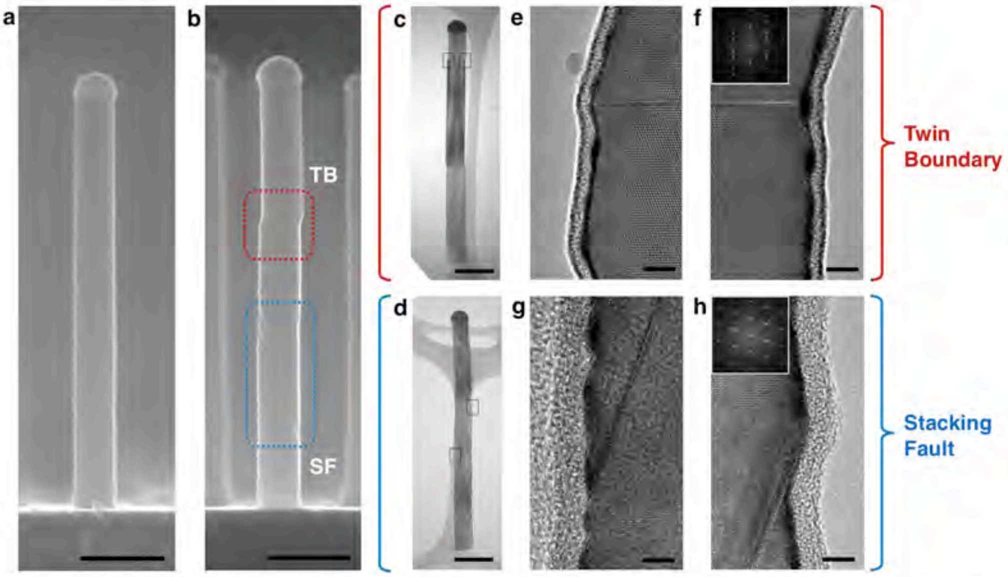


Figure 1. (a) SEM image showing a defect free Si nanowire grown at 400 ^{o}C and 2 x10^{-4} Torr for 35 min. (b) SEM image showing a nanowire exhibiting both a TB and SF grown under the same conditions as (a), but with multiple temperature/pressure pulses. Both (a) and (b) were measured along the <110> direction. Scale bars, 200 nm. (c, d) TEM image of a representative (c) TB and (d) SF. Scale bars, 200 nm. (e,f) High resolution bright field TEM images of the nanowire in (c) showing the structure of each sidewall. The FFT inset confirms the existence of TB. Scale bars, 4 nm. (g,h) High resolution bright field TEM images of the nanowire in (d) showing the structure of each sidewall. The FFT inset shows that the defect is a SF, not a TB. Scale bars, 4 nm.

SURFACTANT ASSISTED GROWTH OF SMOOTH OXIDES ON GAN

J-P. Maria[1]

E.A. Paisley,[1] M. Biegalski,[2] J.M. Lebeau,[1] B. Gaddy,[1] S. Mita,[1] R. Collazo,[1] Z. Sitar,[1] D. Irving,[1] and

[1]Department of Materials Science and Engineering, North Carolina State University, 1001 Capability Dr, Raleigh, NC 27606 USA

and

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

Epitaxial integration of polar oxides with wide band gap polar semiconductors presents the possibility of tunable 2D charge carriers at polar interfaces and integration of non-linear dielectric properties. To achieve such coupling, defect densities must be low, and microstructures must have minimal roughness. However, conventional growth techniques fail to achieve this in materials with such highly dissimilar structure and symmetry. For example, the terminal polar 3D rocksalt surface is determined by the tendency for the high-energy (111) polar orientation to form (100)-oriented low-energy facets. Therefore, realizing smooth polar oxide films on GaN requires the ability to overcome this (100)-faceting tendency. In this presentation we will discuss a new surfactant approach to MBE and PLD growth of rocksalt oxides (MgO, CaO) on GaN, where water vapor is utilized during growth to hydroxylate the rocksalt (111) surfaces, changing the equilibrium habit from cubic to octahedral, eliminating the (100)-faceting tendency. We demonstrate unambiguously using RHEED that surfactant incorporation enables a 2D growth mode of (111) CaO and MgO thin films with a step-and-terrace morphology. For both MgO and CaO, temperature dependent *ab initio* thermodynamic surface energy calculations predict the experimentally observed temperature and pressure window in which 2D growth occurs.

Additionally, solid solutions between MgO and CaO by both PLD and MBE that offer perfect lattice match to (0002) GaN are presented. In all cases, epitaxy stabilizes the system against phase separation and RHEED shows layer-by-layer growth. TEM analysis of defects of the lattice-matched interface will be presented. Current efforts focus on samples designed to probe the possibility of conductive oxide-GaN interfaces.

Collectively, these results demonstrate that one can rationally engineer surface chemistry during growth and create a local equilibrium promoting a specific crystallographic habit and growth mode otherwise unavailable. Demonstrating this using two materials and two growth techniques suggests the generic nature of this methodology. The utility of this method is illustrated by electrical property measurements that reveal drastically reduced leakage current densities (approximately 1000X lower) for surfactant-assisted films as compared to those grown using conventional means.

Finally, current work is now extending surfactant work to include the $BaTiO_3$/GaN interface. Previously, we have demonstrated growth of high quality, epitaxial BT on GaN and recent PFM results suggest coupling between the polarizations across the BT/GaN interface.

CONTRIBUTED TALK
TRACK A - 13:30

Electronic Structure and Quantum Transport Properties of Layered Heterostructures

Alejandro Lopez-Bezanilla, Jingsong Huang, Bobby G. Sumpter
CNMS, Oak Ridge National Laboratory

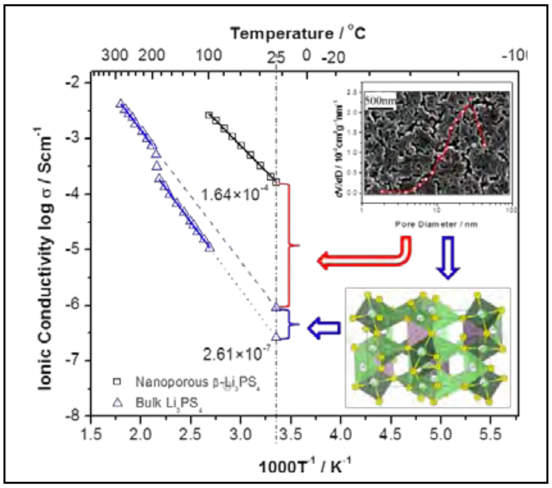
In recently discovered materials such as carbon nanotubes and graphene, the aromatic carbon pi-electrons are laying the foundation for a new field in material sciences that combines organic chemistry and solid state physics. Although carbon is representing the emergence of a new era in material design at the nanoscale, its nearest neighbor elements in the periodic table like B, N and O are equally contributing to the development of new applications ranging from nanoelectronics to solar energy devices. We present computer modeling of a combination of these elements to predict magnetic and electrical properties of layered nanostructures that expand the possible applications of these materials. New functionalities such as metallic and magnetic states have been found on boron nitride nanoribbons (BNNRs) when their zigzag edges are terminated with O and S atoms, and Peierls-like distortions are observed for these atoms along the edges. In contrast, OH edge terminated armchair BNNRs are semiconducting although they exhibit an ondulating geometry at the edges. When BN domains are embedded within graphene nanoribbons, the electronic transport properties of the later are modified, and a wide transport tunability is obtained, from perfect insulating interfaces to asymmetric electron-hole transmission profiles, demonstrating the possibility of engineering mobility gaps to improve device performances. Finally, we present theoretical and experimental results on single and multiple looped graphene sheets. Experimental images of stable closed-edge structures in few layer graphene samples obtained by high-resolution transmission electron microscopy (HRTEM) are compared with results based on first principles density functional theory calculations to show that the electronic properties of graphene with closed edges are not significantly modified with respect to the flat graphene sheet.

Anomalous high ionic conductivity of nanoporous β-Li_3PS_4

Zengcai Liu[1], E. Andrew Payzant[1,2], Zili Wu[1,3], Nancy J. Dudney[2], Adam J. Rondinone[1], and Chengdu Liang[1]

[1] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA, [2] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA, [3] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA

Lithium-ion conducting solid electrolytes hold the promise for enabling high-energy battery chemistries and circumventing safety issues of conventional lithium batteries[1]. Achieving the combination of high ionic conductivity and broad electrochemical window in solid electrolytes is a grand challenge for the synthesis of battery materials. Herein we show an enhancement of room-temperature lithium-ion conductivity of 3 orders of magnitude by creating nanostructured Li_3PS_4. This material has a wide (5 V) electrochemical window and superior chemical stability against lithium metal. The nanoporous structure of Li_3PS_4 reconciles two vital effects that enhance ionic conductivity: (1) The reduced dimension to nanometer-sized framework stabilizes the high conduction beta phase that occurs at elevated temperatures[1a, 2]; and (2) The high surface-to-bulk ratio of nanoporous β-Li_3PS_4 promotes surface conduction[3]. Manipulating the ionic conductivity of solid electrolytes has far-reaching implications for materials design and synthesis in a broad range of applications such as batteries, fuel-cells, sensors, photovoltaic systems, and so forth[1c, 4].



References:

[1] a) R. Makiura, T. Yonemura, T. Yamada, M. Yamauchi, R. Ikeda, H. Kitagawa, K. Kato and M. Takata, *Nat. Mater.* **2009**, *8*, 476-480; b) N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto and A. Mitsui, *Nat. Mater.* **2011**, *10*, 682-686; c) J. Maier, *Nat. Mater.* **2005**, *4*, 805-815.

[2] K. Homma, M. Yonemura, T. Kobayashi, M. Nagao, M. Hirayama and R. Kanno, *Solid State Ion.* **2011**, *182*, 53-58.

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[4] A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon and W. Van Schalkwijk, *Nat. Mater.* **2005**, *4*, 366-377.

Extrinsic Contributions to the Piezoelectric Response of Ferroelectric Nanostructures

Nazanin Bassiri-Gharb[1], Ashley Bernal[1], Alexander Tselev[2] and Sergei Kalinin[2]

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

and

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

e-mail: nazanin.bassirigharb@me.gatech.edu

Ferroelectric (FE) thin films and nanostructures find a wide range of applications in capacitive elements, non-volatile memories, micro- and nano-electromechanical system (MEMS/NEMS) sensors, actuators and transducers, as well as actively tunable photonic and phononic crystals, and energy harvesting nano- and micro-generators. With the drive towards miniaturization, extrinsic size effects have emerged that lead to a reduction in the dielectric, ferroelectric and piezoelectric response of the material. Additionally, patterning ferroelectric materials at the nanoscale poses a continuous challenge for manufacturing methods that need compatibility, in terms of alignments and user-defined shapes, with the device creation requirements. This presentation will address novel processing techniques for creation of FE nanostructures, as well as their properties.

High aspect ratio (3D) ferroelectric nanostructures were processed through soft-template infiltration of precursor sol-gel solutions, followed by thermal treatment leading to removal of organic template and crystallization of the 3D ferroelectric nanostructures. The soft templates were processed through e-beam lithography (EBL). This processing method allows a high-resolution control of the created shapes in terms of location (alignment) and dimensions. A critical size was observed for PZT tube thicknesses of ~ 10-15 nm: for thicknesses below the critical value, the coercive field sharply increased and remanent piezoresponse sharply decreased. Additionally the extrinsic contributions, as measured by nonlinear-BE-PFM, also sharply dropped below the critical thickness. This size effect is attributed to the presence of a critical size below which formation of non-180° domain walls is no longer energetically favorable. The impact of lateral and substrate-induced constraints on the extrinsic contributions to the piezoelectric response in the polycrystalline, ferroelectric nanostructures was also studied. The presence of lateral constraints can lead to a reduction of extrinsic contribution by ~50% with respect to free-standing nanotubes. Similarly, the substrate induced clamping leads to a reduction of ferroelectric response for height-to-outer-diameter ratios ≤3:1.

Submitting author's name:	Nazanin Bassiri-Gharb
Institution:	G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology
Address:	315 Love Bldg, 771 Ferst Dr., Atlanta, GA, USA
e-mail:	nazanin.bassirigharb@me.gatech.edu
CNMS User projects:	CNMS2011-053, CNMS2010-255

INVITED USER TALK
TRACK A - 14:15

Nanoscale Materials Science Challenges for Spin-Torque-Transfer Random Access Memory

William H. Butler

Center for Materials for Information Technology

University of Alabama

In 1989 John Sloncewski proposed that spin-polarized tunneling currents could transfer angular momentum between two ferromagnetic layers. For many years no one paid any attention to his suggestion. In 2001, however, an ORNL team showed that MgO, a wide band gap insulator, could be combined with Fe or CoFe to deliver highly spin polarized tunneling currents at relatively low resistances. In 2005 a team at Grandis, a small silicon valley start-up, demonstrated that these tunneling currents could be used to switch the direction of magnetization of one of these layers and proposed a magnetic memory based on this effect. Today, the largest DRAM companies are anticipating and developing the use of this technology as a replacement for semiconductor DRAM for feature sizes below 20nm. If this happens it would cause major changes in computer architectures because working memory would become non-volatile. In this talk, I will describe the physics associated with the reading and writing of this type of memory cell with special emphasis on the challenges in nanoscale materials science that must be overcome for this technology to succeed.

Support from the Defense Advanced Research Projects Agency and from Grandis, Inc. is gratefully acknowledged.

Center for Nanophase Materials Sciences

Oral Presentations

Track B

2012 User Meeting

INVITED USER TALK
TRACK B - 10:40

Wei-Ren Chen
Oak Ridge National Laboratory

Investigating Polyelectrolyte Dendrimer Solutions using Neutron Scattering and Simulations

Abstract not yet available

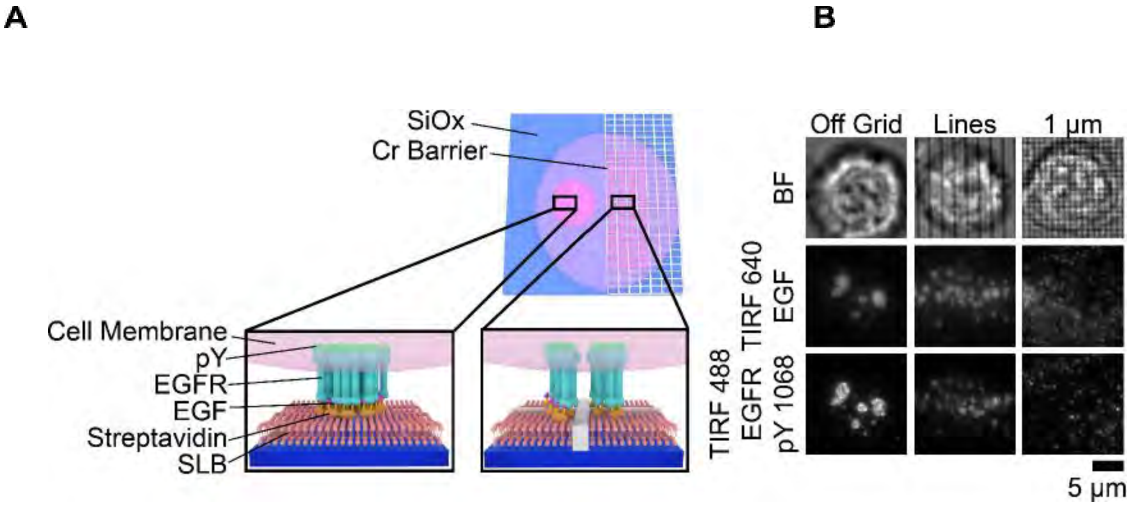
CONTRIBUTED TALK
TRACK B - 11:10

"Nanopatterned Supported Lipid Bilayer Surfaces as Tools for the Study of Receptor Signaling"

Daniel Stabley,[1] Stephen Marshall,[2] Scott Retterer,[3] Khalid Salaita[1]

[1]Emory University, Atlanta, Georgia 30322
[2]Emory University (currently at Caltech for grad school)
[3]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

In order to properly function, cells must communicate using a complex system of ligands and receptors. Classically, signaling through these ligand-receptor pairs was thought to be driven by chemical recognition of ligands. Recently, however, the physical arrangement of the receptors themselves has been seen to play an important role in cell communication. Herein we make use of electron beam nanolithography to fabricate substrates that can control receptor spatial organization and reveal new signaling trends that cannot be studied with traditional biochemical methods.



We employed the nanopatterned supported membrane investigate the epidermal growth factor receptor (EGFR) pathway, which is one of the most well studied cell signaling networks using conventional biochemical methods. Canonically, the EGFR binds its ligand, the epidermal growth factor, dimerizes, and is phosphorylated to initiate signaling networks. Recent work, however, has shown that the EGFR forms nanoscale assemblies at the cell membrane. To better understand the function of these nanoscale clusters, we make use of ligand-functionalized supported lipid bilayers with nanopatterned diffusion barriers to control EGFR clustering in living cells. Supported lipid bilayers are comprised of phospholipid molecules that self assemble into bilayers on a solid support. Importantly, the lipids remain laterally fluid and can be functionalized with a wide range of small molecules and proteins. Through the use of lipids with biotin-modified head groups, these bilayers were functionalized with EGF, which engaged and activated EGFR molecules on the surface of mammalian cells seeded onto the bilayer surface. Metal nanolines fabricated onto the solid support confine the lipid molecules within specific corrals. As a result, ligand-bound receptor molecules that are attached to the lipid bilayer were subject to this geometric pattern (Fig A). By forming nanopatterned chromium barriers of various geometries (~100 nm line width, ~10 nm height, Fig B) we were able to dictate the size of EGFR clusters, which allowed us to determine the role of clustering in receptor phosphorylation. Comparison of cells on patterns of different sizes revealed that clusters of EGFR below 1 µm in size are phosphorylated more efficiently than larger clusters. This result represents the first evidence that large-scale EGFR spatial organization modulates its activation, and opens the door for future studies that make use of nanofabrication to study elements of receptor function that are not accessible using standard biochemical methods.

Conjugated Bottle-Brush Polymers Incorporating Poly(3-Hexylthiophene) as Brush Side-Chains

Suk-kyun Ahn[1]*, Deanna L. Pickel*[1]*, W. Michael Kochemba*[2]*, and S. Michael Kilbey II*[1,2]

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

Regioregular poly(3-hexylthiophene) (rr-P3HT) has received much attention due to its ease of synthesis, high charge carrier mobility, good processability and good power conversion efficiency (PCE > 5%). Therefore, a number of systems incorporating P3HT or copolymers based on P3HT have been developed as potential materials for organic photovoltaics (OPVs). While most research has focused on linear type P3HTs so far, there are also great opportunities for more complex P3HT architectures. Controlling polymer architecture or topology is an efficient way to tailor physical properties of polymers often resulting from the change in their morphology. To this end, we have been interested in exploiting a complex P3HT architecture, the so called “bottle-brush polymer”, as a way to tune the self-assembly as well as physical and electronic properties of the polymers, which may provide another route to develop high performance OPV devices.

In bottle-brush polymers, polymeric side-chains are densely grafted to the polymer backbone. The repulsive interaction between brush side-chains leads to (i) a reduction of entanglements between brush side-chains and (ii) an extension of the polymer backbone. As a result, bottle-brush polymers often adopt worm-like conformations with sizes of hundreds of nanometers, which results in unique self-assembled nanostructures in the melt and solution.

Herein we report a facile synthetic strategy to prepare bottle-brush polymers incorporating P3HT as conjugated polymeric side-chain through the macromonomer approach. Norbornenyl functionalized P3HT macromonomer was synthesized by Kumada catalyst transfer polycondensation (KCTP) followed by end-group modifications using Suzuki and *N,N'*-dicyclohexylcarbodiimide **(**DCC)-promoted coupling reactions. The macromonomer was then polymerized by ring-opening metathesis polymerization (ROMP), producing the conjugated bottle-brush polymer. The length of P3HT brush as well as the polynorbornene backbone of the conjugated bottle-brush polymer is efficiently controlled through KCTP and ROMP chemistries, which may allow the morphology, thermal and electronic properties of resulting polymers to be tailored in useful and interesting ways.

Polypeptoids: Synthesis, Characterization and Materials Properties

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. They have demonstrated biocompatibility and enhanced resistance towards proteolysis relative to polypeptides. Despite lacking the extensive backbone hydrogen bonding interactions that determine the secondary structures of polypeptides, polypeptoids can still fold into well-defined secondary structures (e.g., helices), as dictated by the stereoelectronic properties of the polymer side chains. Compared to polypeptides, a distinct advantage of polypeptoids is their amenability to the thermal processing methods commonly employed for synthetic polymers. The combination of these characteristics makes polypeptoids potentially useful for various biotechnological applications.

This presentation will focus on our recent efforts in the development and mechanistic studies of *N*-heterocyclic carbene (NHC)-mediated living polymerization of *N*-substituted *N*-carboxyanhydrides (R-NCA) which yields cyclic or linear polypeptoids with diverse structures. Polypeptoids can be rendered hydrophobic/hydrophilic or semi-crystalline/amorphous by the introduction of appropriate side-chain structures. Moreover, this structural control can be extended to induce the formation of random coil or helical conformations. The synthesis of polypeptoid copolymers and investigation of their solution properties (i.e., self-assembly and LCST behavior) will also be presented.

Donghui Zhang is an assistant professor in the Chemistry Department of Louisiana State University. She obtained B.S. in Chemistry from Peking University in 1998 and her Ph.D. in organometallic chemistry from Dartmouth College in 2003. After doing 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.

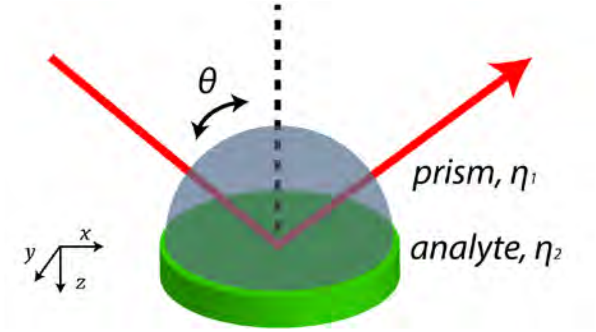
CONTRIBUTED TALK
TRACK B - 13:30

Scanning Angle Raman Microscopy: Measurements of Polymer Film Thickness and Composition

Emily A. Smith, Matthew Meyer, Vy H.T. Nguyen, Kristopher McKee
U.S. Department of Energy, The Ames Laboratory; and Iowa State University, Department of Chemistry, 1605 Gilman Hall, Ames, IA 50011-3111, USA

Scanning angle (SA) Raman microscopy has been developed for studying polymer films and other interfacial phenomena with chemical specificity. The technique uses a sapphire prism optically coupled to a sapphire substrate on which the sample is coated. Raman spectra are collected as the incident angle of the 785-nm excitation laser is precisely varied from approximately 30- to 70-degrees. This range represents angles that span above and below the critical angle for total internal reflection. Angles below the critical angle are used to measure polymers with thicknesses in the 250-nm to 3-µm range using a calibration curve constructed by calculating the electric field distribution as a function of incident angle, distance from the prism interface and polymer thickness. The calculations are used to determine the incident angle where waveguide modes are excited within the polymer film, which corresponds to the angle where the highest Raman intensity is experimentally measured. The average percent uncertainty in the SA Raman thickness determinations is 4%, and the measurements correlate with those obtained from optical interferometery. The calculated electric field distributions are also used to determine the distance dependence of the SA Raman signal; a majority of the signal emanates from the central portion of the polymer film at incident angles below the critical angle. Angles greater than the critical angle are most useful for measuring polymer films with thicknesses of less than a few hundred nanometers. Controlling the incident angle of the laser upon the interface at angles greater than the critical angle allows precise control of the penetration depth of the evanescent wave under total internal reflection, and the depth over which Raman scatter is collected. Far from the critical angle the instrument provides 30-nm depth resolution, which is significantly better than the depth resolution achieved in confocal Raman measurements. Since the sample volumes probed in TIR measurements are small, measurements of weak Raman scattering polymers have been problematic and signal enhancement is required for the analysis of these samples. The use of tailored substrates fabricated at CNMS to enhance the Raman signal and analyze weak Raman scattering samples will be discussed.

Scanning Angle Raman Microscopy Sample Geometry:



Spontaneous wrinkling-type patterns in azlactone based functional polymer thin films

Muruganathan Ramanathan[1]*, Brad S. Lokitz*[1]*, Jamie M. Messman*[1]*, and S. Michael Kilbey II*[1, 2]

[1]*Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN 37831 USA. .*
[2]*Department of Chemistry, University of Tennessee, Knoxville, TN.*

Introduction

Wrinkling of polymer thin films are viewed, more optimistically, for the potential development of next generation hi-tech devices such as stretchable electronics, microlens arrays, and smart surfaces.[1-3] Besides these hi-tech applications, Stafford and coworkers have demonstrated that surface wrinkling can be used as a versatile platform for measuring a number of thin film properties such as elastic moduli, stiffness, strength, and ductility.[4-8] Despite the fact that wrinkling formation in polymer thin films is a spontaneous process, it usually involves multiple steps to obtain periodic wrinkling patterns on any polymer thin film surfaces. Most common way of producing polymeric wrinkles is through application of a mechanical, osmotic or thermal stress to a thin elastic film, which is coated on top of a pre-strained soft substrate. Here for the first time, we report a one-step process for developing wrinkling patterns where the wrinkles are formed, *truly* spontaneously, by casting an Azlactone based polymer solution onto a substrate, without applying any external stress to the system. We further demonstrate that the directionality of these wrinkles can be tailored simply by changing the mode of deposition onto the substrates.

Experimental details

The wrinkling patterns presented in this work are directly created from Poly 2-vinyl-4,4-dimethly Azlactone (PVDMA, Mw 5.9kg/mol, PDI=1.02). Casting the PVDMA solution (1wt % in $CHCl_3$) onto a SiO_x substrate, results in the formation of periodic, microscopic wrinkles (shown in Fig 1a). These patterns are also produced on a number of other substrates; in Figure 1 we present the PVDMA wrinkles, respectively, on a nitride (Si_3N_4), on a metal (Au) and on a transparent insulator (glass slide). The wrinkles have long-range order, as the periodicity is maintained over large topographic areas. Structures formation has been testified on 4 mm^2 chips all the way to the 12" wafers.

Results and Discussion

The topographical orientation of these periodic wrinkles presented in this work depends on the mode of deposition of the polymer solution onto a substrate. For instance, spin casting the PVDMA solution onto any of the aforementioned substrates results in a radial pattern, whereas, tilt casting results in unidirectional patterns. Casting the films on transparent substrates allows us to get further structural insights through the transmission optical microscopy (TOM). Observed TOM images reveal a long-range ordered, uni-directional patterns that are obtained by tilt casting a drop of the polymer solution on a microscopic glass slide.

We further found that these wrinkling structures are prevalent beyond the PVDMA thin films to PVDMA brush-like layers. In thin films the thickness is about 60 nm and the film is not covalently anchored to the substrate. Sonication of these films in a good solvent essentially removes all the polymers and subsequently the surface becomes featureless. On the other hand, in brushes and brush-like layers the polymer is covalently anchored to a substrate via a linker molecule/end-group. We have synthesized a block copolymer of Poly(Glycidyle Methacrylate) PGMA-*block*-PVDMA (MW: 43K with 1:3 block ratio of PGMA and PVDMA and PDI: 1.24).[9] The epoxide group on the PGMA covalently attaches to the hydroxyl groups on piranha cleaned SiO_x substrate. PVDMA "brush-like layers" are created after annealing and sonication in a good solvent to remove all the unattached polymers. These brushes are very thin (less than 40 nm in thickness) but still exhibit these remarkable wrinkling patterns. However, there are certain characteristic differences between the structures in PVDMA thin films and in PGMA-*b*-PVDMA brushe-like layers but the fact is that the solution casting of PVDMA polymer either in thin film form or in a brush form develops wrinkling morphologies. We postulate two mechanisms for the physical origin of these wrinkling type patterns: a) this could arise from the evaporation of solvents from the thin film polymer solutions that generates vertical temperature gradients in the films, and made them susceptible to Benard-Marangoni convections.[10] Vitrification might freeze the convection patterns and produce these wrinkling patterns in PVDMA films. b) it is conceivable that the PVDMA forms a skin layer atop surface adsorbed/anchored PVDMA, as the solvent evaporates a local strain is developed that makes the skin layer to wrinkle.

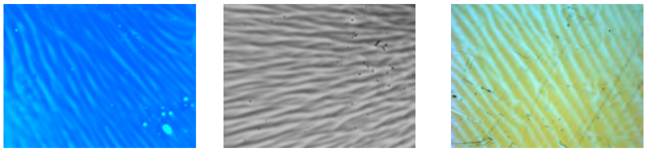


Figure 1. Optical micrographs of wrinkling patterns that are formed by spin casting the 1wt% of PVDMA from $CHCl_3$ at a spin sped of 1K or 5K rpm. Fig 1a, 1b and 1c respectively represent the PVDMA wrinkles on variety of substrates such as nitride (Si_3N_4), oxide (SiO_x) and metal (Au) representing the versatility of the process. Scale bar represent 200 mm.

Conclusions

In summary, we demonstrate the formation of submicron wrinkle patterns and their compatibility to various substrates (nitrides, oxides, metals etc.), geometries (2D and 3D), and well-controlled structural orientation of these wrinkles that simply depends on the mode of deposition. Long-range ordering in these wrinkles are apparent through the formation of a uniform, sinusoidal wrinkling pattern from top to bottom of a 12" wafer after tilt casting the PVDMA solution. We expect that this simple, straightforward strategy for wrinkle formation on stimuli responsive thin films with a possibility of highly stable brush-like layer formation with PGMA will lead to a rich and exotic field of fundamental research in polymer thin film/brush instability.

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

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Thermal transport through van der Waals interfaces between individual nanostructures

Deyu Li
Department of Mechanical Engineering
Vanderbilt University
Nashville, TN 37235-1592

Nanostructures possess unique thermal transport properties because of nanoconfinement effects. However, nanostructures are usually in contact with other nanostructures or substrates. For example, in various nanostructured microfibers, thin films, and bulk nanocomposites, which have been projected as structural materials for aerospace vehicles and for energy conversion applications, individual nanostructures are often in contact with other nanostructures or host materials through van der Waals (vdW) interactions. Thermal transport through these vdW interfaces could play critical role in the overall thermal transport properties of the nanostructured materials. Therefore, it is important to study thermal transport through vdW contacts between individual nanostructures. We report on experimental studies of thermal transport through contacts between individual nanostructures, which includes (1) thermal transport through vdW interfaces between individual boron nanoribbons [1], and (2) contact thermal resistance between individual carbon nanotubes.

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Nanoscale Carbon Based Electronic Junction Control Devices

Andrew G. Rinzler

University of Florida, Gainesville, Florida, USA

The low density of electronic states of reduced dimensionality carbons (nanotubes, graphene) implies large shifts of their chemical potential, and thus their work function, depending upon their charge state. Since the work function line-up across the interface between two materials dictates the junction transport properties, the ability to tune the work function in these systems provides a new degree of freedom for tuning electronic transport. We initially considered chemical charge transfer doping as one means to achieve such junction engineering but soon became intrigued by the idea of using field gating for an electronically tunable control over the trans-junction transport. That led to a radical redesign of the organic thin film transistor to a vertical architecture that exploits carbon nanotubes or graphene as a field gated source electrode. The architecture readily lent itself to making a vertical light emitting transistor, which has defined a new state of the art in such devices. In another direction we also realized junction control in a nanotube/n-Si Schottky junction solar cell, enhancing performance by 30%. These developments and latest progress will be discussed.

Center for Nanophase Materials Sciences

Poster Abstracts

2012 User Meeting

Pillar arrayed chips for planar separation and detection
CNMS-2012-218

[1]Teresa Kirchner, [1]Nichole Crane, [1]Chris Freye, [2]Nickolay Lavrik, [1]Michael Sepaniak
[1]UTK Chemistry, [2]CNMS

Abstract:

Unlike HPLC, there has been little advancement in the stationary phases (size and functionality) used for planar chromatography. Advantages in modernizing planar chromatography stationary phases include the ability to separate multiple samples simultaneously, orthogonal separation media and imaging of the separation without rigorous temporal demands. In this poster we present a highly ordered pillar array that has been chemically modified for spatial chromatography using fluorescence microscopy or surface enhanced Raman spectroscopy (SERS) to detect analyte bands. The pillar arrays were created using photolithograpy in combination with anisotropic deep reactive ion etching to create reproducible silicon pillars. The pillar diameters and pitch variations are approximately 1 to 3 microns with a total pillar array area of 3 by 1 centimeters. The pillar arrays were imaged using SEM in order to measure the pillar diameter and pitch as well as analyze the pillar sidewalls after etching and stationary phase functionalization. We are using these fluidic arrays to explore the impact on mass transport (Figure 1) and chromatographic efficiency caused by reducing the diameter and gap of the pillar array. Analysis of a variety of stationary phases that may be compatible with this system is being performed to evaluate the possibility of creating tunable solute retentive properties on the pillar surfaces. The focus of our current work is to optimize the pillar array morphology and surface chemistry for the planar chromatography systems to achieve separation and detection performance beyond traditional TLC media.

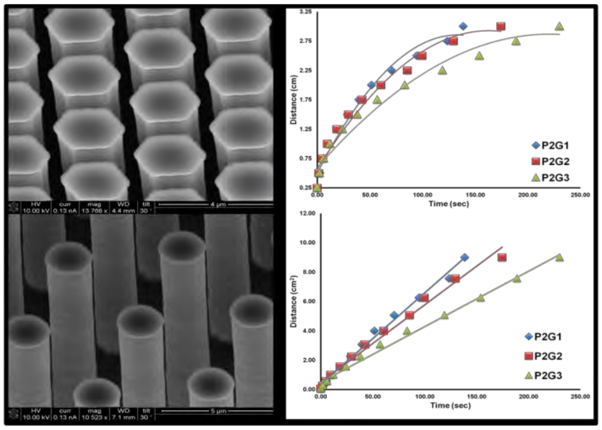

Figure 1. SEM images of 2 micron pillars with varying pitch (left). Preliminary solvent front flow kinetics comparison studies of 2 micron pillars with varying pitch (right).

Silicon nanopillars for field enhanced surface spectroscopy

CNMS-2011-040

Jennifer Charlton,[1] Sabrina Wells,[1] Michael Kandziolka,[1] Igor Merkulov,[2] Ivan Kravchenko,[2]
Nickolay Lavrik,[2] James Bradshaw,[3] and Michael Sepaniak[1]
[1] UTK Chemistry, [2] CNMS, [3] Y-12

Abstract:

Silicon nanowire and nanopillar structures have continued to draw increased attention in recent years due in part to their unique optical properties. Herein, electron beam lithography combined with reactive-ion etching is used to reproducibly create vertically-aligned, silicon nanopillars in varying sizes, shapes, and heights. By adjusting etching conditions, individual and arrays of pillars with diameters in the 80-150 nm range and with high aspect ratios as well as nearly parallel side walls are created. Finite difference time domain numerical analysis predicts enhancements in localized fields in the vicinity of appropriately-sized and coaxially-illuminated silicon nanopillars of approximately two orders of magnitude. By analyzing experimentally measured strength of the silicon Raman phonon line (500 cm^{-1}), it was determined that nanopillars produced field enhancement that are consistent with these predictions. Additionally, we demonstrate non-plasmonic surface enhanced Raman for a thin film on the pillar surface (Figure 1). Finally, silicon nanopillars of cylindrical and elliptical shapes were labeled with different fluorophors and evaluated for their surface enhanced fluorescence (SEF) capability. The SEF derived from analysis of the acquired fluorescence microscopy images indicate that silicon nanopillar structures can provide enhancement comparable or even stronger than those typically achieved using plasmonic SEF structures without the limitations of the metal-based substrates. It is anticipated that scaled up arrays of silicon nanopillars will enable SEF assays with extremely high sensitivity, while a broader impact of the reported phenomena are anticipated. Preliminary experiments are being conducted to explore these structures for applications in fluorescence-based bioassays and actinide detection.

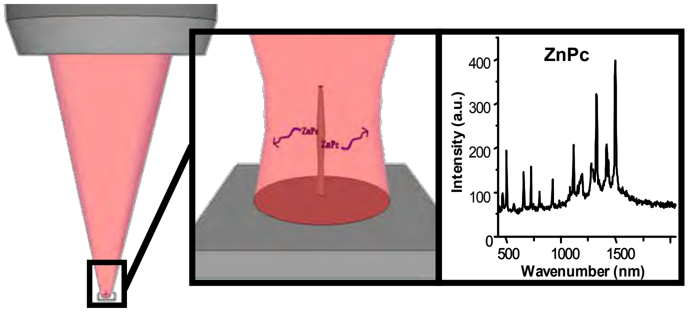

Figure 1. Schematic illustration of our experiments illustrating a single individual silicon nanopillar. The Raman spectrum is for a thin layer of zinc phthalocyanine .

Extraordinary optical transmission of multimode quantum correlations via localized surface plasmons

Benjamin Lawrie, Philip Evans, Raphael Pooser

Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
lawriebj@ornl.gov

With the recent growth of interest in quantum plasmonics, the ability to couple squeezed light sources into localized and propagating surface plasmons is a topic of growing importance that will allow for applications ranging from plasmonic continuous variable quantum information processing to sub-shot noise nano-imaging and bio-sensing. Quadrature squeezed surface plasmon polaritons have recently been demonstrated in Au waveguides [1], but the transduction of squeezed light by localized surface plasmons (LSPs) has not yet been demonstrated.

Recent literature has shown clear evidence for LSP mediated EOT in nano-hole arrays [2,3]. We demonstrate the coherent transduction of multi-spatial mode squeezed light by Ag LSPs in LSP mediated EOT, and demonstrate that squeezing as a function of transmission matches closely with experimental and theoretical linear attenuation models.

Arrays of triangle holes with base 230 nm, height 300 nm, and pitch 400 nm were fabricated in 80 nm Ag films by electron beam lithography (Fig. 1a). The transmission through the nanohole arrays was simulated with commercial finite difference time domain (FDTD) software (Fig. 1b) and measured by confocal microscopy (Fig. 1c) as a function of polarization. The FDTD electric field profile in Fig. 1d demonstrates that the near IR resonances result from LSP modes while the additional simulations have demonstrated that the visible resonances are the result of propagating plasmon polaritons modes.

Quantum correlated probe and conjugate beams were generated via four-wave mixing in Rb, and the probe was coupled through the hole-array while the conjugate was proportionately attenuated by a neutral density filter. Fig. 1e illustrates the relative intensity noise and shot noise, with 1.28 dB squeezing for a polarization of 60° or 150°. A linear attenuation model was used theoretically and experimentally to model the loss of squeezing in the presence of a variable neutral density filter, and Fig. 1f illustrates that except in the low transmission regime the EOT mediated squeezed light is well-described by such a model.

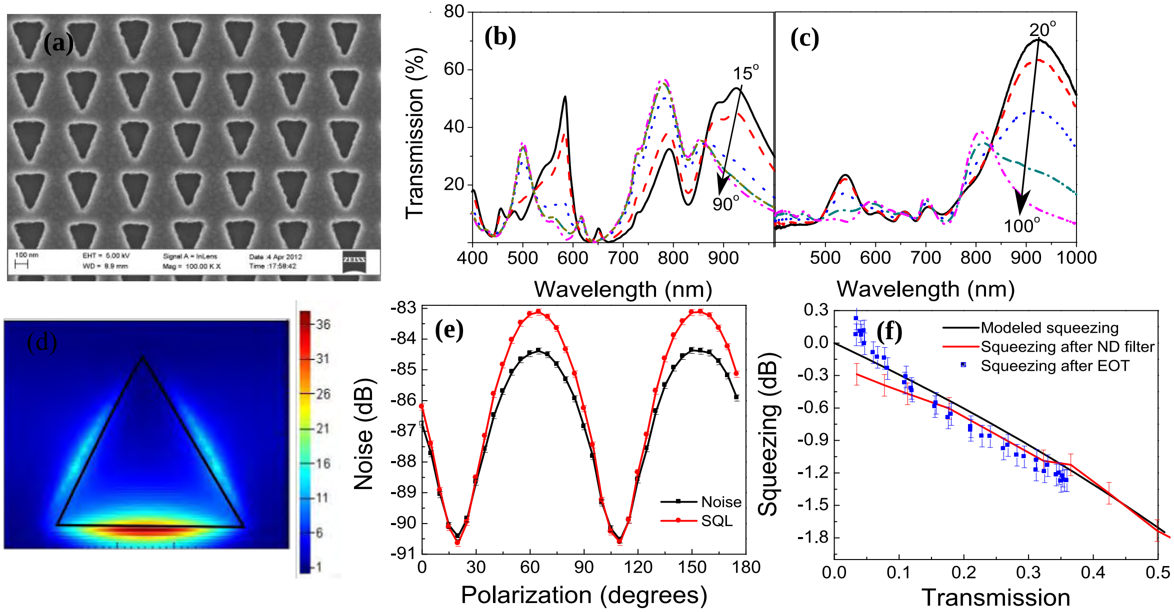

Fig. 1. SEM image (a) of Ag triangle hole array, with FDTD (b) and experimental transmission (c) spectra. 200 μm x 200 μm Electric field profile for 0° polarization illustrates near-IR LSP mode (d). The relative intensity noise and standard quantum limit for probe light coupled through the hole array (e), and the squeezing after EOT with the experimental and modeled results for attenuation by a variable ND filter (f).

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Nanophotonics: From novel fabrication technologies to reconfigurable photonics

Shuren Hu[1], Judson D. Ryckman[2], Yang Jiao[2], Jeremy W. Mares[2], and Sharon M. Weiss[1,2]

[1]*Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA*
[2]*Department of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, Tennessee 37235, USA*

The collaboration between CNMS and the Weiss group involves two themes: (1) Innovating new methods to push forward inexpensive mass production of nanophotonic sensors, and (2) Enabling ultra-fast, highly sensitive, power efficient devices for reconfigurable photonics.

1.) Direct imprinting of porous substrates (DIPS). One of the bottlenecks limiting the popularization of photonic devices and sensors is the fabrication cost and complexity. Our technique, DIPS, is a direct-to-device technique for mechanically deforming porous nanomaterials to produce well-defined micro- and nano-structures. While repeatably producing nanoscale features (<100nm), the overall process is remarkably simple, rapid, and low-cost. Different subprojects, related to label-free biosensors and tunable drug delivery, have been advanced due to implementation of the DIPS process.

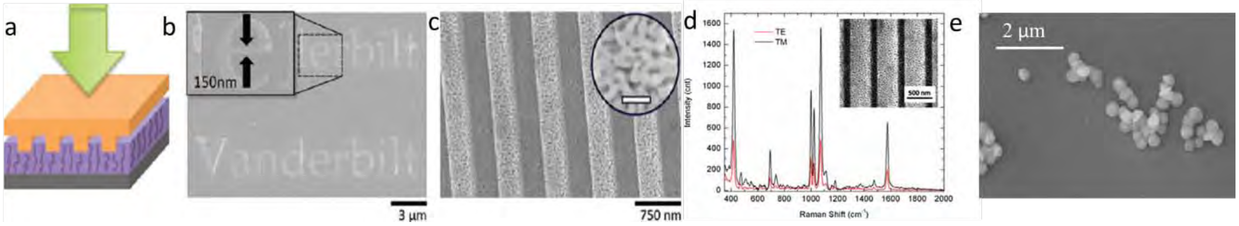

Fig1. (a) Illustration of DIPS. A reusable stamp imprinted into the porous material using an applied pressure on the order of 100 N/mm^2. (b) Porous silicon imprinted with 3µm font "Vanderbilt" text. (c) Nanoporous gold (NPG) grating (Λ= 750 nm). Inset reveals the original pore morphology (scale bar = 100 nm). (d) SERS spectra of benzenethiol molecules adsorbed on patterned NPG substrate with a 550 nm grating pitch, activated by TE (red) and TM (black) polarized light. (e) Ultrasonicated particles after DIPS. These nanosized particles are ready to be used for drug delivery

2.) Hybrid Silicon / Vanadium Dioxide Modulator. Motivated by the need for compact silicon-compatible optical switches operating at THz speeds, we demonstrate an optical modulator based on a silicon ring resonator coated with vanadium-dioxide (VO_2). VO_2 is a functional oxide that undergoes a semiconductor-to-metal transition (SMT) near 67°C. While the SMT can be induced optically by ultra-fast laser excitation in less than 100fs, in our initial work we utilize photothermal excitation. Optical modulation greater than 10dB is shown from modest quality-factor (~10^3) resonances, as well as a large –1.26nm change in resonant wavelength, resulting from the large change in the dielectric function of VO_2 in the SMT.

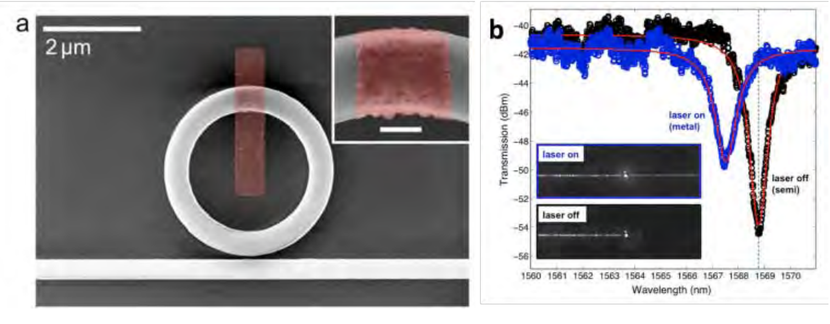

Fig2. (a) SEM image of a hybrid Si-VO_2 micro-ring resonator with 1.5µm radius. The lithographically placed VO_2 patch is highlighted in false-color. (Inset scale bar is 250nm). (b) Optical transmission of the 1.5µm radius hybrid Si-VO_2 ring resonator before and after triggering the SMT with a 532nm pump laser. Inset: IR camera images revealing vertical radiation at a fixed probe wavelength, λ=1568.78nm (dashed line).

RAMAN PLASMONIC ENHANCEMENT BASED ON BIOMIMETIC METAL NANOSTRUCTURES

Héctor I. Areizaga[1], Raymond A. Velez-Calder[1]; Marco A. De Jesús[1], Michael J. Sepaniak[2]; Nickolay V. Lavrik[3]; Ivan I. Kravchenko[3]

1. Department of Chemistry, University of Puerto Rico, Mayagüez, P.O. Box 9000, Mayagüez, PR 00681
2. Department of Chemistry, University of Tennessee, Knoxville, 552 Buehler Hall 1420 Circle Dr , Knoxville TN 37996-1600.
3. Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN, 37831-6496

Construction of high performance plasmonic nanomaterials for bio-sensing and trace chemical detection is a field of intense theoretical and experimental research. Consequently the need for plasmonic substrates capable of producing intense field enhancements with high surface areas for the rapid detection of trace bioactive agents of biomedical and environmental significance is ever more pressing. Bio-inspired designs offer the opportunity to develop hybrid nanostructures with the potential to exhibit highly intense and reproducible plasmonic fields over extended areas of complex-periodicity. This work uses nanolithographic and spectroscopic techniques for the construction, characterization and performance testing of asymmetric, bilateral and radially symmetric silver composites for surface enhanced Raman scattering (SERS) detection. The developed patterns consist of 40 × 40 µm nanoarrays with 150-120 nm particle benchmark size and 50 nm minimum inter-particle gaps. Designs are inspired on evolutionary successful schemes of fractal-based spirals (sunflower seeds and romanesco broccoli); bilaterally symmetric (acacia leaves, and honeycombs) and radially symmetric (orchids and lilies). CNMS fabrication sequence consisted of spin-coating, e-beam lithography, PECVD coating of SiO_2, and silicon reactive ion etching (RIE) Metallization with Ag by electro-evaporation rendered a SERS active surface. Studies conducted at 632.8 nm demonstrated Raman enhancements factors greater than 10^7 for the acacia leaf, sunflower and lilies patterns. Finite-difference time-domain (FDTD) simulations of the constructed devices are being employed to improve pattern performance and to evaluate experimental results with the theoretical predictions. Recent SERS studies in addition to FDTD simulations projects an improvement in the plasmonic responses at 785 nm given the actual inter-particle density, periodicity and morphology of the constructed patterns. The substrate characterization and SERS performance of the developed substrates as well as the strategies to improve the design performance are presented. The viability of the developed Raman substrates for routine trace analysis of bioactive agents is discussed.

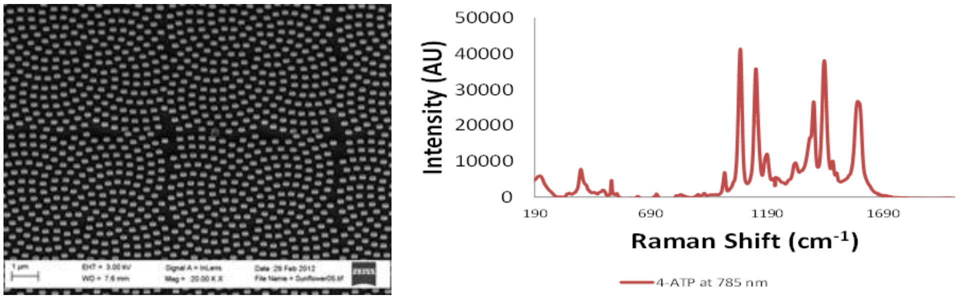

Figure 1: Field Emission Scanning Electron Microscope Image of a bio-Inspired Sunflower Nano-array (Left) and 4-aminothiophenol SERS Spectrum obtained with an excitation of785 nm (right)

Keywords: Surface Enhanced Raman Spectroscopy, bio-Inspired nano-arrays, plasmonic nanocomposites, bioactive agent detection.

Single-molecule mobility in confined and crowded femtoliter chambers

C. Patrick Collier

The effects of increased crowding and confinement on the mobility of individual fluorescent molecules were studied using Fluorescence Correlation Spectroscopy (FCS) and a microfluidic device with sealable femtoliter-volume chambers. When crowding and the degree of confinement were increased simultaneously, extended correlation times of fluorescent intensity fluctuations were observed compared to varying either crowding or confinement alone. The data suggests these extended correlation times were due to both enhanced hydrodynamic coupling and increased adsorption-desorption events at a wall. Such events are attributed to increases in local, effective concentrations of fluorophores at the wall in the presence of crowders. In the smallest sealed chambers, photobleaching had an increasingly important role in the dynamics. The data in increasingly confined and crowded chambers described here captures some of the salient features of crowding in cell-like environments.

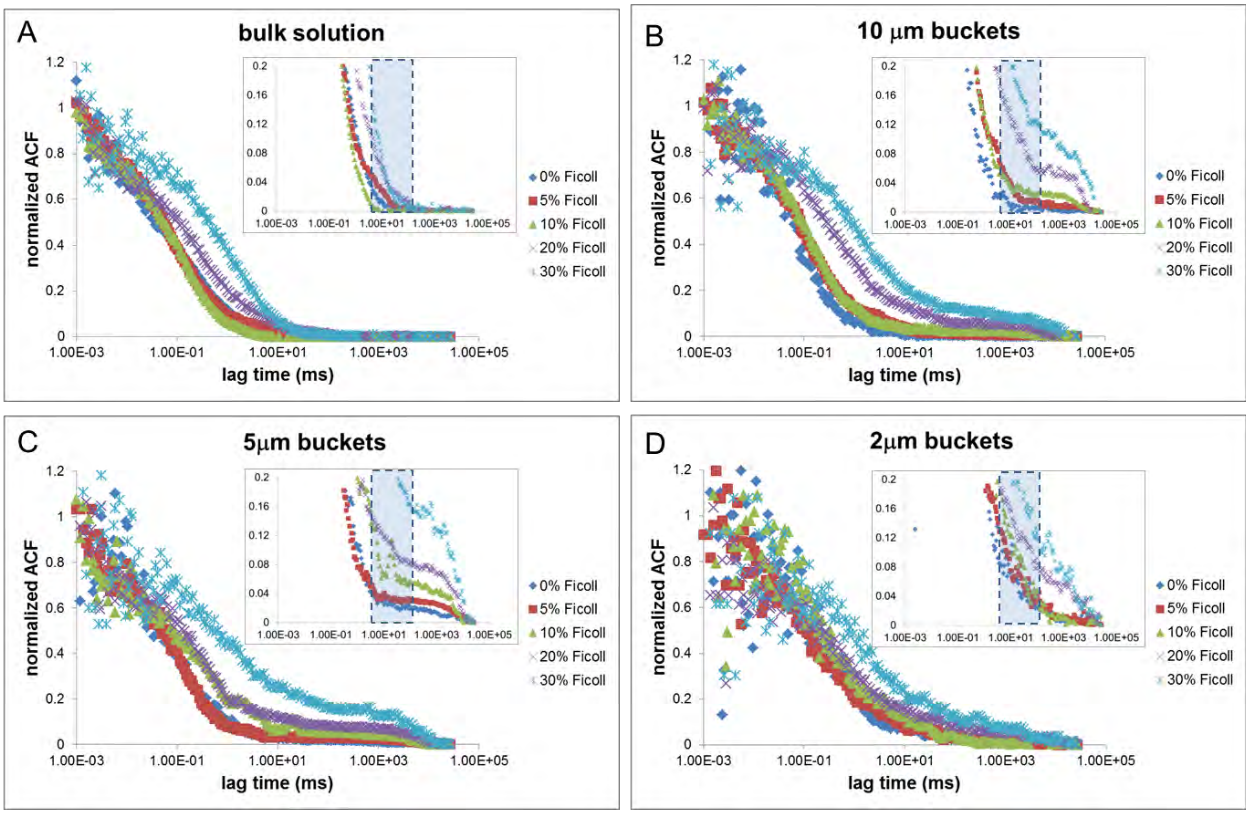

Fig. 1 Series of FCS measurements of AF555 fluorophores in increasingly confined and crowded femtoliter-volume sealed chambers. Insets highlight enhanced long lag time correlations in confined environments (panels B-D,) not observed for fluorophores outside the chambers in bulk solution in the microchannel (panel A). These long lag time correlations were amplified in the presence of crowding molecules like Ficoll-70. Rectangular regions in insets span the range of decorrelation times in bulk solution for increasing Ficoll concentrations, and are meant to underscore the different behavior in chambers.

Directed selfassemblage of soft matter nanostructures on inorganic surfaces

S. Vespucci,[2] S. Retterer,[1] S. Baschieri,[3] C. Cantale,[3] M. Caruso,[2] C. Dalmastri,[3] C. Lico,[3]
L. Mosiello,[3] P. Morales[3]

[1]Center for Nanoscale Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee
[2]The NAST Center, Tor Vergata University Unit Viale della Ricerca Scientifica 1, 00136 Roma, Italy
[3]ENEA, Centro Ricerche Casaccia and NAST Center Via Anguillarese 301 00123 Roma, Italy

Fabrication of nanoarchitectures and their directed assemblage on inorganic surfaces, based on specific biomolecular interactions, is attempted with the aim of building complex systems by hybrid technologies. Experimental investigation of the “DNA motherboard” concept feasibility involves the selfassemblage of predesigned DNA nanostructures, advanced nanolithography of selected inorganic materials, specific biomolecule-inorganic surface interactions and specific biomolecule-biomolecule interactions. Advances of the META project WP1 will be reported, showing ordered spots in the 10 nm range produced by e-beam lithography and first syntheses of ordered DNA nanostructures. Problems arising in the assemblage of such nanostructures on the surface mediated by specific and aspecific interactions will also be discussed.

Bio-inspired Assembly of Silica at the Nanoscale

Juan Pablo Hinestrosa[1], *Jonathan E. Sutton*[2], *David P. Allison*,[3,4] *Mitchel J. Doktycz*[1,3], *Jamie M. Messman*[1], *Scott T. Retterer*[1,3]

[1]Center for Nanophase Material Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
[2]Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716
[3]Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
4Department of Biochemistry & Cellular & Molecular Biology, University of Tennessee, Knoxville, TN 37996

Bio-inspired assembly and layer-by-layer construction of inorganic materials from lithographically defined organic templates enables the fabrication of nanostructured systems at low temperatures and mild pH, opening the door to low-impact manufacturing and facile recycling of nanostructured materials with unique mechanical, optical and electrical properties. Here, templated layer-by layer assembly of silica was achieved using a combination of electron beam lithography, chemical lift-off and aqueous solution chemistry. A nanopatterned mask of lines, honeycomb-lattices, and dot arrays was defined in electron beam resist. Subsequently, an amine-silane monolayer was vapor deposited onto the patterned substrates and was reacted at room temperature with silicic acid solutions made in buffers of varying pH and salt content. Vapor treatment and solution reaction could be repeated multiple times to perform layer-by-layer deposition while keeping the nanoscale ordering intact. The conditions for the silicic acid deposition, namely pH, salts and solution age, had a strong effect on the thickness of each layer and the morphology of the amorphous silica formed. Following silica deposition, the nanopatterned mask can be removed by sonication in acetone leaving only the silica nanostructures on the substrates. 'Defects' in the arrays of silica nanostructures were relatively minor and do not affect the overall organization of the layers. These defects were attributed to incomplete removal of the resist mask from underneath the deposited silica. The number of defects increased with the addition of each silica layer. The bio-inspired method described here allows for the bottom-up assembly of well-defined, inorganic nanostructures and provides a path, via layer-by-layer processing, to expand nanopatterns into the third dimension and enables the construction of layered hybrid materials under mild conditions.

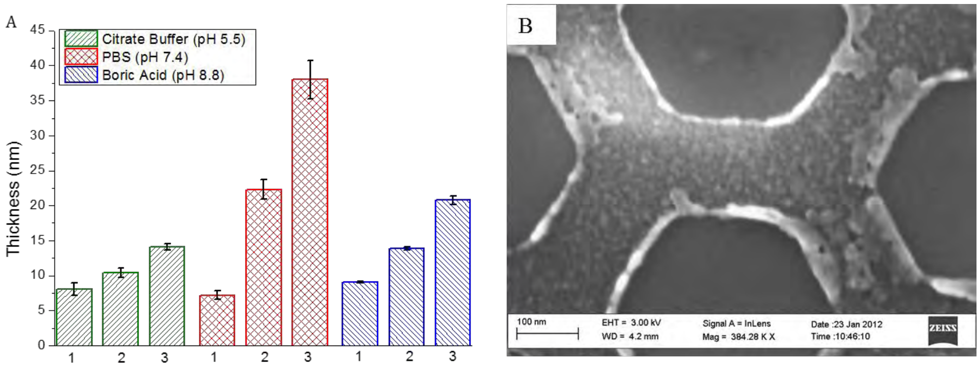

Figure. A. Evolution of silica layer thickness for each deposition step at the three pH conditions studied. B. SEM image of honeycomb-lattice of silica deposited from citrate buffer.

FRACTURE STRENGTH OF SMALL DIAMETER FIBERS WITH FIB AND NANO-TENSILE TESTING

M. Kant[1], D. Penumadu[1]
[1] Civil and Environmental Engineering, University of Tennessee, Knoxville, TN USA

Nano-fabrication tools at CNMS have been employed by the authors to study the fracture strength of single carbon fibers by introducing single-edge notches using focused ion beam. This technique has the advantage of direct application failure initiation site on small diameter (seven microns in this study) carbon fibers, while previous techniques relied on the approximation of the flaw causing failure after fracture [1]. Special attention was given to develop a milling procedure that would produce repeatable notch geometry in the fiber. Nano-tensile testing was carried out at the University of Tennessee with unique gripping and mounting procedure developed specifically on a single 7 micron T700 carbon fiber that was mounted (prepared for tensile extension), notched (milled in FIB), and tested (failed in tension) without any sample rearrangement. Using a nano UTM, a system derived from nano-indentation, failure loads were measured with nano-newton precision.

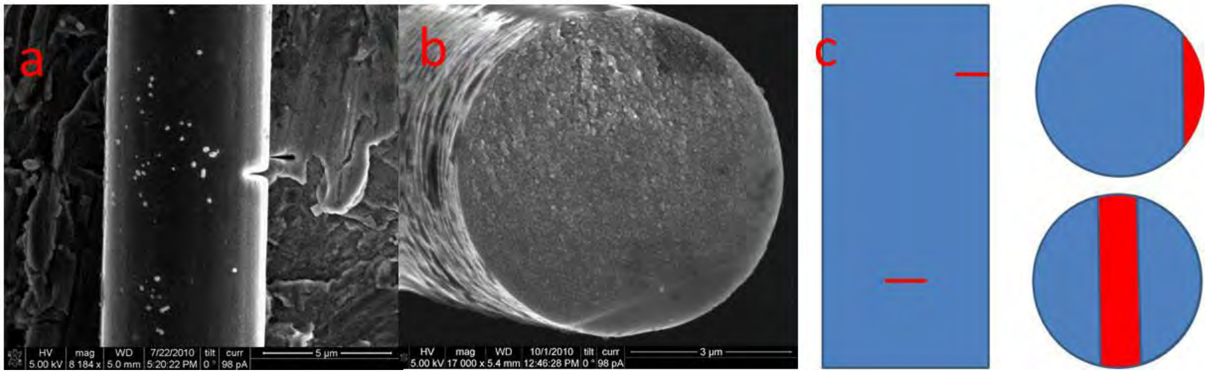

Figure 1 – a) Example edge notch on single carbon fiber. b) Example failure surface of single carbon fiber from FIB notch. C) demonstration of edge notch geometry (top) and center notch geometry (bottom). Red inicates locations of nano-fabrication.

The notch produced a stress concentration from which the failure load determined the fibers fracture strength according LEFM as in equation 1.

$$K_{IC} = \sigma_f Y \sqrt{\pi a_c} \qquad (1)$$

Currently, a KIc fracture strength of focused ion beam side notch geomtry has been determined for T700 carbon fibers to be 1.5 MPa*m$^{1/2}$. Future study involves the use of Focussed Electron Beam (FEB) to mill hole type geometries, seen in Figure 1c (bottom). It is of particular interest to observe property variation due to strucutral sheath/core inhomogeneity that is known to exist for carbon fibers, resulting from carbonisation process. However, it was found that the FIB was not an adequate tool for milling direct holes due to the inability to accomplish material removal, which resulted in hole broadening and approximately, a 1 micron depth limit. Thus, ongoing work is to create failure initiation sites of known size with hole type geometries by FEB. This approach has the added benefit of removing uncertainty associated with Galium impregnation by FIB milling.

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A triple beam microscope: focused laser processing in a scanning ion/electron microscope

N. A. Roberts[1,2], G. A. Magel[1], C. D. Hartfield[1], T. M. Moore[1], J. D. Fowlkes[3] and P. D. Rack[2,3]

1 Omniprobe, Inc., an Oxford Instruments Company, 10410 Miller Rd., Dallas, Texas 75238

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

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

In situ laser processing in a dual scanning electron/ion microscope can offer tremendous utility for direct–write micro– and nano – scale synthesis. Laser assisted electron beam induced deposition (LAEBID) introduces new microscope functionality including localized thermal processing (e.g., annealing) which can enable *in situ* observation of phase transformations or coupled with energy dispersive x ray analysis enables *in situ* chemical analysis. Presented here is the confluence of localized thermal processing and standard focused electron and ion beam induced processing – spatially overlapping electron and photon pulses induce the thermal desorption of reaction by-products, produced during electron beam induced deposition (EBID), effectively purifying the growing deposit on a layer–by–layer basis. EBID is a nanoscale direct write synthesis method where a focused electron beam locally induces the dissociation of a substrate-adsorbed precursor molecule. A portion of the dissociated molecule condenses at the electron-substrate-precursor interface containing the metal of interest as well as a contaminant by–product. Current results demonstrate the purification of platinum deposits (reduced the carbon content of the final deposit by ~50%) with the addition of synchronized laser pulses during deposition as well as a significant reduction in deposit resistivity. Moreover, the *pulsed* photon strategy diminishes issues associated with bulk substrate heating, which can shorten the precursor residence time and degrade pattern fidelity due to thermal drift. In addition, deposit spatial resolution improves. LAEBID deposits were found to be ~25% smaller than comparable EBID deposits. In addition to LAEBID, the focused laser processing has also been utilized for the dewetting of thin metallic films, localized chemical vapor deposition and etching (local to the laser spot).

Characterization of phase-separated, self-assembled, epitaxial Cu_2O-TiO_2 nano-pillar arrays for advanced photovoltaics

Daniela F. Bogorin, Tolga Aytug, Andrew R. Lupini, Sergei Kalinin, Evgheni Strelcov, Ivan I. Kravchenko, Adam J. Rondinone, Ilia N. Ivanov
(Oak Ridge National Laboratory, Oak Ridge, TN 37831)

Victor Maroni
(Argonne National Laboratory, Argonne IL 60439)

As components of the solar energy harvesting and conversion devices, nanostructured assemblies with well-defined geometrical shapes have emerged as high efficiency and economically viable alternate over planar junction thin film architectures. However, fabrication of inorganic nanostructures generally requires complicated and multiple step processing techniques, making them less suitable for large-scale manufacturing. Using *rf*- sputtering technique we have exploited phase-separated self-assembly and developed epitaxial, nanostructured composite films composed of phase separated, and vertically oriented *p-n* interfacial nanocolumns of Cu_2O (p type; bandgap ~2eV) and TiO_2 (n type; ~3.2 eV). The characteristic band gaps of these phases allow extension of the solar capture from ultraviolet to a visible wavelenght. The composite films were grown on perovskite substrates and exhibit single crystalline epitaxy in both phases. We have investigated crystalline structure and phase, interfacial quality, optical absorption and charge carrier transport properties of the nanopillar arrays using XRD, TEM, SEM, conductive-AFM, UV-vis, and Raman spectroscopy. Here, we present nearly complete atomic order at Cu_2O-TiO_2 interface and an absorption profile that captures a wide range of solar spectrum extending from ultraviolet to visible wavelengths. Compared to layered thin film architectures, the use of such vertically aligned nanostructures in solar cells can promote cost-effective fabrication of high efficiency photovoltaic devices by providing low defect concentrations, improved absorption and light trapping capabilities, along with increased minority carrier diffusion lengths.

Ab initio based multi-scale modeling of segregation in solids

Hyunwook Kwak[1], Yun-kyung Shin[2], Adri C. T. van Duin[2], and Alex V. Vasenkov[1]

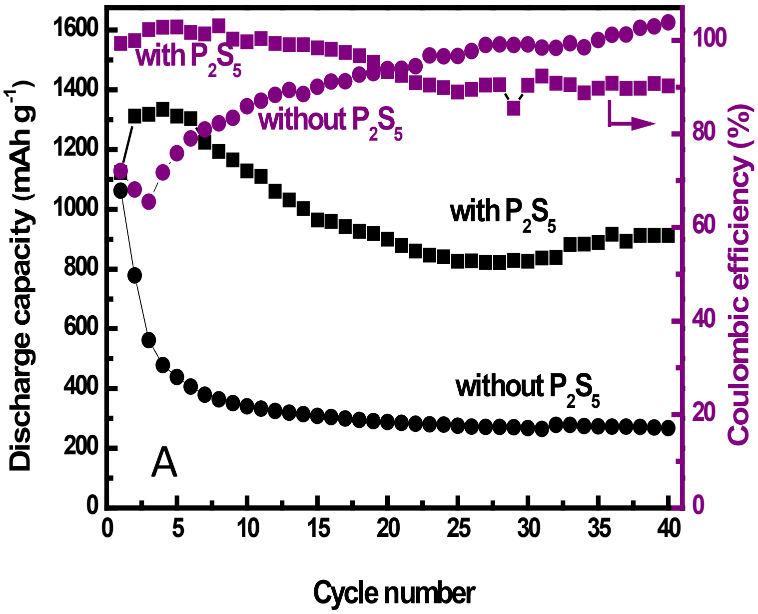
Ab initio multiscale model for segregation was formulated for multi-component condensed-phase materials by bridging the gap between first-principles DFT and large-scale MD-MC hybrid scheme using the ReaxFF reactive force field formalism. The model enables first-principles-based quantitative prediction of composition changes in ordered and disordered condensed-matter phases at different temperatures. Feasibility of the model was demonstrated via the analysis of segregation in FeAl binary alloy surfaces and sulfur atoms diffusion and segregation in the grain boundaries of aluminum and alumina. The model provides detailed description of the segregation mechanism as well as atomic composition predictions well in agreement with experiment. Based on the model's prediction capabilities, potential application of the model to the analysis of multi-component systems undergoing rapid chemical reactions will be discussed.

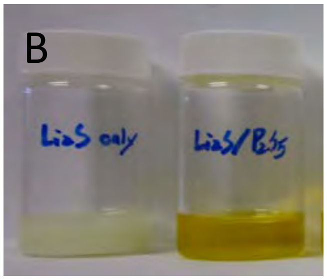
Affiliations:
[1] CFD Research Corporation, 215 Wynn Drive, Huntsville, AL 35805
[2] Pennsylvania State University, University Park, PA 16802

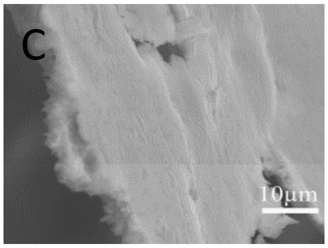
Phosphorous pentasulfide as a novel additive for high-performance lithium-sulfur batteries

Zhan Lin[1], Zengcai Liu[2], Wujun Fu[2], Nancy J. Dudney[1], and Chengdu Liang[2*]
1, Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6124, USA
2, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6493, USA

Lithium-sulfur (Li-S) batteries suffer from rapid capacity decay and low energy efficiency because of the low solubility of lithium sulfide (Li_2S) in organic solvents and the intrinsic polysulfide shuttle phenomenon. Here, we report a novel additive of phosphorus pentasulfide (P_2S_5) in organic electrolyte to boost the cycling performance of Li-S batteries. The function of the additive is two-fold: (1) P_2S_5 promotes the dissolution of Li_2S and alleviates the loss of capacity caused by the precipitation of Li_2S; and (2) P_2S_5 passivates the surface of lithium metal and therefore eliminates the polysulfide shuttle phenomenon. A Li-S test cell demonstrates a high reversible capacity of 900-1350 mAh g^{-1} and a high coulombic efficiency of ≥90% for at least 40 stable cycles at 0.1 C. Figure A: Comparison of Li-S cells with and without P_2S_5. Figure B: Photograph of insoluble Li_2S in tetraglyme, the common organic liquid electrolyte for Li-S batteries. Addition of P_2S_5 (right vial) results in fully dissolved complexes. Figure C: SEM image of a solid-electrolyte interphase (SEI) layer peeled off from the Li anode.







Cr, N, -Codoped TiO_2 Mesoporous Microspheres for Li-ion Rechargeable Batteries

Zhonghe Bi[1], Craig A. Bridges[1], Bingkun Guo[1], Xiao-Guang Sun[1], Raymond R. Unocic[2],
Harry M Meyer III[2], Sheng Dai[1], and M. Parans Paranthaman[1]

[1]Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

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

In recent years, TiO_2 has been identified as one of the most promising materials for electronic devices including solar cells and Li-ion rechargeable batteries (LIBs), because of its relatively high abundance in nature, low toxicity, and safe to handle.[1] However, its' intrinsic physicochemical properties of low electronic conductivity leads to relative poor rate capability owing to the poor electron transport when utilized as a host for Li-ion intercalation, which limits its practical application. Meanwhile, promising TiO_2 based mesoporous sphere materials have been widely reported as electrode materials for LIBs.[2] Micrometer sized sphere has also been considered as the optimal material morphology in conventional electrode fabrication technique, since this kind of architecture has the function of ensuring high contact area between electrolyte and electrode, short diffusion distances for Li^+ transport, good accommodation of strain during cycling, as well as high packing density.[2] However, one concern for mesoporous materials is the long transport distance of electrons in micron sized particles, especially for low conducting TiO_2. Therefore, increasing the electronic conductivity of TiO_2 becomes more important for mesoporous TiO_2 materials. According to our previous study, it predicted that Cr-N is the preferred codopant pair using first-principles calculations.[3] And also Cr-N codoped TiO_2 nanoparticles indeed exhibited substantially narrow band gaps, as well as dramatically enhanced photoabsorption and photoactivity in the visible spectral region. Therefore, it is highly desirable to develop a Cr-N codoped TiO_2 with the morphology of mesoporous microsphere that could combine the advantages of the mesoporous structure, spherical morphology, and higher electronic conductivity, this combination which has not been reported before. We will report in detail about a facile synthesis of Cr-N codoped mesoporous TiO_2 microspheres with enhanced electrical conductivity as high power anode materials for LIBs, which exhibit high capacity, good cycling performance, and high rate capability.

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TiO_2 Nanotube Arrays on Porous Ti Foam for Rechargeable Lithium and Sodium Ion Batteries

M. Parans Paranthaman,[1] Zhonghe Bi,[1] Paul A. Menchhofer,[2] Ryan R. Dehoff,[2] Craig A. Bridges,[1] Miaofang Chi[2], Bingkun Guo,[1] Xiao-Guang Sun,[1] Sheng Dai[1]

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

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

Abstract

Self-organized amorphous TiO_2 nanotube arrays (NTAs) were successfully fabricated on both Ti foil and porous Ti foam through electrochemical anodization techniques. The starting Ti foams were fabricated using Additive Manufacturing Facility, ARCAM's Electron Beam Melting (EBM) technology. The TiO_2 NTAs on Ti foam were used as anodes in lithium ion batteries; they exhibited high capacities of 103 $\mu Ahcm^{-2}$ at 10 μAcm^{-2} and 83 $\mu Ahcm^{-2}$ at 500 μAcm^{-2}, which are two to three times higher than those achieved on the standard Ti foil, which is around 40 $\mu Ahcm^{-2}$ at 10 μAcm^{-2} and 24 $\mu Ahcm^{-2}$ at 500 μAcm^{-2}, respectively. This improvement is mainly attributed to higher surface area of the Ti foam and higher porosity of the nanotube arrays layer grown on the Ti foam. In addition, a Na-ion half-cell composed of these NTAs anodes and Na metal as the counter electrode showed a self-improving specific capacity upon cycling at 10 μAcm^{-2}. These results indicate that TiO_2 NTAs grown on Ti porous foam are promising electrodes for Li-ion or Na-ion rechargeable batteries.

This work was sponsored by the Materials Science and Engineering Division, Office of Basic Energy Sciences, U.S. Department of Energy. Microscopy work was conducted at the ORNL CNMS-SHaRE user facility, which is sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy. Drs. Z. Bi and B. Guo acknowledge the support of the ORISE postdoctoral fellowship.

Graphitic Mesoporous Carbons as the Supports of Promoted Rhodium and Molybdenum Carbide Catalysts for Alcohol Production from Synthesis Gas

Song-Hai Chai [a], Jane Y. Howe [b], Viviane Schwartz [c], Michelle Kidder [a], Steven H. Overbury [a,c], Sheng Dai [a,c,d], De-en Jiang [a]

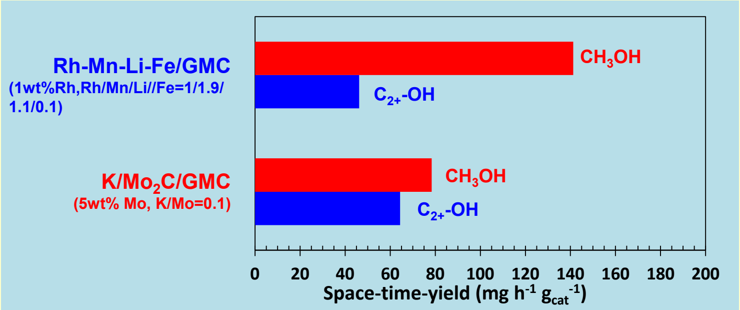
[a] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[b] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[c] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[d] Department of Chemistry, University of Tennessee, Knoxville, TN 37966, USA

ABSTRACT

Graphitic mesoporous carbon (GMC), synthesized via a facile soft-templating route, was used as the support of Mn, Li, and Fe triple-promoted Rh catalysts for synthesis of light alcohols (C_1–C_3) from synthesis gas (CO + H_2). A significant inhibition on the formation of undesired CH_4 and light hydrocarbons was observed over the GMC-supported catalyst compared with the conventional SiO_2-supported counterpart, while the formation rate of desired C_2H_5OH was maintained. The reaction-induced growth of active Rh nanoparticles over GMC was found much slower than that over SiO_2. In addition, GMC as support showed higher catalytic activity for C_2H_5OH formation than other carbon materials such as amorphous mesoporous carbon and non-porous carbon black. The preferable performance of GMC could be associated with unique electron structure of graphitic carbon providing a specific metal-support interaction, as well as its featured nanochannels offering a confinement environment for metal particles. The surface modification of GMC by wet oxidation with HNO_3 can further enhance the catalytic activity for C_2H_5OH formation. On the other hand, we also studied the use of GMC as the support of molybdenum carbide (β-Mo_2C) catalysts, which are the promising alternatives to expensive Rh-based catalysts for the synthesis of C_1–C_3 alcohols from synthesis gas. The CO conversion rate over β-Mo_2C/GMC was six-time higher than that over precious Rh/GMC counterpart. The selectivity and formation rate of C_2–C_3 alcohols were enhanced considerably by introducing a minor amount of K_2CO_3 into the β-Mo_2C/GMC catalysts, while undesired light hydrocarbons were suppressed simultaneously. The K_2CO_3-promoted β-Mo_2C/GMC exhibited comparable selectivity and space-time-yield for C_2–C_3 alcohols to a typical Rh-Mn-Li-Fe/GMC catalyst with optimized composition.

Catalytic performance of GMC-supported Rh and Mo_2C catalysts

(573 K, 3.0 MPa, H_2/CO=2, GHSV = 36,000 ml h^{-1} g_{cat}^{-1})



Catalyst	CO Conv. (%)	S_{CO2} (mol-C%)	Carbon Selectivity (mol-C%, CO_2-free)					
			CH_4	C_{2+}-HC	CH_3OH	C_2H_5OH	1-C_3H_7OH	Other C_{2+}-oxy.
Rh-Mn-Li-Fe/GMC	2.0	17.0	14.6	1.3	53.4	22.5	2.0	6.2
K/Mo_2C/GMC	3.1	33.6	22.0	17.9	24.2	22.9	5.6	7.4

Zeolite LTA-Polyimide Nanocomposite Membranes for Natural Gas Separations

Megan Lydon[1], Kinga Unocic[2], Christopher Jones [2,3], Sankar Nair[3]

[1]School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, GA
[2]Oak Ridge National Laboratory, Oak Ridge, TN
[3]School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA

Natural gas is emerging as one of the most important energy sources. It often includes large amounts of impurities such as CO_2 that need to be removed prior to use. Large improvements in the efficiency and cost of natural gas separation/purification are needed. Zeolite materials are of interest for natural gas separations because their angstrom-scale pores can be chosen or tuned to provide excellent selectivity between gases of different kinetic diameters. Nanocomposite membranes consisting of a bulk polymer phase and a dispersed selective zeolite phase are gaining attention for improving the membrane gas separation capabilities of traditional polymer membranes while avoiding the high processing costs of purely inorganic zeolite membranes. However, poor adhesion between the polymer and zeolite phase leads to nonselective pathways for gas molecules around the more selective zeolite particles. Functionalization of the zeolite with MgO_xH_y inorganic surface nanostructures has been shown to improve compatibility between phases in these membranes and eliminate or minimize the gap.

In this work, four unique methods of surface roughening are presented on the aluminosilicate zeolite LTA and the functionalized nanoparticles are characterized using high resolution transmission electron microscopy, nitrogen adsorption characterization of surface area and pore volume, X-ray diffraction, and elemental analysis. Additionally, we show how these nanostructures impact the various properties of polyimide nanocomposite membranes including gas selectivity, mechanical properties, and phase compatibility using CO_2/CH_4 gas permeation, nanoindentation, and TEM imaging of membrane cross sections. We will show that one method, ion exchange induced surface deposition, shows significantly improved interfacial compatibility with the glassy polymer while maintaining the intrinsic structure and gas separation properties.

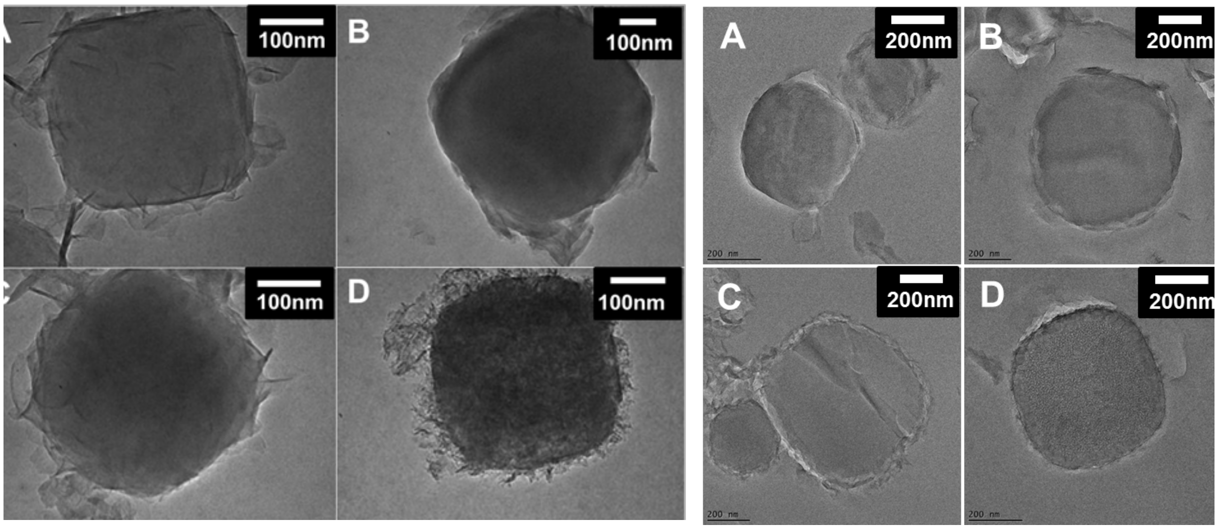


Figure 1: LTA functionalized by the A) Grignard B) Solvothermal, C) Modified solvothermal, and D) Ion exchange methods (Left) and a cross section of the functionalized LTA particles in a Matrimid nanocomposite membrane.

Are the Surfaces of Oxide Nanocrystals With Defined Facets as Perfect as They Appear? – A Case Study of Nanoshaped Ceria Catalysts

Zili Wu, Meijun Li, Steven H. Overbury

Chemical Science Division and Center for Nanophase Materials Sciences
Oak Ridge National Laboratory, Oak Ridge, TN 37831. Email: wuz1@ornl.gov

Heterogeneous catalysis takes place on the surface of catalytic materials and undoubtedly the surface structure plays an essential role in catalysis. However, the complexity and heterogeneity of traditional catalysts prevents a full understanding of the interplay between surface structure and catalytic behavior. Recent advances in nanomaterials synthesis make it possible to achieve nanocrystals with crystallographically defined surface terminations and high surface area. Application of these well-faceted nanocrystals in catalysis has generated interesting catalytic function that is dependent on the surface structure of the nanomaterials. To understand the structure dependence, a prerequisite is the full characterization of the surface sites of these nanocrystals during the catalytic process.

In this research, we investigate the surface structure of nanoshaped catalyst via probe molecules and probe reactions. Nanostructured CeO_2 crystals, rods, cubes and octahedra, are chosen with each exhibiting well-defined crystallographic planes. Methanol[1] and di-oxygen[2] were employed to probe the surface sites of these nanoshapes under oxidized and reduced condition, respectively. The reactivity of the different surfaces was also probed by a prototype reaction, CO oxidation.[3] Through detailed *in situ/operando* infrared and Raman spectroscopic studies, the surface species and reaction pathways were clearly identified on the ceria nanoshapes. We found that although the three ceria nanoshapes are well-structured on the surface, they are not perfectly faceted but contain defects on the surface and in the bulk that can have a profound effect on the surface chemistry during ceria catalysis. It is suggested that the surface structure of ceria controls the catalytic performance through the structure-dependent surface vacancy formation energy, defect sites and coordinatively unsaturated sites on ceria. Our study implies that the catalytic properties of ceria nanoparticles could be mediated and tuned by controlling their shape and thus surface sites, which points to a strategy for both the improvement of current heterogeneous catalysts and the design of highly efficient catalyst without the change of the catalyst composition.

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Solution-Based Lithium Incorporation and Delamination of Magnesium Diboride

Daniel R. Sexton, Matthew T. Davidson, Christopher A. Barrett and Tina T. Salguero

Department of Chemistry, University of Georgia, Athens, Georgia 30602, USA

The metal diborides (MB_2) are an underdeveloped class of high performance ceramic materials. The most famous member is MgB_2, known for its excellent superconducting properties at relatively high temperature (T_c = 39 K); in addition, there is significant commercial interest in MgB_2 because of its simple structure and inexpensive source components. In this contribution, we report the preparation and characterization of MgB_2 and MgO nanosheets derived from bulk MgB_2 via exfoliation and delamination processes. The composition, morphologies, crystal structures, and properties of these nanosheet materials were elucidated using a combination of TEM, SEM, PXRD, EELS, solid state NMR, and SQUID analysis.

In situ synthesis of oxynitrides

Craig Bridges
Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

The development of the chemistry of nanophase oxyanion synthesis is an important area, as this may expand the role these materials play in the future for both energy storage and conversion. The synthesis of oxynitride phases has typically required the formation of an amorphous or small particle precursors, due to the relatively slow diffusion of the nitride anion at typical synthesis temperatures. Here we examine in detail the correlation of synthesis conditions in the formation of oxynitrides. Nanoparticles and bulk particles have been prepared through a variety of methods to obtain well defined precursors for ammonolysis. In situ diffraction results will be presented, and this work provides insight into the underlying factors controlling anion transport for this particularly difficult class of oxyanion synthesis.

Synthesis of Cadmium Selenide (CdSe) Quantum Dots via an Aerosol Route

He Jing and Da-Ren Chen

Washington University in St. Louis, One Brookings Drive, St. Louis, Missouri, 63130

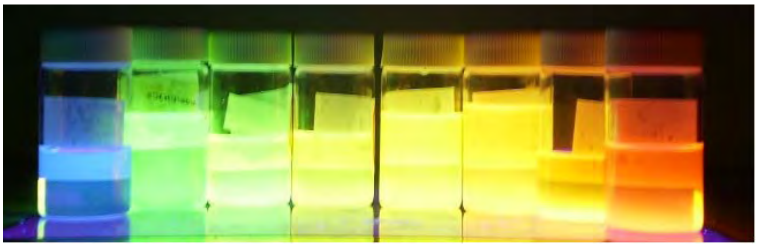

Figure 1 *Representative samples of CdSe Quantum Dots under UV illumination*

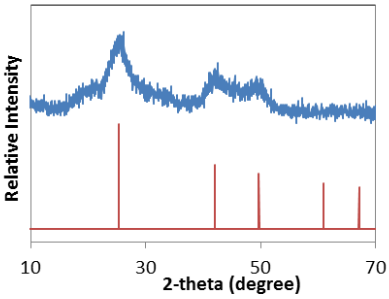

Figure 2 *X-ray diffraction of CdSe nanoparticles*

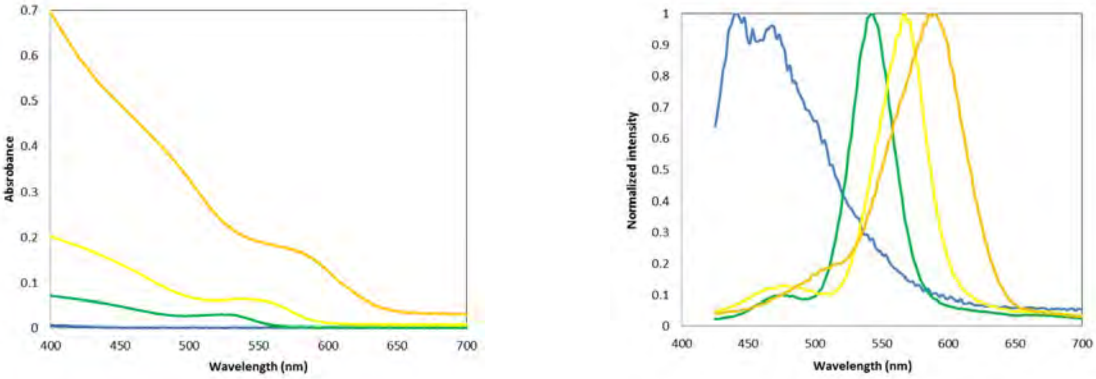

Figure 3 *Absorbance (left) and photoluminescence (right) spectra of CdSe Quantum Dots with the emission light of various colors in the visible light region*

In this study, an aerosol route was applied to synthesize CdSe Quantum Dots, which could have the benefit for continuous and scale-up production. The synthesis route includes the atomization of reactants via a custom-made atomizer producing polydisperse droplets of the mean size of 0.3 µm, passing the droplets through a tube furnace and the collection of resultant particles via bubblers. The reaction rate and time of the synthesis can be controlled by varying the reaction temperature and carrying gas flow rate. As a result, quantum dots with emission light peaks of 465 nm to 609 nm were obtained. The qualities of the quantum dots were comparable with those obtained by the hot-injection approach. Furthermore, the effect of molar ratio for two used reactants (i.e., Cadmium acetate and Selenium) on the quality of prepared QDs was also investigated. Under the same operational condition, the higher Cd:Se molar ratio resulted in QDs having the longer emission light peak wavelength. Except the case that a large excess of the Cadmium precursor presented (Cd:Se = 5:1), the full width at half maximum (FWHM) of the emission spectra remained close.

SAXS studies of alkyl chain, temperature, and confinement effects on the structure of room temperature ionic liquids

José Leo Bañuelos,[1] Song Li,[2] Guang Feng,[2] Pasquale F. Fulvio,[1] Nikolas Arend,[3] Gernot Rother,[1] Antonio Faraone,[4] Lawrence M. Anovitz,[2] Patrick Hillesheim,[1] Jianchang Guo,[1] Robert W. Shaw,[1] Sheng Dai,[1] Peter T. Cummings,[2,5] David J. Wesolowski[1]
[1]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee
[2] Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee
[3]Jülich Center for Neutron Science at the Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee
[4] NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland
[5]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee

The application of room temperature ionic liquids (RTILs) in various technological applications, for example, as solvents, stabilizers, in hydrolysis, and as electrolytes in energy storage applications, is made possible by the wide range of tunable properties of these designer molten salts. Specificity is achieved by fine-tuning the functional groups of the weakly coordinating organic cation and inorganic/organic anion. Imidazolium-based, and more recently, pyrrolidinium-based RTILs have been the subject of investigation in energy storage applications due to their wide electrochemical stability windows of 4.9 V and 5.9 V, respectively. From the large body of work devoted to studying these systems, a consensus of the laws governing the structure and properties for these classes of RTILs is beginning to emerge. However, there is a lack of experimental insight about the structure of RTILs at interfaces and under nano-confinement; both of which are conditions encountered in electrical energy storage systems. Small angle X-ray scattering (SAXS) measurements were conducted to investigate the alkyl chain length and temperature effects on the structural properties of the [C_nMPy] [Tf_2N] family of RTILs with n=3-10 and at temperatures from 23 to 90 ^{o}C. In combination with atomistic molecular dynamics simulations, the observed behavior is described in terms of competing electrostatic and van der Waals interactions. SAXS studies of various RTILs loaded at varying degrees into mesoporous carbon frameworks were carried out and the findings combined with various neutron scattering techniques to obtain insight on the interfacial structure and dynamics of confined RTILs.

Enhanced Dispersion and Stability of Platinum on SiO_2 by Surface Modification with ZrO_2 and TiO_2 – Impact on CO Oxidation Performance

Mi-Young Kim, Jae-Soon Choi*, Todd J. Toops, Viviane Schwartz, Jihua Chen
Oak Ridge National Laboratory, USA
Eun-Suk Jeong, Sang-Wook Han
Chonbuk National University, South Korea

Effective use of platinum group metals (PGM) is important to meet ever tightening emission standards while minimizing catalyst cost. Alumina is the most widely used PGM support due to hydrothermal stability and ability to maintain Pt dispersion, but its high reactivity toward SO_x causes drastic performance degradation. Silica is relatively inert toward SO_x, but PGMs dispersed on SiO_2 are easily sintered due to weak metal-support interaction. We have reported that the thermal stability of Pt particles on SiO_2 can be greatly enhanced by incorporating a layer of TiO_2, ZrO_2, CeO_2, or V_2O_3, and subsequently treating with H_2O_2 [1]. In this presentation, we will discuss the promising potential of these materials as automotive catalysts by investigating performance in CO oxidation at fresh, sulfated, and hydrothermally aged states.

Catalysts were prepared by impregnating 1 wt% Pt on TiO_2- or ZrO_2-modified SiO_2 (Pt/Ti-Si-H_2O_2, Pt/Zr-Si-H_2O_2) as described in [1]. Pt catalysts supported on SiO_2 or Al_2O_3 (Pt/Si, Pt/Al) were also prepared as references. The catalysts were sulfated at 400 °C for 3 h in 30 ppm of SO_2, 4% O_2, 5% H_2O, and Ar balance, desulfated by temperature programmed reduction to 800 °C in 1% H_2, 5% H_2O, and Ar balance, and finally hydrothermally aged at 800 °C for 2 h. After each treatment, catalyst physicochemical properties were examined using XRD, *in-situ* XAFS, TEM, BET, CO_2 and NH_3 temperature programmed desorption (TPD). Catalytic performance was evaluated using CO oxidation reaction (1% CO + 4% O_2 + 5% H_2O in Ar balance).

Pt/Ti-Si-H_2O_2 and Pt/Zr-Si-H_2O_2 showed higher catalytic activity in CO oxidation than Pt/Al and Pt/Si regardless of treatment type. The Ti- and Zr-incorporation led to higher dispersion as shown in Figure 1, stronger interaction with the support and greater electron deficiency of Pt, resulting in excellent fresh-state performance. The Ti- and Zr-incorporated catalysts were also easier to desulfate than Pt/Al due to their lower basicity. The performance of these catalysts was superior even after severe hydrothermal aging at 800 °C, especially with incorporation of a Zr-layer.

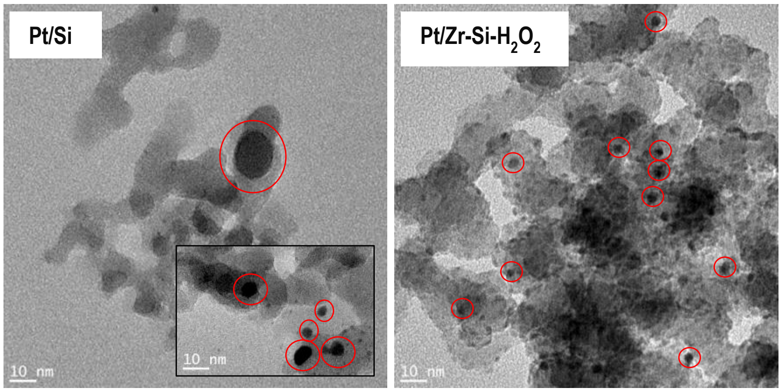

Figure 1. TEM images of Pt catalysts.

This study demonstrates the feasibility of developing highly stable, sulfur-tolerant oxidation catalysts with reduced Pt use via controlled surface modification of silica supports with transition metal oxides.

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Effect of Solvent Quality on the Chain Conformation of Poly(3-Hexylthiophene) (P3HT) in Solution and the Crystalline Morphology of Solution-Casted Thin Film

Jong Kahk Keum,[1*] Kai Xiao,[2] Ilia N. Ivanov,[2] Kunlun Hong,[2] James F. Browning,[1*] Gregory S. Smith,[1] Ming Shao,[2] Kenneth C. Littrell,[1] Adam J. Rondinone,[2] Andrew E. Payzant[2]

[1]Neutron Scattering Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[2]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Understanding the chain conformation of conjugated polymers in casting solution and its impact on the crystalline morphology of solution-casted thin film is crucial in many optoelectronic applications. Using small-angle neutron scattering, we show that well-dissolved poly(3-hexyl thiophene) (P3HT) chains in good solvent (chloroform) abruptly grow into long lamellae upon increasing the fraction of poor solvent (hexane), i.e., coil-to-lamella transition. The growth of lamella is due to the strong π-π interaction of P3HT chains, which becomes dominant with increasing poor solvent proportion above a certain critical point. Various P3HT solutions with different chain conformation were then drop-casted onto Si-wafers to prepare thin films and the films were examined by X-ray diffraction. The results indicated that the grown lamellae in solution induce much more improved crystallinity and crystal orientation in the casted thin film than disordered chains do.

End Functionalized Conjugated Polymers for Potential Self Assembly and Optoelectronic Applications

T. David[1], S. Sun[1], D. Pickel[2], and K. Hong[2]
[1]Center for Materials Science (CMR), Norfolk State University
[2]Center for Nano Materials Science (CNMS), Oak Ridge National Lab

Organic Materials, especially conjugated organic materials and polymers have been the focus of research for sensors, organic field effect transistors, organic solar cells, and many other electronic and optoelectronic devices. In addition to the ease of processing and cost efficiency, organic materials and polymers also exhibit attractive properties for optoelectronic devices such as flexibility, property tenability, chemical functional tailorbility, etc. Charge mobility in typical polymeric electronic semiconductor devices are still relatively low (typically less than 1.0 cm^2/vs) compared to typical crystalline semiconductors. However, it has been observed that charge mobility appears much more efficient in organized molecular wires and self assembled monolayers, where single molecules or oligomers (<20 repeat units) are chemisorbed or physisorbed to a conductive substrate via interactive (docking) functional end groups (such as RNH_2, -RSH, -RCN, and $-RSiR_3$). This research focused on the synthesis, characterization, and optoelectronic studies of end-functionalized conjugated polymers for self-assembly on conducting surfaces and for optoelectronic application studies. In this presentation, our preliminary results on the synthesis and characterization of the end functionalized polymer will be presented.

Charge regulation and local dielectric function in planar polyelectrolyte brushes

Rajeev Kumar[1], Bobby G. Sumpter[2] and S. Michael Kilbey II[2,3]
[1] National Center for Computational Sciences, Oak Ridge National Laboratory, Oak Ridge, TN-37831
[2] Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN-37831
[3] Department of Chemistry, University of Tennessee, Knoxville, TN-37996

Understanding the effect of inhomogeneity on the charge regulation and dielectric properties, and how it depends on the conformational characteristics of the macromolecules is a long-standing problem. In order to address this problem, we have developed a field-theory to study charge regulation and *local* dielectric function in planar polyelectrolyte brushes. The theory is used to study a polyacid brush, which is comprised of chains end-grafted at the solid-fluid interface, in equilibrium with a bulk solution containing monovalent salt ions, solvent molecules, and pH controlling acid. In particular, we focus on the effects of the concentration of added salt and pH of the bulk in determining the local charge and dielectric function. Our theoretical investigations reveal that the dipole moment of the ion-pairs formed as a result of counterion adsorption on the chain backbones play a key role in affecting the local dielectric function. For polyelectrolytes made of monomers having dipole moments lower than the solvent molecules, dielectric decrement is predicted inside the brush region. However, the formation of ion-pairs (due to adsorption of counterions coming from the dissociation of added salt) more polar than the solvent molecules is shown to increase the magnitude of the dielectric function with respect to its bulk value. Furthermore, an increase in the bulk salt concentration is shown to increase the local charge inside the brush region.

Temperature Gradient Interaction Chromatography: An inside look at polymer heterogeneity

Deanna L. Pickel, George C. Morar, David W. Uhrig, S. Michael Kilbey, II

Polymer chemists have traditionally relied on Size Exclusion Chromatography (SEC) to provide information about the heterogeneity in synthetic polymer samples. Unfortunately, SEC separates based on the hydrodynamic size of a molecule, which is dependent on the polymer architecture, chemical make-up and other factors, which is a particular problem for branched polymers. Temperature gradient interaction chromatography (TGIC) separates molecules based on the degree of polymerization (i.e. number of repeat units) by taking advantage of the enthalpic interactions between the polymer and the solute and stationary phase, resulting in separation that is independent of architecture. TGIC has recently been incorporated into the suite of characterization techniques within the Macromolecular Nanomaterials Group. This technique has been utilized to better understand the composition of star-shaped molecules synthesized in-house. In particular we have found that stars prepared with a C_{60} core are significantly more heterogeneous in the distribution of arms than SEC suggests. Two-dimensional chromatography was manifested in this was: Samples were fractionated by TGIC, and subsequently characterized by SEC using MALLS and viscometry detectors for complete characterization of the branched materials.

Ab-initio calculations and molecular dynamics simulations of peptide adsorption onto metal oxide surfaces

C. Arcangeli [1,2], I. Borriello [1,2], M. Celino [1,2], M. V. Falessi [1], P. Morales [1,3], N. Pellicciotta[1] B. G. Sumpter [4]

1. NAST Centre, Nanoscience & Nanotechnology & Innovative Instrumentation, Università dgli Studi di Tor Vergata, Via della Ricerca Scientifica, 1 I-00133 Roma, Italy
2. ENEA, UTTMAT-DIAG, Casaccia Research Center, Via Anguillarese 301, I-00123 Roma Italy
3. ENEA, UTTMAT-SUP, Casaccia Research Center, Via Anguillarese 301, I-00123 Roma Italy
4. Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN USA

Peptides that bind inorganic surfaces are of great interest for the self- or directed assembly of nanodevices, with wide ranging applications such as electronics, biomaterials, energy production, and medicine. These surface-binding peptides can be identified by phage-display peptide libraries, but little experimental information is available for developing an understanding of the relationships between the peptide sequence, its structure at an inorganic surface, and its surface adhesion. To aid in this development, first principles simulations based on Density Functional Theory (DFT) and classical Molecular Dynamics (MD) simulations are carried out to investigate the structure and stability of single amino acids and of the full peptide adsorption on TiO_2 anatase (101). Our results shed light on the role played by some amino acids that are known to be essential in selective adsorption on TiO_2, as well as their structural conformation upon the surface. The critical role for the adhesion mechanism played by the water molecules at the organic-inorganic interface adhesion is also revealed by our results.

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Applications of Scanning Probe Microscopy in Biology

V. Reukov[1], A.S. Shaporev[1], G.L. Thompson[2], M. Nikiforov[3], S.Jesse[4], S. Kalinin[4], A. Vertegel[1]

[1]Clemson University, Department of Bioengineering, Clemson, SC
[2]Air Force Research Laboratory, San Antonio, TX
[3] Argonne National Laboratory, Chicago, IL
[4] Oak Ridge National Laboratory, Center for Nanophase Materials Science, Oak Ridge, TN

Over the past years, different variations of scanning probe microscopy (SPM) have emerged as a powerful tool for imaging the surface of biological cells under physiological conditions with nanometer resolution. The advancements of multimodal SPM have enabled measurements of the mechanical properties of living cells using piezo-response microscopy. Here, we present results of several experiments on imaging of living cells in physiologically-relevant conditions using Force-volume mapping and Band Excitation Piezoresponse Force Microscopy (BEPFM) and have begun to correlate the mechanical properties derived from each SPM technique in order to establish BEPFM in the biological realm.

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A search model for topological insulators with high-throughput robustness descriptors

Kesong Yang[1], Wahyu Setyawan[2], Shidong Wang[1], Marco Buongiorno Nardelli[3,4] and Stefano Curtarolo[1,4,5]

Topological insulators (TI) are becoming one of the most studied classes of novel materials because of their great potential for applications ranging from spintronics to quantum computers. To fully integrate TI materials in electronic devices, high-quality epitaxial single-crystalline phases with sufficiently large bulk bandgaps are necessary. Current efforts have relied mostly on costly and time-consuming trial-and-error procedures. Here we show that by defining a reliable and accessible descriptor χ_{TI}, which represents the topological robustness or feasibility of the candidate, and by searching the quantum materials repository aflowlib.org, we have automatically discovered 28 TIs (some of them already known) in five different symmetry families. These include peculiar ternary halides, Cs{Sn,Pb,Ge}{Cl,Br,I}$_3$, which could have been hardly anticipated without high-throughput means. Our search model, by relying on the significance of repositories in materials development, opens new avenues for the discovery of more TIs in different and unexplored classes of systems.

[1]Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708, USA,

[2]Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352, USA,

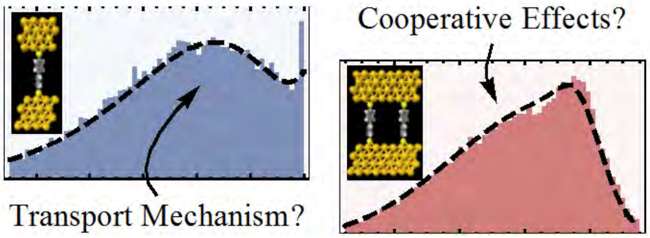
[3]Department of Physics and Department of Chemistry, University of North Texas, Denton, Texas 76203, USA,

[4]Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6367, USA,

[5]Department of Physics, Duke University, Durham, North Carolina 27708, USA.

On The Information Content of Conductance Histograms: Transport Mechanisms, Cooperative Effects, and Junction Symmetries

Patrick D. Williams[1,2] and Matthew G. Reuter[2,3]



We present a computational investigation into the line shapes of peaks in conductance histograms, finding that they possess high information content. In particular, the histogram peak associated with conduction through a single channel elucidates the electron transport mechanism and, particularly for the case of resonant tunneling, asymmetry in the junction. A statistical analysis of the peak corresponding to conduction through two channels reveals the presence of cooperative effects between the channels and also provides insight into the underlying conduction eigenchannels. This work describes tools for extracting additional interpretations from experimental statistical data, helping us better understand electron transport processes.

[1]Oak Ridge High School, Oak Ridge, TN 37830, USA
[2]Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[3]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Electrochemical nanowriting on CeO_2 thin films

Nan Yang [a,c] , Sandra Doria [b], Amit Kumar [d] , Antonello Tebano [a], Silvia Licoccia [c], Sergei Kalinin [d] and Giuseppe Balestrino [a]

[a] *INFM-CNR SPIN and Department of Informatica Sistemi e Produzione, University of Rome, Tor Vergata, Via del Politecnico, 00133, Rome, Italy.*
[b] *Departement of Physics, University of Rome, La Sapienza, Piazzale Aldo Moro 5, 00185, Rome, Italy.*
[c] *Department of Chemical Science and Technologies & NAST Center, University of Rome, Tor Vergata, Via della Ricerca Scientifica, 00133, Rome, Italy.*
[d] *The Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.*

CeO_2 is an oxide with variable chemical properties due to the external band structure, influenced by the f-orbitals of the rare earth metal Cerium. Previous studies estabilished that, under reducing conditions, CeO_2 tends to loose a fraction of oxygen ions, leaving oxygen vacancies, and becoming $CeO_{2-\delta}$. In the latter, the oxidation state of Cerium changes from +4 to +3.
We found multiple bias induced processes in oxide ceria thin films 350nm thick, grown on different substrates by Pulsed Laser Deposition. Our measurements showed the formation of irreversible deformations on the oxide surface, as a consequence of the bias applied to the AFM tip. The exchange of electrons between tip and sample plays a pivotal role in the explanation of the electrochemical process.
The change in stoichiometry has been studied in detail, to figure out the nature of the deformations, the preferential directions, the temperature and bias dependence, the degree of reversibility and the internal structure.
The presence of a conductive substrate seems to facilitate electrochemical writing, that occurs between + 5 V and + 41 V, and, for negative bias, in the range between -26 V and -35 V. The lateral dimensions of the deformations exceed considerably the tip-surface contact area, and the expansion of 7% of the total thickness is found to be compatible with the formation of oxygen vacancies in the material surface, with subsequent ions migration.

Acknowledgments. *Local electrochemical characterization of Sm-doped-CeO2 epitaxial thin films [CNMS2012-016].*

Search for New Materials - a Computational Approach

P. Ganesh

We are conducting cluster-expansion based computational searches to discover potentially new ferroelectrics, multiferroics for electronic applications as well as battery-electrode materials for Na/Mg ion battery applications. Our recent findings over a simple rock-salt arrangement of simple mixtures of alkaline-earth oxides, such as BaxSr(1-x)O and BaxMg(1-x)O has revealed new low energy phases in the former over the whole composition range, some of which are ferroelectric and could possibly be stabilized by creating a surface or thin-films. Our study reveals interesting trends in the polarization and Born-effective charges across the whole composition range, and gives insight into why there are many known BaSr-based ferroelectrics in nature as opposed to BaMg-based ones. Contrast of these trends with different class of structures, for example those based on perovskites, will also be presented.

Na-based intermetallic alloys are expected to be excellent anode materials for Na-batteries, owing to their low voltages and increased capacity as evidenced by many stable intermetallic phases over a wide composition range. We are investigating Na-M binaries, predicting structures and computing voltage-profiles to compare with electrochemically made Na-M conversion materials. XRD, XPS and Mossbauer characterizations are further compared with predicted structures of these materials.

Epitaxial growth of highly conductive IrO2 thin films by pulsed laser deposition

Liang Qiao and Michael D. Biegalski

Center for Nanophase Materials Sciences, Oak ridge National Laboratory

Abstract

Iridium oxide (IrO2) is one of a few naturally highly conductive transitional metal binary oxides and has very unique material properties, such as single stoichiometry, high thermal and chemical stability, and excellent diffusion barrier for oxygen, which make it a very interesting material from both fundamental and applications. Here we show that IrO_2 can be epitaxial grown on commercially available oxide substrates, e.g. $SrTiO_3$, $LaAlO_3$, MgO, and Al_2O_3, by pulsed laser deposition. X-ray diffraction demonstrates that crystallographic structure of epitaxial IrO_2 thin films are strongly affected by both lattice mismatch and crystal symmetry mismatch between film and respective substrates. Consequently, IrO_2 grown on MgO substrates, with the rock salt structure, exhibits a single domain structure, while epitaxial film on perovskite and corundum substrates exhibit complicated in-plane domain configuration with film lattice rotating and tilting with respective to substrate lattices. Electronic structure of epitaxial IrO2 film is determined by x-ray photoelectron spectroscopy and first-principle calculations, where both measured and calculated valence band spectrum shows a distinct inflection of the density of state right at Fermi level, indicating a high electron density. Further electrical transport measurement demonstrates various conducting mechanisms as a function of temperature. The obtained highly conductive epitaxial IrO2 thin film is a promising electrode material for application of oxide electronic devices.

Femtosecond Laser Micro-/Nano-machining of Holes and Lines in Fused Silica

B. K. Canfield, L. Costa, D. Rajput, A. Terekhov, W. H. Hofmeister, and L. M. Davis
Center for Laser Applications, University of Tennessee Space Institute, 411 B. H. Goethert Pkwy, MS 35,
Tullahoma, TN 37388

Machining materials with femtosecond lasers has broad technological applications, including lab-on-a-chip microfluidic devices for biological and chemical assays. The high peak intensity delivered by a tightly focused fs pulse allows highly localized damage due to nonlinear absorption mechanisms, while the ultrashort duration restricts undesirable thermal damage from spreading over a larger area. Femtosecond laser processing can thus provide a rapid, cost-effective means of producing sub-micron-scale features in a wide range of materials, including metals and ceramics. In this work we demonstrate two variations of fs laser machining in fused silica: high-aspect ratio nanoscale holes using a round beam, and microchannels written by focusing the beam to a line. Features are formed in single-shot mode, that is, one pulse per hole or line.

The amplified Mira fs laser at CNMS provides the pulses and is externally controlled through a custom LabVIEW program. The 1 kHz amplifier outputs 1.6 mJ per pulse, more than 300 times higher than that available at the University of Tennessee Space Institute's Center for Laser Applications. The higher pulse energy enables machining of long lines, where the energy density is distributed along the line focus, as well as machining of high aspect nanoholes of greater depth than those of previous experiments.

The optical setup relies on a 0.68 numeric aperture molded glass aspheric lens to focus the pulses tightly. Although a high-magnification microscope objective can focus more tightly, the asphere offers several advantages: it provides a relatively long working distance of 1.7 mm; it has known optical parameters for modeling using Zemax optical design software; it significantly reduces spherical aberration of collimated beams that fully fill its aperture; and it costs under $100.

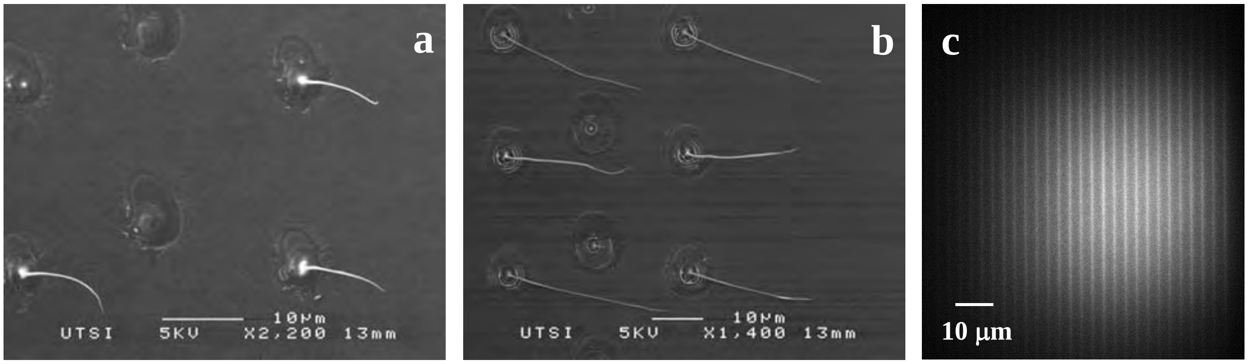


Figure 1. Femtosecond laser-machined structures: acetate replicas of high-aspect ratio holes using minimal LSA of +2 µm (a) and using maximum positive LSA of +41 µm (b); (c) micron-scale subsurface channels written by line-focusing.

To machine round, high-aspect ratio holes, the beam size and divergence (which affects the longitudinal spherical aberration, or LSA, of the focus) are first adjusted by spacing a series of spherical lenses so that the beam just fills the asphere's entrance pupil. The lens spacings are predetermined using calculations in Zemax. We have found that using large LSA and attenuating the pulse energy to tens of microjoules enables drilling of very deep, narrow holes, as can be seen by comparing the scanning electron micrographs of acetate replicas for two limiting LSA conditions using ~12 µJ pulses in Figs. 1(a) and (b). The use of the asphere should thus help elucidate the role of LSA in the formation of deep holes.

For line-focus experiments, a set of cylindrical lenses, which reshape the round beam into a line, are placed before the aspheric lens. Line features nearly 1800 µm long, less than 1 µm wide and ~6 µm deep have been obtained by this method. Moreover, the line features can be written entirely within the material, as observed optically under wide-field illumination in Fig. 1(c). Access wells may then be machined and the features chemically etched to yield an array of parallel microfluidic channels.

The Role of Hydrogen During Si Nanowire Growth

Naechul Shin and Michael. A. Filler

Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA

Semiconductor nanowires are promising building blocks for a diverse range of next generation electronic and photonic devices. The physical properties of these materials, and nanostructures in general, are intimately connected to their structure, which must be controlled with nanoscale precision. This remains a challenging task in many systems and stems from an inadequate chemical understanding of common synthetic routes. To this end, we report on the first *in-situ* spectroscopic investigation of vapor-liquid-solid semiconductor nanowire growth and reveal the dominant, and as of yet unrecognized, role of surface chemistry near the triple-phase boundary. We specifically show that chemical bonding is responsible for "kinking" as well as defect formation. Real-time transmission infrared measurements of Si nanowire growth from Si_2H_6 coupled with post-growth electron microscopy imaging demonstrate that covalently-bound hydrogen, resulting from precursor decomposition, drives the well-known <111> to <112> growth direction change, creates an axially oriented twin boundary, and controls Au diffusion on the sidewall. The temperature, pressure, and time dependent infrared spectra shown in Figure 1 show that the intensity of two characteristic ν(Si–H) vibrational modes, centered near 2075 and 2090 cm^{-1}, increase as the temperature is reduced. Importantly, the transition between <111> and <112> growth coincides with the appearance of these spectral features. Furthermore, the exposure of H atoms to <111>-oriented nanowires causes an immediate kink toward the <112> direction during growth and confirms the importance of surface hydrogen. The extensive use of hydride chemistries for group IV and III-V semiconductor nanowire syntheses suggests significant implications for a variety of material systems. These findings open a new avenue to rationally engineer semiconductor nanowire crystal structure, which we leverage to fabricate complex nanowire-based superstructures.

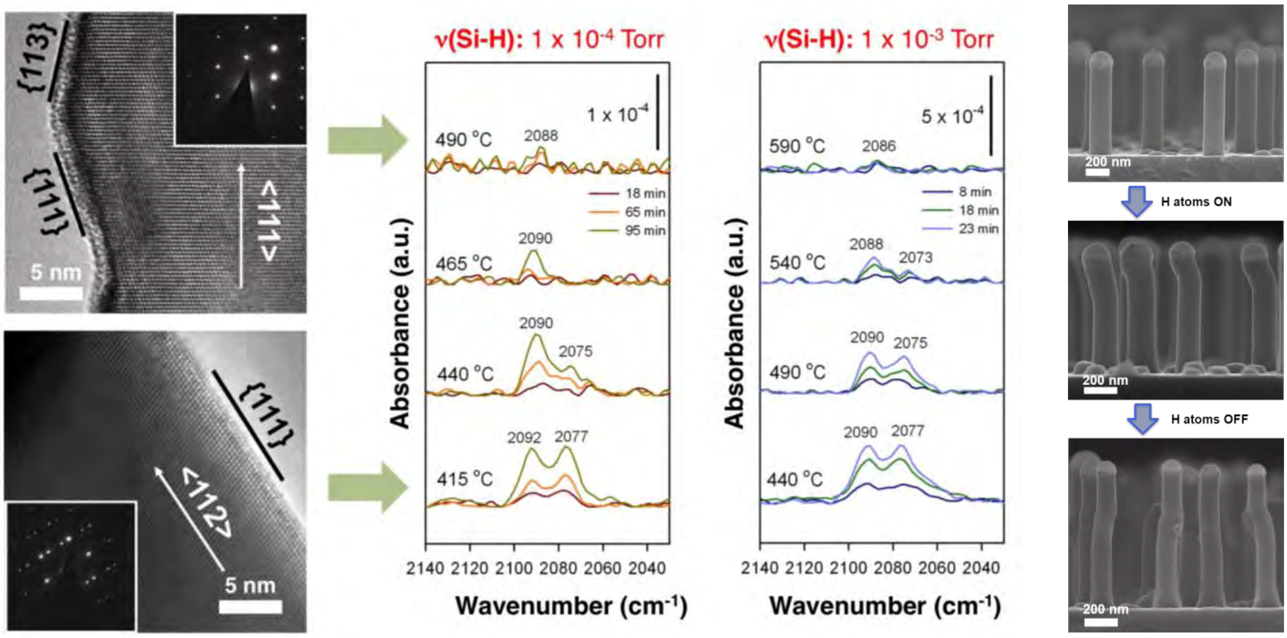


Figure 1. *(**Left**) Post-growth transmission electron microscopy imaging of Si nanowires and (**Middle**) real-time infrared spectra show that covalently-bonded hydrogen is present on the nanowire surface only during <112>-oriented elongation. (**Right**) H atom exposure induces kinking to the <112> direction with growth conditions that usually yield <111>growth.*

Phonon Engineering of Si Nanowires by Controlled Chemical Doping

M. Babaeian[1], M. Ontl[2], T. Jayasekera[1], A. Calzolari[3], M. B. Nardelli[4,5]

[1]Department of Physics, Southern Illinois University, Carbondale, IL

[2] South Western Illinois College, REU Participant at Southern Illinois University, Carbondale, IL

[3] Theory@Elettra Group, DEMOCRITOS National Simulation Center CNR-IOM Istituto Officina dei Materiali, I-34014 Trieste, Italy

[4] Department of Physics and Department of Chemistry, University of North Texas, Denton, Texas 76203, USA

[5] Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6359, USA

Using first principles Density Functional Theory calculations, we have investigated electronic and dynamical properties of Si nanowires in [111] direction with different diameters in the presence of impurities such as Ge. Our analysis find that the thermal transport properties of Si nanowires highly depend on the Ge impurities and the quantitative effect depends on both the dopant concentration and the dopant pattern of impurity atoms. By controlled doping, nanowires can be engineered to reduce the thermal transport with electrical transport less interrupted, such that their thermoelectric properties can be enhanced.

Resonant Infrared Matrix-Assisted Pulsed Laser Evaporation of P3HT-based Bulk Heterojunctions: Small-Angle X-ray Scattering and Photovoltaic Device Characterization

Adrienne D. Stiff-Roberts and Ryan D. McCormick
Duke University, Department of Electrical and Computer Engineering, Box 90291
Durham, NC 27708-0291

The prototypical conjugated polymer-based photovoltaic device features bulk heterojunctions of poly(3-hexylthiophene) (P3HT) and methanofullerenes (PCBM). Despite achieving some of the highest device efficiencies that have been demonstrated, these P3HT-PCBM nanocomposites suffer from the low hole mobility in P3HT. Interchain hopping conduction dominates charge transport in conjugated-polymer thin films, and is strongly dependent on the internal morphology of the polymer film [1]. Therefore, this ORNL CNMS User Program project (in collaboration with Dr. Andrew Payzant and Dr. Kai Xiao) will determine if a novel polymer deposition technique (resonant infrared matrix-assisted pulsed laser evaporation, RIR-MAPLE) can increase the P3HT hole mobility, as well as the resultant solar cell device efficiency, by promoting a thin-film internal morphology with enhanced interchain interactions.

RIR-MAPLE is a promising approach to optimizing P3HT chain morphology in order to improve charge transport because it can control and tune many aspects of nanoscale morphology [2-4]. RIR-MAPLE is most successful when the incident laser wavelength is tuned to an absorption peak in the host matrix that is absent from the guest material. Therefore, a novel approach using target emulsions of a desired guest material and corresponding solvent with water has been developed that is compatible with a table-top Er:YAG laser with a fixed emission wavelength at 2.9 µm.

The overall project will proceed as follows. P3HT thin films will be deposited by RIR-MAPLE, as well as drop-casting and spin-casting for comparison. Small-angle X-ray scattering (SAXS) will be used to determine the internal morphology of the thin films. The corresponding hole mobilities will be measured using time-of-flight (TOF) photoconductivity or field-effect transistor techniques. P3HT-PCBM solar cells will be fabricated using optimized RIR-MAPLE recipes and characterized. It is expected that emulsion-based RIR-MAPLE deposition will demonstrate the ability to preferentially deposit a given P3HT thin film orientation in order to maximize hole mobility and solar cell device efficiency. To date, the following steps have been completed: emulsion-based RIR-MAPLE deposition of P3HT thin films; drop-casting and spin-casting deposition of P3HT thin films for comparison; and SAXS measurements of P3HT thin films. Initial results of the SAXS measurements are shown in Figure 1. These preliminary results and the overall project will be presented.

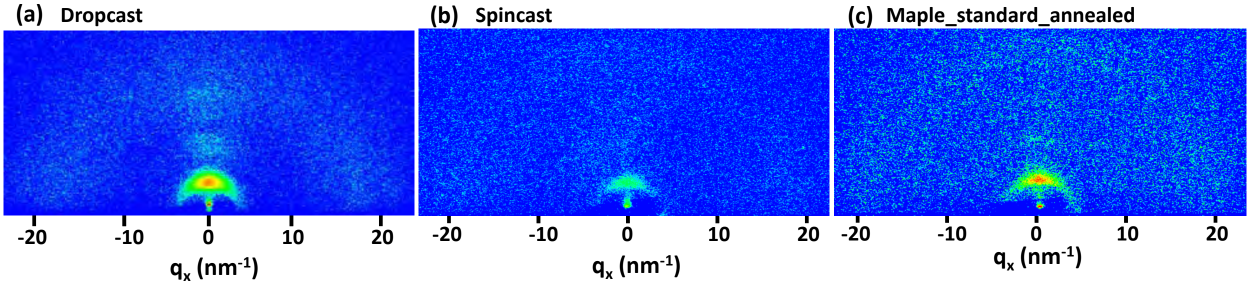


Figure 1. SAXS data for (a) drop-cast, (b) spin-cast, and (c) RIR-MAPLE deposited thin films of P3HT.

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NOVEL FULLERENE ACCEPTOR MATERIALS FOR APPLICATION IN ADVANCED ORGANIC PHOTOVOLTAIICS

Youjun He, Ming Shao, Kai Xiao, Sean C. Smith, Kunlun Hong

Center for Nanophase Materials Science, Oak Ridge National Laboratory,
P.O. Box 2008, Oak Ridge, TN 37831-6496

Organic photovoltaics (OPVs) have witnessed great development due to advances in new material synthesis, optimized interface contact, and improved device-processing condition. The power conversion efficiency (PCE) of for *tandem OPVs* has reached over 10%. According to the calculation, the highest PCE for *a single layer device* should be near 15%.[1] Though, many reported polymer donor materials have the suitable band gap, their actual PCE is far away from 15%. One important reason is their high energy levels, compared with that of PCBM, which not only induced big energy loss, but also decreased the open circuit voltage of the device, and thus limited their performance. In order to address this problem, we designed and synthesized several fullerene-based acceptors with higher LUMO levels (compared to that of PCBM). The OPVs based on P3HT, our fullerene derivatives and PCBM as acceptor materials have been fabricated. The PCE of these OPV based our fullerene material as acceptor showed very promising results.

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