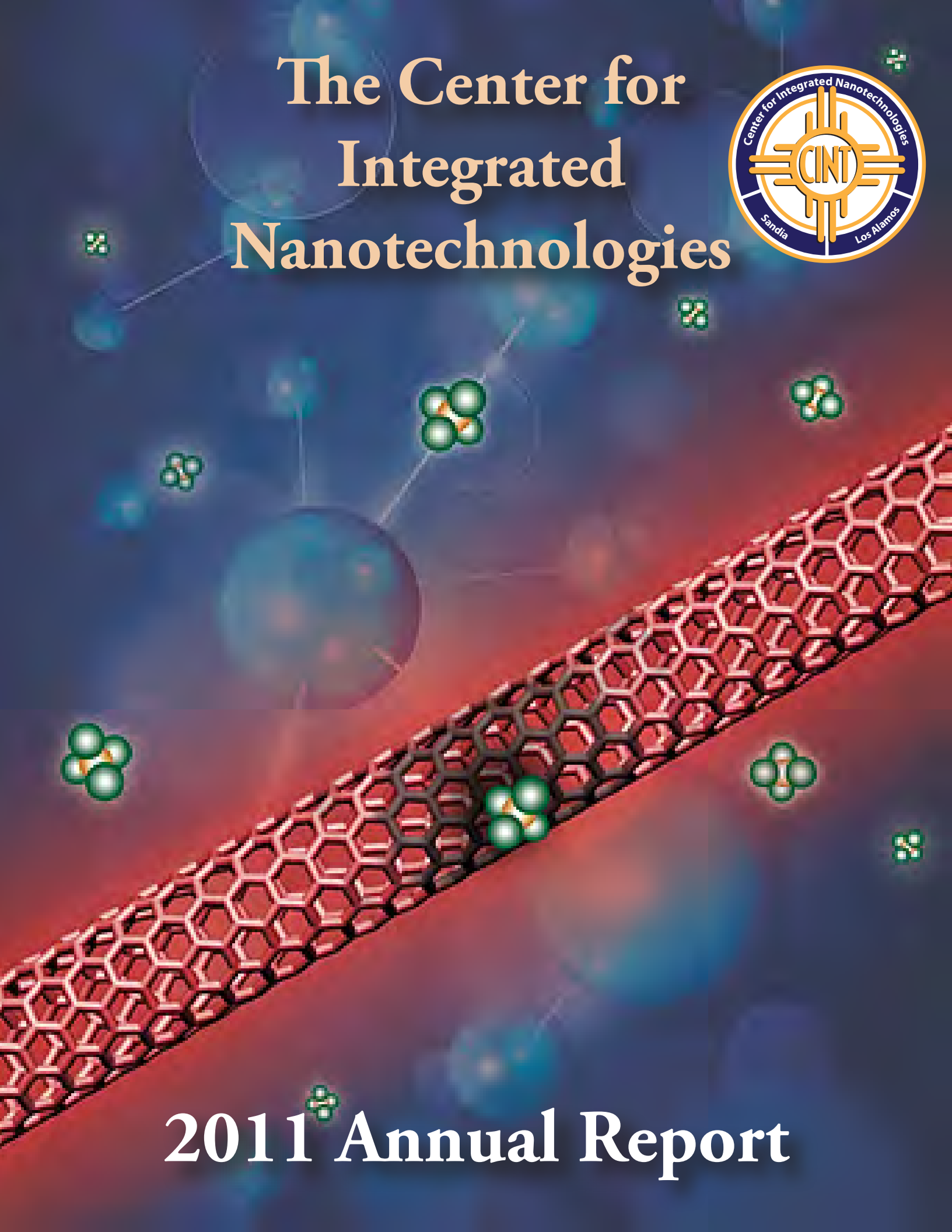
The Center for Integrated Nanotechnologies



2011 Annual Report

Center for Integrated Nanotechnologies
2011 Annual Report

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Cover art - Artist's concept of nanotubes on the liquid surface. Image from Los Alamos National Laboratory

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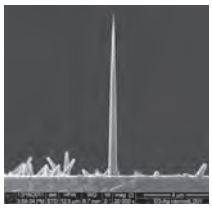


From the Directors' Office

We are pleased to share with you this 2011 edition of the Annual Report from the Center for Integrated Nanotechnologies (CINT) and the growing excitement we feel around cementing our brand as a leader in integration nanoscience. This can be seen most readily in the momentum we have achieved in our signature Integration Focus Activities (IFAs). These efforts unite our scientists across our four scientific Thrust areas with our users to concentrate research on larger-scale nanoscience integration challenges for specific classes of nanomaterials, systems, and phenomena. All three of our current IFAs (p. 10) now have a full head of steam, and nearly 30% of our current user projects map in some meaningful way to one of these IFAs. As part of our redoubled effort to increase our industrial user base, we are also looking to leverage these IFAs to build a stronger link to and spur recruitment within our industrial user community. We believe that the IFAs are a natural community-building tool with an intrinsic value proposition for industry; an R&D pipeline that can lead to more mature, more commercially well-positioned technologies. Finally, as nanoscience and nanotechnology are maturing, we as a research community are beginning to see our efforts extend in many exciting new directions. Our focus on nanoscience integration positions us very well to capitalize on new opportunities including the emerging Mesoscale Initiative within the DOE Office of Science. Many aspects of mesoscale science are embodied in the integration of nanoscale building blocks.

We are equally proud of our continuing strong performance in support of our user program. We have fully transitioned to our new user proposal database providing enhanced convenience and flexibility for proposal submission and review. In our two regular proposal calls this year we received a total of 225 proposals, an increase of 10% over our 2010 performance. Our official count on number of users for the period remains at ~ 350 and continues to reflect full engagement of our scientific staff. We are also seeing a steady increase in our industrial user base, with the number of industrial proposals (including Rapid Access proposals) doubling in 2011. We attribute this in part of our outreach efforts including our focused industrial session in each of our past two annual User Conferences (p. 20)

As always, we welcome feedback and invite suggestions from our users and all stakeholders on all aspects of our user program and Center operations. We hope you find this annual report informative and, more importantly, that it will motivate you to continue your engagement with CINT or to become a CINT user.

David Morris, Director

Neal Shinn, Co-Director

S. Tom Picraux, Chief Scientist

Heather Brown, User Program Coordinator

Antonya Sanders, Communications Coordinator

The Center for Integrated Nanotechnologies (CINT) is a Department of Energy/Office of Science Nanoscale Science Research Center (NSRC) operating as a national user facility devoted to establishing the scientific principles that govern the design, performance, and integration of nanoscale materials. Jointly operated by Los Alamos and Sandia National Laboratories, CINT explores the continuum from scientific discovery to use-inspired research, with a focus on the integration of nanoscale materials and structures to achieve new properties and performance and their incorporation into the micro- and macro worlds. Through its Core Facility at Sandia National Laboratories and its Gateway Facility at Los Alamos National Laboratory, CINT provides open access to tools and expertise needed to explore the continuum from scientific discovery to the integration of nanostructures into the micro- and macro worlds. In its overall operations, CINT strives to achieve the following goals common to all Nanoscale Science Research Centers:

1. Conduct forefront research in nanoscale science;
2. Operate as a user facility for scientific research;
3. Provide user access to the relevant BES-supported expertise and capabilities at the host national laboratory;
4. Leverage other relevant national laboratory capabilities to enhance scientific opportunities for the nanoscience user community;

These additional goals are specific to the unique CINT mission:

5. Establish and lead a scientific community dedicated to solving nanoscale science integration challenges;
6. Create a single user facility program that combines expertise and facilities at both Los Alamos and Sandia National Laboratories.

The CINT user program provides the international scientific community with open access to world-class scientific staff and state-of-the-art facilities for theory and simulation, nanomaterials synthesis and characterization, and unique capabilities for nanoscale materials integration, from the level of nanoscale synthesis to the fabrication of micro- and macroscale structures and devices. The staff of CINT includes laboratory scientists, postdocs and technical support staff who are leaders in the nanoscience research programs in CINT scientific thrust areas:

- Nanoscale Electronics and Mechanics,
- Nanophotonics and Optical Nanomaterials,
- Soft, Biological and Composite Nanomaterials, and
- Theory and Simulation of Nanoscale Phenomena.

The thrusts have been developed over the past several years by engaging the broader scientific community through discussions with potential CINT users and with attendees at CINT workshops, as well as by attracting some of today's top nanoscience talent to become CINT staff.

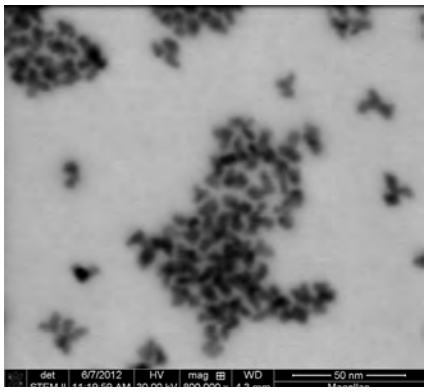
News from 2011: New Capabilities

CINT Technologist Chris Sheehan putting a sample into the Magellan SEM

Featured capability:
CINT Magellan HRSEM (High Resolution Electron Microscope)
The FEI Magellan 400 SEM provides sub-nanometer spatial resolution from 1kV to 30 kV. By using low voltages, only the surface of the sample interacts with the electron beam and thus insulators/beam sensitive samples can be imaged without the need for conductive coatings and the amount of surface data is maximized. These capabilities make this tool ideal for investigations of nanotubes, nanowires, nanocomposites, and other materials where workhorse SEMs do not have the low-voltage resolution required for sensitive surface imaging. This system features:

- Schottky thermal emission source with UniCo-lore mode to give a highly coherent beam (less than 0.2 eV energy spread)
- spatial resolutions of 0.8 nm at 1kV and above in secondary electron mode.
- EDAX Apollo XV Energy Dispersive Spectroscopy (EDS) detector for elemental analysis.
- EDAX Hikari Electron Backscatter Diffraction (EBSD) detector for crystallographic orientation determination.
- Nabity electron beam lithography patterning capability.
- annular STEM detector (spatial resolution of 0.7 nm).

Scientific contacts: Chris Sheehan and Nathan Mara



InP/ZnSe quantum dots taken in STEM mode, looking through very thin carbon film with the QDs sitting on it. These measured to be 5 nm, +/- 1nm.

Other new capabilities:

Holographic Optical Trapping Microscope
The holographic trapping microscope enables the non-contact optical manipulation of soft materials and nanoparticles and can also mechanically and spectroscopically probe such materials in situ. Force measurements based on optical manipulation methods can be used to investigate the viscoelastic properties of soft and biological materials or probe adhesion forces. Contact: Walter Paxton

Nanoink Dip-Pen Nanolithography
Dip-Pen Nanolithography is a scanning probe lithography technique where a "tip" (e.g., an AFM tip or tip-array) is used to "write" liquid-phase "inks" onto any substrate with 50 nm to 10 μm resolution. The inks can comprise solutions of self-assembled-monolayer-(SAM) forming molecules, pure liquids, nanoparticles, biomolecules, sol-gel precursors, etc. DPN operates under ambient conditions and is fully compatible with biomolecules, polymers, and quantum nanostructures. Contact: Jennifer Hollingsworth

IChrome TVIS Super Continuum Source
This versatile light source serves as an excitation source for measuring photoluminescence lifetimes down to 1 ps, enables photon correlation measurements (when paired with the recently procured time-correlated single-photon counting instrumentation), provides a bright tunable source for single-nanoelement PL imaging/spectroscopy and for pump-probe measurements, and serves as the basis for new imaging modes and spectroscopy including Rayleigh scattering imaging and absorbance spectroscopy at single-element levels. Contact: Steve Doorn

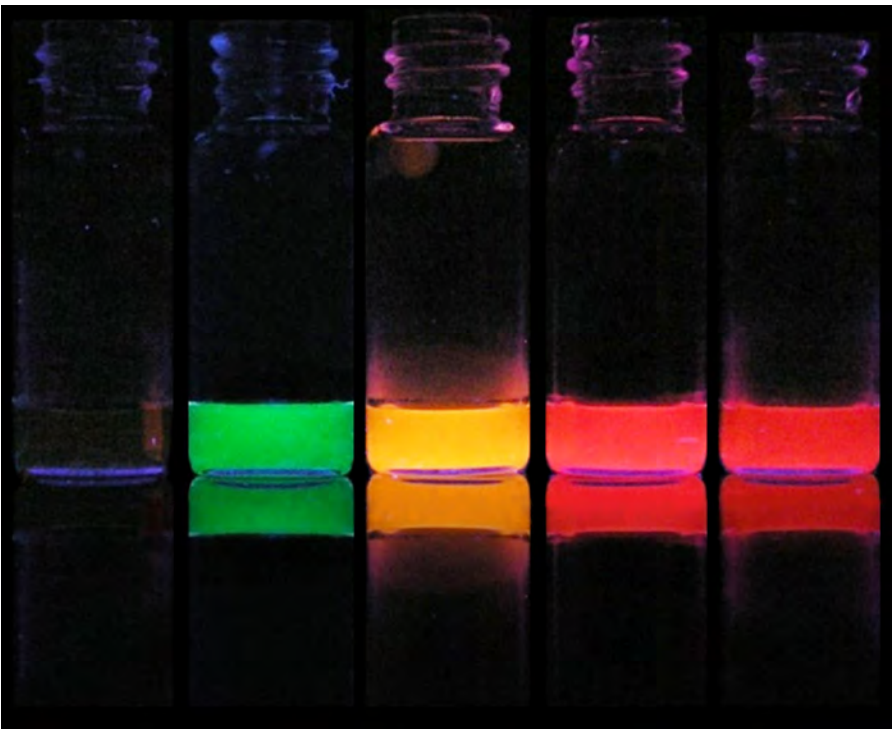
Hysitron PI-85 SEM Picoindenter
This in-situ SEM strain stage represents a significant capability enhancement in support of CINT's signature efforts in in-situ nanomechanics. The system has a load range from 1μN to 30mN, offers in-situ indentation, bending, compression and tension testing capabilities, includes a heating stage rated to 400°C, an electrical characterization package and has outstanding resolution of both load (<1μN) and displacement (<1nm). Contact: Nate Mara

Simultaneous TGA/DSC Analyzer
Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA/DSC) are complementary techniques to investigate material's response to different temperatures: mass change (e.g., decomposition or sublimation temperatures) and thermal changes often unaccompanied by the mass change as a function of temperature (e.g., melting, glass transition, second order phase transition, enthalpy and heat capacity measurements). Both techniques have become indispensible in the design of new metal precursors and understanding the structure/composition of nanocomposites. Contact: Dale Huber

Variable Angle Spectral Ellipsometer
The Variable Angle Spectroscopic Ellipsometer (VASE) has spectral coverage from 0.24-2.5um, is equipped for ellipsometric measurements on a small sample area, and can be used as scatterometer. These features are particularly useful for metamaterials, photonic crystals, gratings and nano-antenna arrayed with only a small patterned area. This instrument can also perform reflection and transmission measurements to yield absorption information, and attenuated total reflection measurements to study surface photonic states. Contact: Willie Luk

R&D 100 Award: NanoCluster Beacons

CINT scientists won one of R&D Magazine's 2011 R&D 100 Awards for their work with NanoCluster Beacons. Recognized as the "Oscars of Invention" by the Chicago Tribune, these awards honor the top 100 proven technological advances of the past year.



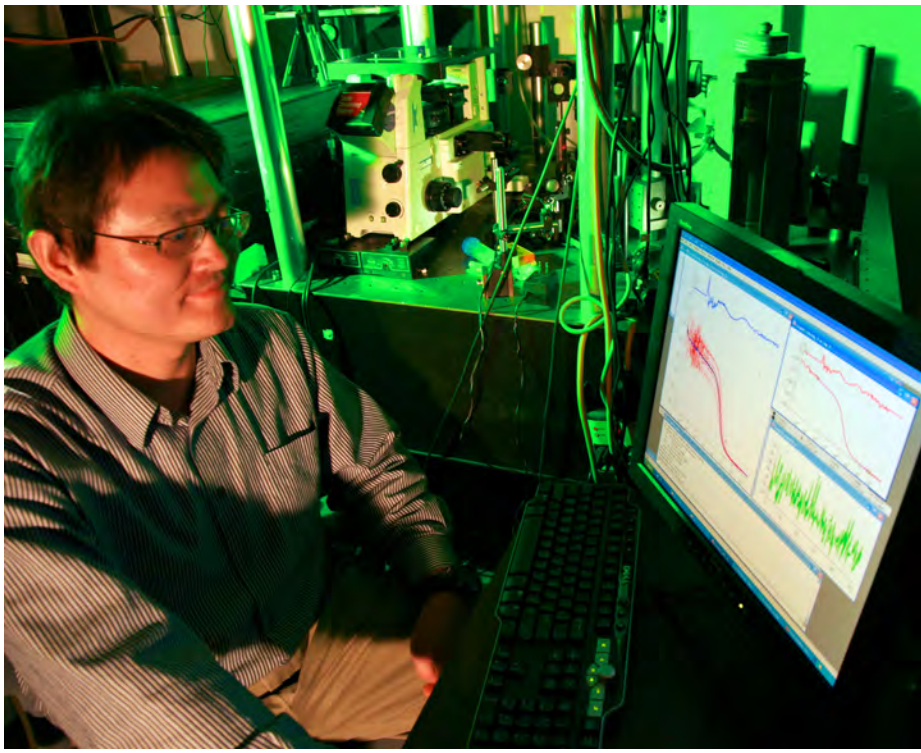
NanoCluster Beacons are collections of silver atoms maneuvered to illuminate when bound to specific nucleic acids, such as the DNA of particular pathogens. Created by Hsin-Chih (Tim) Yeh, James Werner, Jaswinder Sharma, and Jennifer Martinez, these beacons can be used to probe for diseases that threaten humans by identifying the nucleic acid targets that represent a person's full genome, and allow for personalized medication. They also can be used in quantitative biology applications, such as counting individual molecules inside a cell.

Once bound with a specific target, a NanoCluster Beacon lights up, emitting fluorescence approximately 200 times greater than in the unbound state and easily viewed by the naked eye under ultraviolet light. The beacons come in an array of colors for multiplexed analyses, are more photostable than beacons used today, and can be turned on and off reversibly. Inexpensive, easy to use, and reversible, NanoCluster Beacons are superior molecular probes for detecting specific targets, human oncogene (cancer) sequences, and molecular disease sequences (such as sickle cell anemia).

CINT Postdoc Hsin-Chih (Tim) Yeh was part of the NanoCluster Beacons team.

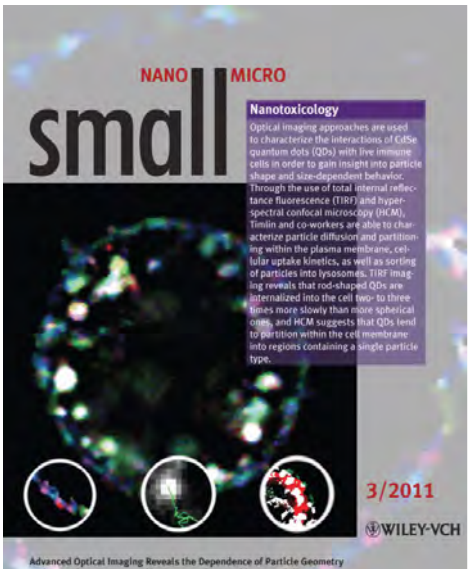
Patents

CINT Scientists were involved in the following patent applications in 2011-2012 (does not include disclosures).

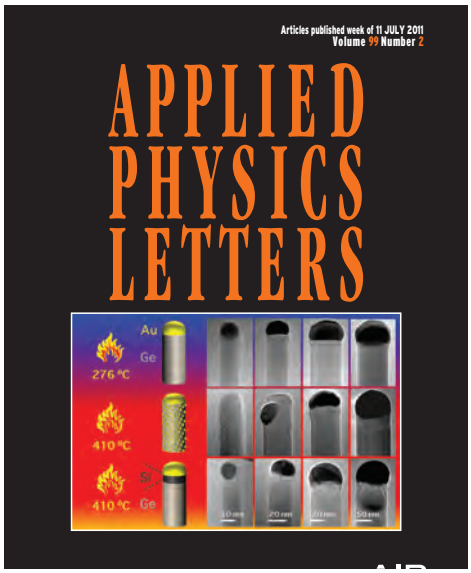


- Thick-shell nanocrystal quantum dots. Jennifer Hollingsworth et al., US Patent US 7,935,419 B1 Issued May 3, 2011.
- Polymer-assisted deposition of films. T. M. McCleskey, A. K. Burrell, Q. X. Jia, and Y. Lin, US Patent No. 8,124,176, Issued Feb. 28, 2012.
- Fibrous composites comprising carbon nanotubes and silica. H. Peng, Y. T. Zhu, D. E. Peterson, and Q. X. Jia, US Patent No. 8,034,448, Issued Oct. 11, 2011.
- Buffer layers for coated conductors. L. Stan, Q. X. Jia, and S. R. Foltyn, US Patent No. 8,003,571, Issued Aug. 23, 2011.
- Carbon microtubes. H. Peng, Y. T. Zhu, D. E. Peterson, and Q. X. Jia, US Patent No. 7,959,889, Issued June 14, 2011.
- Preparation Of Anode Comprising Silicon Nanowires. J.-H. Cho and S. T. Picraux Provisional application (S121,996). Filed.
- Carbon nanotube/metal carbide composites with enhanced properties. G. Zou, Y. Zhang, A. K. Burrell, T. M. McCleskey, and Q. X. Jia, Filed.
- Room temperature ferromagnetism insulating thin films. J. MacManus-Driscoll and Q. X. Jia, Filed.
- Mid-Infrared Tunable Metamaterials , I. Brener et al., Filed
- Magnetic Agglomeration Method for Size Control in the Synthesis of Magnetic Nanoparticles, D. Huber, US Patent No. 7972410, Issued July 5, 2011.
- High-Yield synthesis of bookite TiO2 nanoparticles, D. Huber and T.C. Monson, US Patent No. 7943116, Issued May 17, 2011

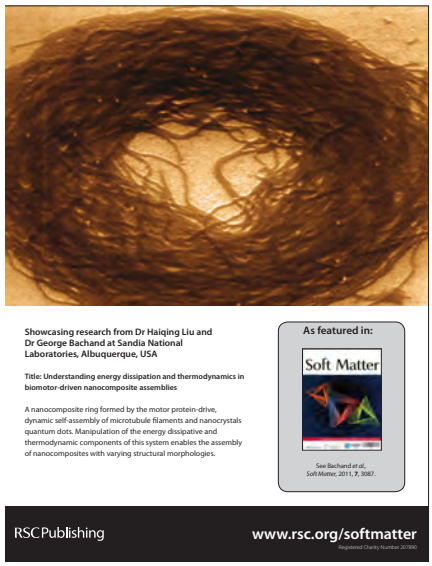
Journal & Book Covers



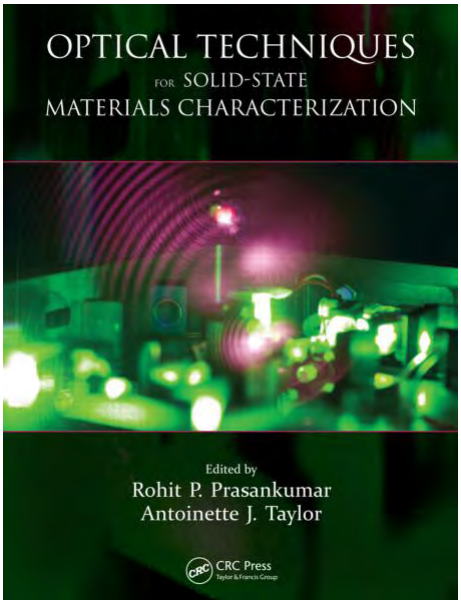
Optical imaging approaches are used to characterize the interactions of CdSe quantum dots (QDs) with live immune cells in order to gain insight into particle shape and size-dependent behavior. Through the use of total internal reflectance fluorescence (TIRF) and hyper-spectral confocal microscopy (HCM), Timlin and co-workers are able to characterize particle diffusion and partitioning within the plasma membrane, cellular uptake kinetics, as well as sorting of particles into lysomes. TIRF imaging reveals that rod-shaped QDs are internalized into the cell two-to-three times more slowly than more spherical ones, and HCM suggests that QDs tend to partition within the cell membrane into regions containing a single particle type.
CINT Contact: George Bachand



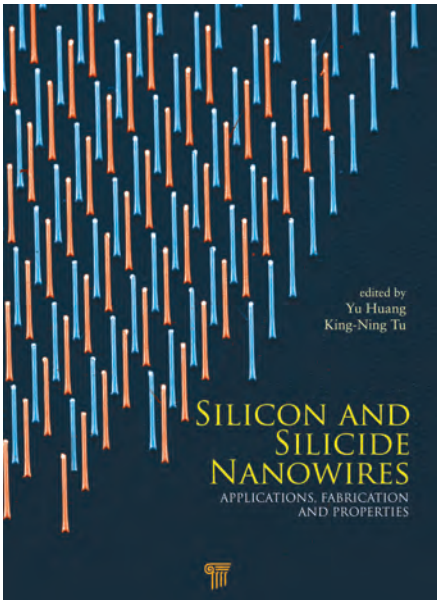
Synthesis of germanium/silicon (Ge/Si) core/shell nanowire heterostructures is typically accompanied by unwanted gold (Au) diffusion on the Ge nanowire sidewalls, resulting in rough surface morphology, undesired whisker growth, and detrimental performance of electronic devices. Here, we advance understanding of this Au diffusion on nanowires, its diameter dependence and its kinetic origin. We devise a growth procedure to form a blocking layer between the Au seed and Ge nanowire sidewalls leading to elimination the Au diffusion for in situ synthesis of high quality Ge/Si core/shell heterostructures.
CINT Contact: Tom Picraux



A nanocomposite ring formed by the motor protein-drive, dynamic self-assemblyof microtubual filaments and nanocrystals quantum dots. Manipulation of the energy dissipative and thermodynamic components of this system enables the assembly of nanocomposites with carying structural morphologies.
CINT Contact: George Bachand



CINT Scientist, Rohit Prasankumar, and CINT Distinguished Affiliate, Toni Taylor edited a book in 2011, titled "Optical Techniques for Solid-State Materials Characterization."



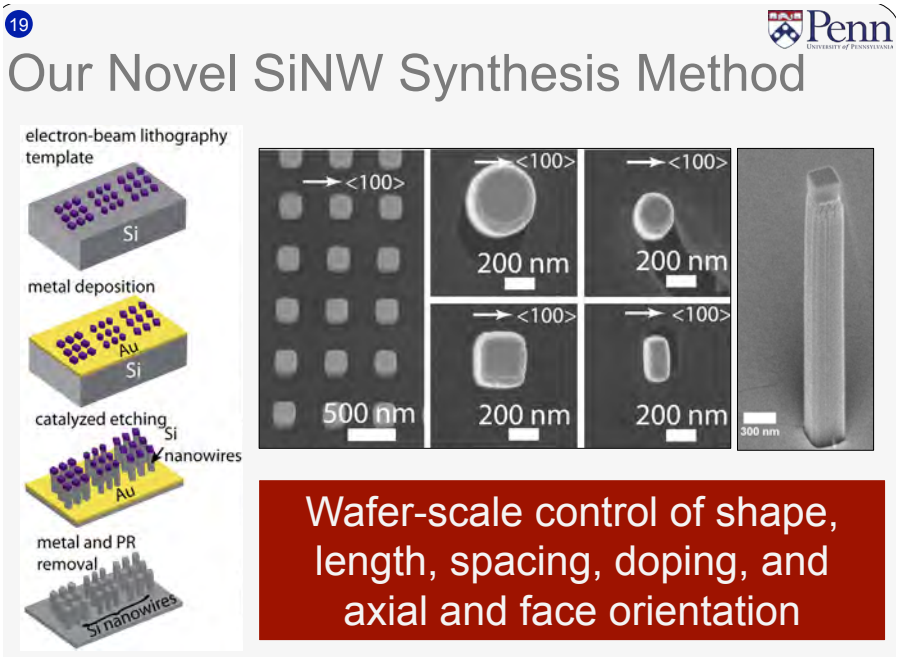
A nanowire image from Tom Picraux's team was edited and used for the book cover of "Silicon and Silicide Nanowires: Applications Fabrication and Properties."

NSRC Events

NSRC Contractors meeting

From May 31-June 2, 2011, representatives from the Department of Energy Basic Energy Science Nanoscale Science Reserach Centers (NSRCs) and E-Beam Micro-characterization Centers gathered in Maryland for the 2011 Contractors' Meeting. The purpose of the Contractors' Meeting is to bring together researchers - facility scientists and facility users of the BES EBMC and NSRC facilities and leading experts across the multi-disciplinary spectrum served by these facilities - to foster discussion of the latest research results, catalyze collaborations, and stimulate ideas for promising new directions for investigation. Dynamic exploration of research ideas and capability needs will also help DOE in assessing the needs of the research community to chart future program directions.

CINT was featured in the meeting with presentations by CINT Scientist Jianyu Huang titled In-Situ TEM Electrochemistryof Li-Ion Battery Materials, and CINT User Dan Gianola from University of Pennsylvania with a talk on Quantative In-Situ Mechanical Testing of Nanowires. There were also 12 poster presentations from a combination of CINT Users, scientist, and postdocs.



MRS Meeting

The NSRCs continue to work to attract new users. One method is to host a booth at some of the larger technical conferences that attract potential users. In 2011, the NSRCs joined together at the Materials Research Society Fall Meeting in Boston.
Left to right - Grace Webster from the Center for Functional Nanomaterials (CFN), Laura Edwards representing the Center for Nanophase Materials Sciences (CNMS), Antonya Sanders from CINT, and Denean McArthur also of CFN.

Integration Focus Activities

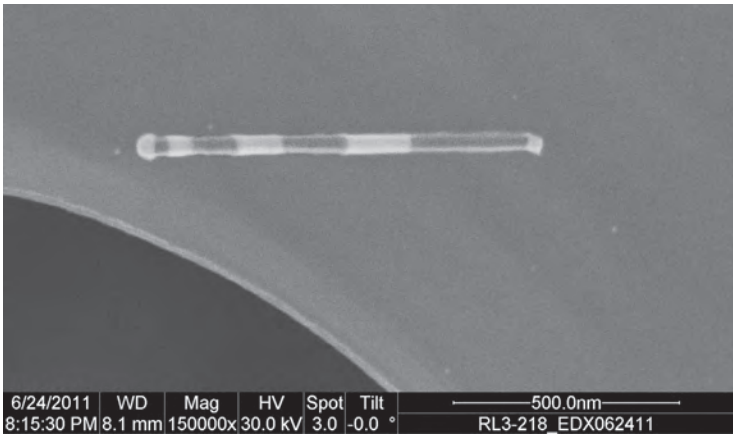
Integration Focus Activities (IFAs) are initiatives aimed at nanoscale integration challenges within the context of specific classes of materials, systems, or phenomena that will have high scientific and technological impact. These topics are developed from a "bottoms-up" process within the CINT community. They are cross-thrust activities, which provide canonical examples of integration science and are intended to become strong attractors for users and collaborators. The IFAs both emerge out of a particular thrust effort and build on areas of strength across thrusts. The studies center on particular classes of materials, systems, or phenomena and derive their integration focus through a use-inspired science approach. These focused efforts bring an interdisciplinary approach by CINT scientists and users to a particularly timely area of integration science. They enable rapid progress in specific areas of common interest, attract and build user communities, and are variable term in nature. Each IFA is supported by two dedicated postdoc positions whose research is targeted towards linking the work of CINT scientists and the user community in specific high-impact areas.

Nanowires for New Energy Concepts IFA

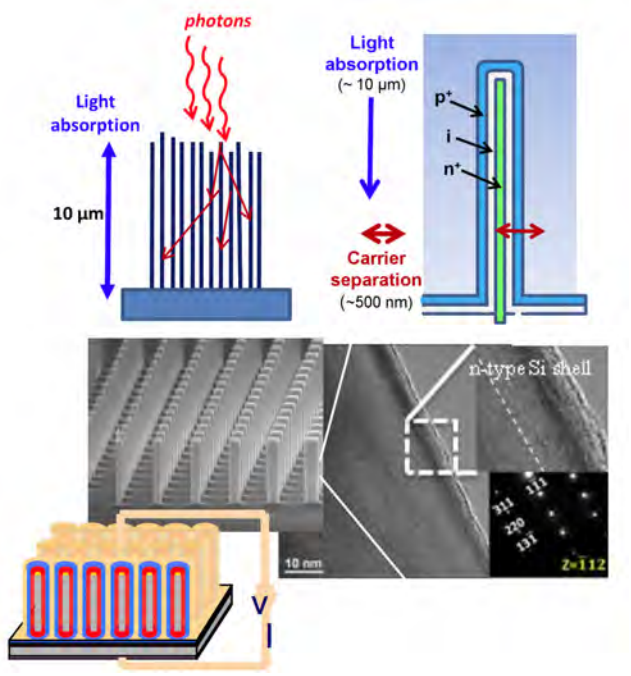
The novel properties of nanowires offer tremendous opportunities for transformative energy applications. These multi-purpose materials combine nanoscale and even quantum-confinement effects with enhanced transport properties. CINT scientists together with our user community are focusing to understand and control the functionality and integration of heterogeneous semiconducting nanowires for new energy harvesting and storage concepts. We emphasize heterogeneous nanowires to realize an unprecedented level of control over material performance by tuning interface, strain, and materials-mixing effects. We combine new synthesis strategies with structural, electrical, optical, and thermal characterization, initially at the single-nanowire level to answer critical science questions underlying new nanowire materials concepts for photovoltaics, thermoelectrics, and energy storage. We also drive toward functional integration of nanowires into two- and three-dimensional architectures.

Selected Recent Highlights:

- Flow-reactor solution-liquid-solid nanowire synthesis. We've developed a flow reactor for solution phase growth of heterostructured nanowires. In contrast to traditional "beaker" chemistry the volume of reactants in the flow cell is very small. This enables rapid and precisely controlled switching of the reactants that makes growing axially heterostructured nanowires possible. Using this technique we have shown the first example of an eight-segment ZnSe-CdSe axially heterostructured nanowire. By controlling the growth rate in the flow reactor we measured the length-diameter dependence of CdSe and ZnSe nanowires and determined for the first time that the solution-phase growth mechanism involves both the Gibbs-Thomson effect and surface diffusion.

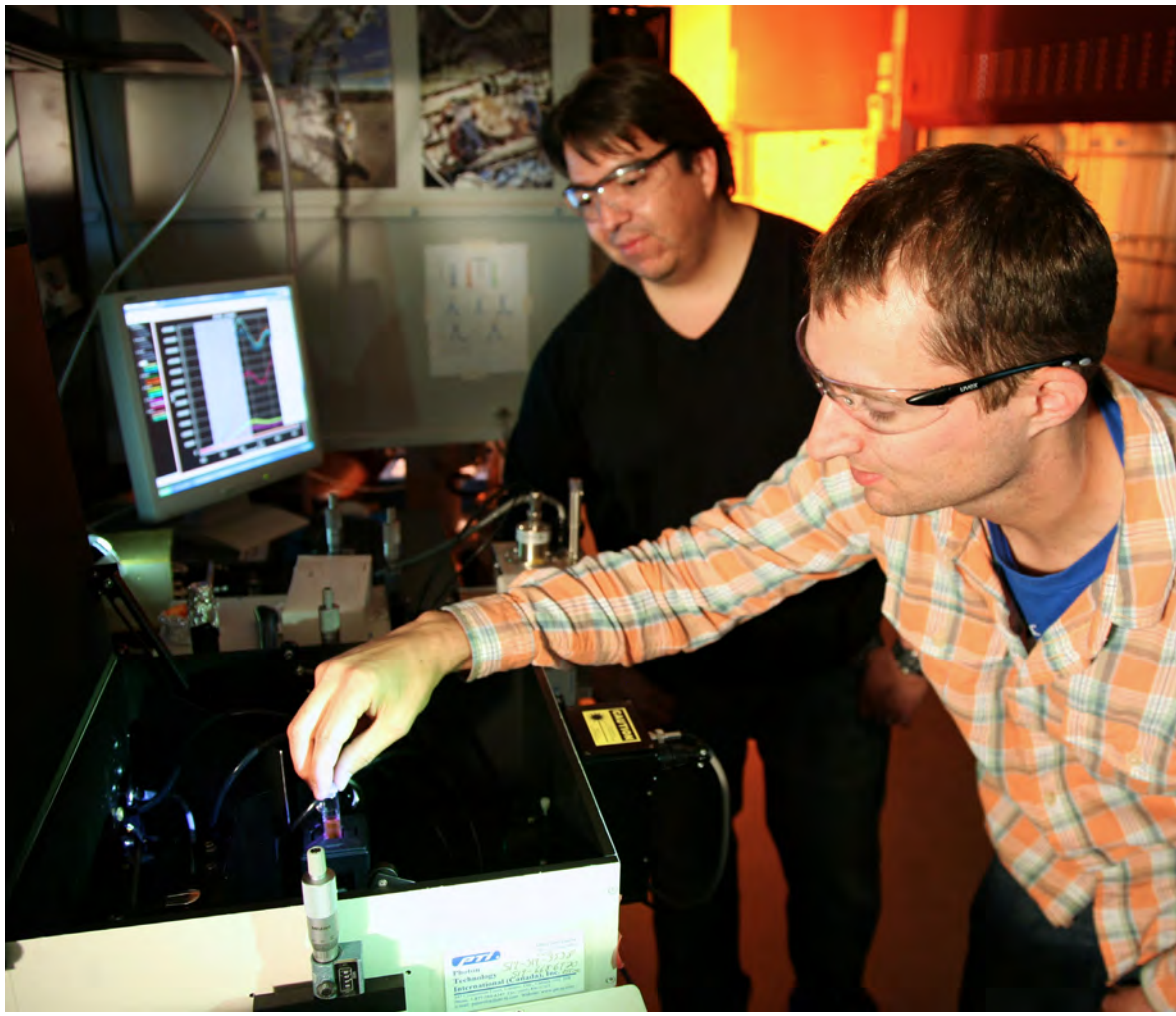


- Ultrafast optical spectroscopy. The ultrafast optical microscopy (UOM) system uses a femtosecond pump-probe laser setup and microscope objectives to measure carrier dynamics and carrier velocities in single nanowires with high temporal and spatial resolution in a non-contact, non-invasive manner. We showed the first measurement of carrier-lifetime increase by surface passivation on a single Si-SiO2 nanowire. By spatially separating the pump and the probe along the nanowire we extracted the carrier transport along the nanowire axis. We also used this system to perform the first measurement of GaN/AlGaN core/shell nanowires that revealed the influence of the AlGaN shell on carrier relaxation.



- Toward Si colar cells with single crystal efficiency at thin film cost. Using radial p-i-n nanowire arrays, we aim to decouple optical absorption and carrier collection. We have gained new insight into nanoscale radial epitaxial, low-temperature single crystal growth and fabrication of large-area nanowire arrays. We have measured external and internal quantum efficiencies by conducting wavelength dependent photovoltaic and optical absorption measurements in collaboration with our industrial partners.

Programmable Membrane-Based Nanocomposites IFA



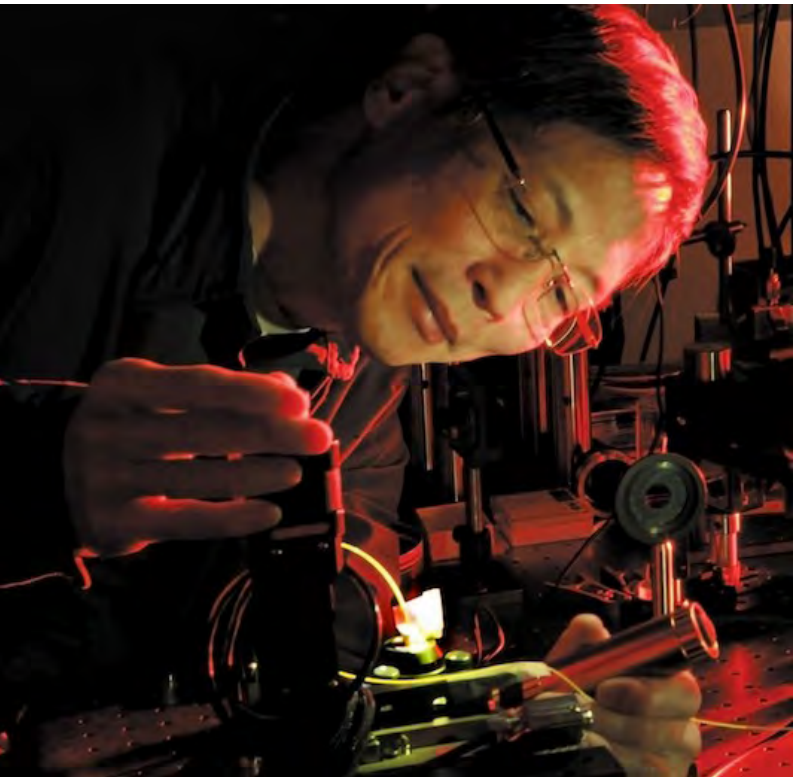
The focus of the Programmable Membrane-Based Nanocomposites (PMBN) Focus Area is to investigate the interactions between nanoscale materials and membrane-based composites such as lipid and polymer vesicles and membrane architectures. The ultimate goals of the research involve learning how to replicate many of the complex behaviors associated with cellular membranes within artificial nanocomposites and integrated systems. These integrated nanomaterials could be utilized in applications including electrical energy storage (the artificial electric eel), artificial photosynthesis, environmental remediation (reversible CO2 sequestration and water purification), and responsive sensors and adaptive materials for Homeland Defense applications.

The starting point for understanding the behavior of complex membranes involves understanding the fundamental interactions between membrane hosts, nanoparticles, and substrate surfaces. Initially, research in this IFA focused on investigating interactions of nanoparticles with lipid-based membrane systems, including: 1) nanoparticle adsorption, insertion, migration, and aggregation as a function of particle size, shape, and surface chemistry, 2) lipid responses as mediated by substrate interactions, including diffusion and transport, mechanical stability, domain formation and component partitioning, and 3) membrane-mediated nanoparticle organization.

Over the last year, research has shifted focus to polymer-based membrane materials. Polymers have the advantage of added versatility providing a greater means of tuning functionality, molecular weight, and robustness, while allowing for self-assembly into similar membrane organization with similar properties observed in lipid-based systems. We recently showed the ability of forming hybrid polymer bilayer/monolayer structures by surface chemistry in a one-step procedure using polymer micelles as the starting material. The hybrid layers resulted in self-assembled independent compartmentalization with differing properties. These hybrid systems are being further investigated as hosts for nanoparticles and as biomimetic films.

Over the next year we will continue developing polymer-based membrane materials from self-assembly of block copolymers. Systems being developed are more elaborate with an emphasis placed on functional properties to enhance nanomaterials interaction and control. As an example, responsive polymers and functional polymers (e.g. conjugated) are being explored as potential polymer blocks. We are also beginning work on a new project area that incorporates theoretical simulations, chemical synthesis, and experimental verification to define parameters for controlling the interaction and organization of nanoparticles with polymer brushes. Using mixed polymer brushes, consisting of locally phase separated regions of two polymers, functionalized nanoparticles will be localized spatially. For polymers that are responsive to the either the pH of the solvent or temperature, the nanoparticles can be captured and released in a controlled manner. For this work, we are using grafted polymer brushes in order to control the amount of each polymer in mixed systems. Uniform sized and shaped nanoparticles, essential to nanoelectronic engineering with defined predicted properties, will be synthesized. The polymer layer will be designed with specific interactions to drive self-assembly. Molecular simulations will correlate the interactions on the nanometer length scale with the macroscopic assemblies in solutions and at interfaces. Both explicit atom and coarse grained models will be used to cover the large range of time and length scale inherent in polymeric systems. Both experiment and simulation will follow the infiltration of nanoparticles from solution into the polymer brush in solution and the subsequent structure of the nanoparticle/brush film after the solvent is removed. The properties of the composite film, both mechanical and responsiveness will be studied for potential applications.

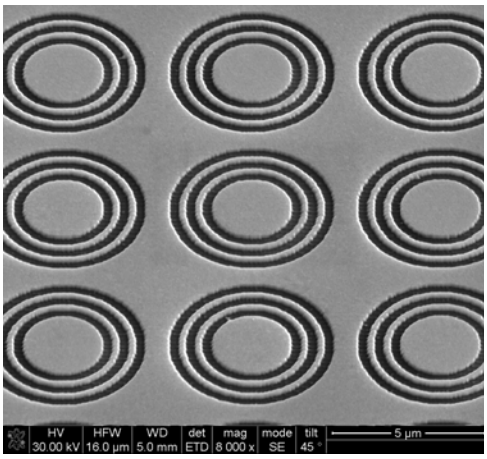
Metamaterials and Plasmonics IFA

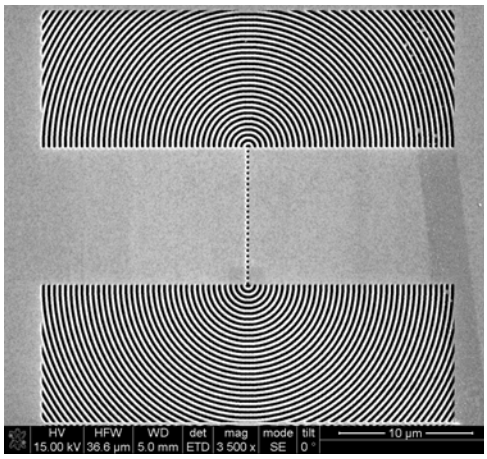


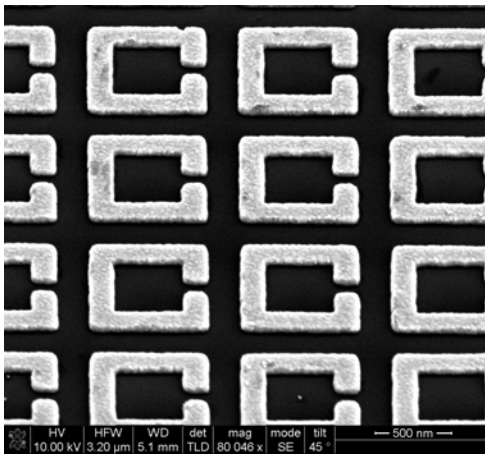
Artificially structured metamaterials and plasmonics provide novel properties that are difficult or impossible to achieve using naturally occurring materials. The new class of electromagnetic artificial materials greatly extends our ability to manipulate electromagnetic radiation (light), and has led to the demonstration of unique behavior such as negative refraction, cloaking, and superlensing. The Metamaterials and Plasmonics Integration Focus Activity builds upon the extensive activities at CINT in this field over the past few years spanning from terahertz to optical wavelengths. The goals of these activities are to understand and design metamaterial and plasmonic structures capable of enhanced interactions with light, and to accomplish novel functionalities from tunable and nonlinear hybrid metamaterials through integration of semiconducting and/or complex oxide materials and structures. During the past years CINT has demonstrated leadership in this field through the groundbreaking work in novel metamaterial structures, active and dynamical metamaterials and plasmonics, and their applications to sensing and imaging.

During the last year the research in this IFA has largely focused on the enhanced light-matter interactions when metamaterial or plasmonc structures are introduced. We found that the phonon vibrations in the integrated (substrate) materials or the intersubband transitions in semiconducting quantum wells can be strongly coupled to the metamaterial resonances, which might result in loss reduction in metamaterials and the creation of unique spectral features. Enhanced nonlinear response was predicted in the early days of metamaterial research, and recently it has become an important research direction. We found that, in addition to their wide range thermal and optical tunability of the resonant response, high-temperature superconducting metamaterials exhibit strong nonlinear response under intense terahertz irradiation. Recent highlights also include the prediction of nonresonant broadband light transmission in a nano plasmonic structure, the demonstration of broadband metamaterial perfect absorbers and identification of the mechanism, and the demonstration of all-dielectric low loss metamaterials in the infrared.

Through a vibrant network of users and research groups at both National Labs, this IFA will continue its work and leadership in these areas of Metamaterials and Plasmonic research. Additional expansion into new directions include integrated active metamaterial devices as diffraction modulator for terahertz imaging, active or dynamical tuning of chirality in 3-D metamaterials and electromagnetically induced transparency in superconducting metamaterials, light polarization control and conversion, using spoof plasmon for thermal emission control and enhanced emission, integration of metamaterial and plasmonic resonators with epitaxial bandgap engineered heterostructures and complex oxides for enhanced nonlinear responses, including superconducting Josephson junctions towards quantum metamaterials, and the coupling of plasmonic structures with optical nanoparticles such as quantum dots, nanowires, carbon nanotubes and other semiconductor heterostructures.

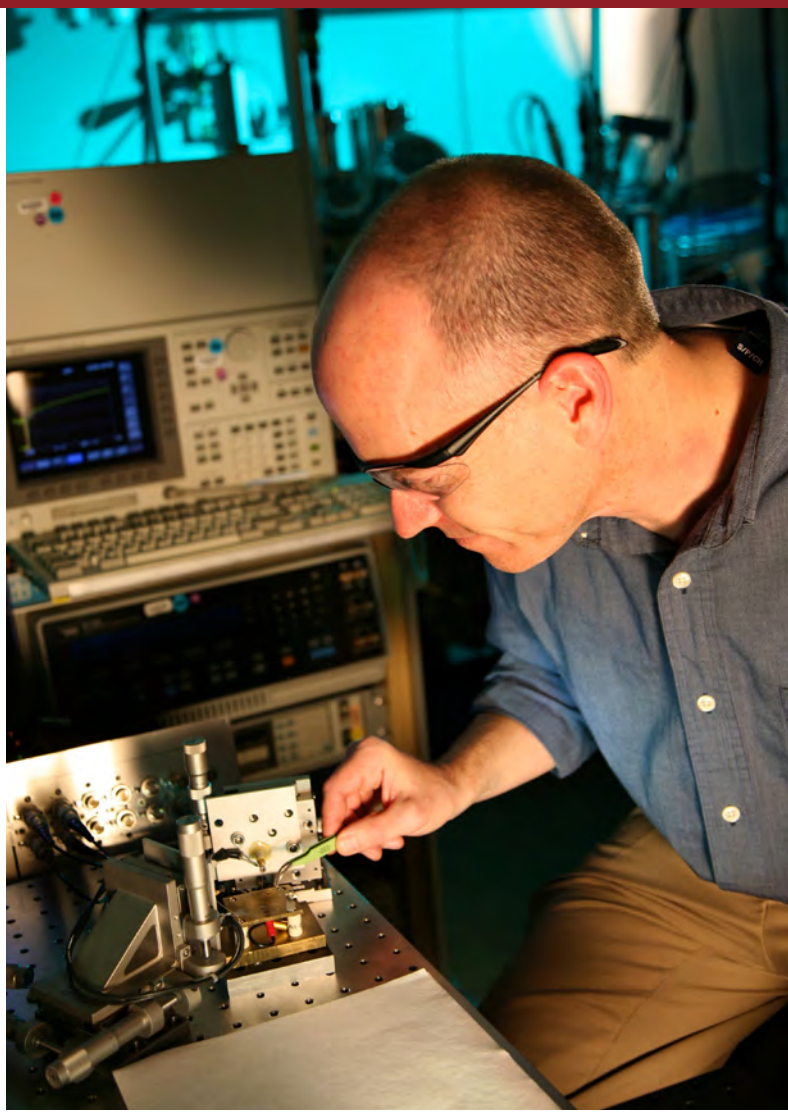






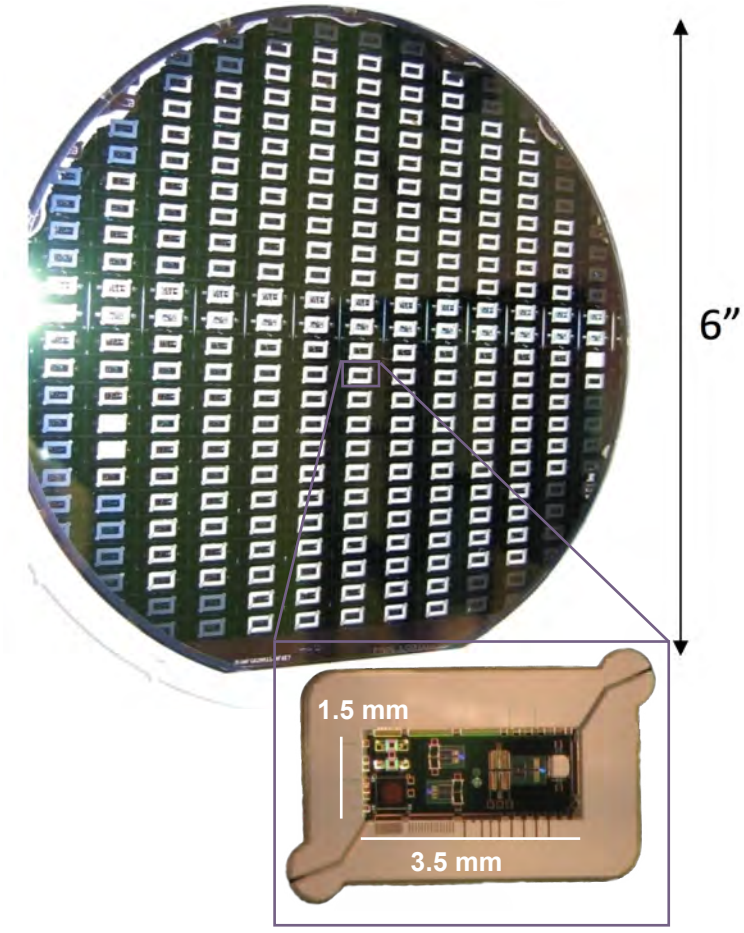
Discovery Platforms™

The thrusts develop a variety of new instrumentation to advance the science in their areas. One effort unique to CINT is the Discovery Platform™. These platforms are modular micro-laboratories designed and batch fabricated by CINT to allow easy integration of nanomaterials into microscale structures. Their purpose is to facilitate studies of nanomaterial properties and their integration. They should allow easy connections, a range of diagnostic and experimental measurement conditions, and a degree of standardization and reproducibility in nanoscale measurements. The inception, creation and evolution of Discovery Platforms have evolved in close collaboration with our user community.



Nanowire Discovery Platform (NWDP)

One configuration of the CINT Nanowire Discovery Platform (NWDP), the lateral nanowire (NW) platform, has completed fabrication at Sandia's microelectronics fabrication facility and has been under initial testing. This platform contains a high density array of metallic interconnects with buried bottom gates for the assembly and electrical characterization of semiconducting nanowires. The electrodes were designed to enable the assembly of nanowires from solution using dielectrophoresis (DEP). Scoping experiments using silicon nanowires showed successful DEP assembly with future work being focused on electrical characterization of the assembled nanowires. A second version of the NWDP, the silicon nanowire DP, has almost emerged from full fabrication.



This DP is distinguished by the monolithic integration of silicon nanowires as an intrinsic part of the platform, i.e. the NWs are fabricated as part of the NWDP fabrication process. The integrated NWs are designed to enable concepts of NW-based device and sensor characterization without need for post-fabrication NW integration. The third version of the NWDP, the vertical NW DP, has completed partial processing, but issues with the thick isolation dielectric were found. This platform is being held from further processing until a solution to the dielectric failure issue can be found.

Our future work on the NWDP will be focused on evaluation of the completed lateral NW platform. We will use dielectrophoresis to assemble semiconducting nanowires across electrodes and over the top of buried electrical interconnects. The evaluation will use silicon and silicon-germanium nanowires synthesized in the CINT VLS NW growth facility, with a special interest in investigating axially-doped wires (i.e. having axial pn junctions). Following assembly, the buried gates will be used to modulate the NW conductance for evaluation of the performance of these NWs in nanoelectronics and NW-based sensing.

Nanomechanics and Thermal Transport Discovery Platform (NMTTDP)

CINT's 'Nanomechanics and Thermal Transport Discovery Platform' (NMTTDP) has been heavily used by researchers for the study of the nanomechanics of semiconducting and metallic nanowires. In work performed by CINT user Prof. Dan Gianola and his research group at U. Penn, the NMTTDP was used to measure the piezoresistance of (100)-oriented silicon nanowires as a function of wire diameter and length. These studies required electrical testing during straining, which is one key feature that was added in the second generation of this nanomechanics test platform. Their studies revealed gauge factors comparable to values reported for thin film silicon and in contrast to the giant piezoresistance previously reported for silicon nanowires. In other work from the Gianola group, the NMTTDP was used to measure the temperature dependence of the onset of plasticity and fracture in FCC metal nanowhiskers [see Fig. 1(a)]. Gianola's group observed that the temperature and strain rate dependence to plasticity onset in Pd nanowhiskers did not follow conventional beliefs of thermally-activated dislocation nucleation, suggesting that plasticity onset in metal nanowhiskers is more complex than previously envisioned. This work was featured in nanomechanics symposia at the MRS and SES meetings with manuscripts in preparation. The NMTTDP was also used to study stress generation mechanisms in Li-ion battery anode electrode materials. In work that was performed in collaboration with CINT user Prof. Gerald Gulley of Dominican Univ., arrays of cantilever beams were coated with copper followed by a thin layer of silicon. The silicon-coated beams were cycled in battery electrolyte against a Li metal counter electrode, and the beam deflection was recorded as a function of cell potential [see Fig. 1(b)]. The cantilever deflection was recorded over several charge-discharge cycles in order to observe mechanical degradation in the silicon electrodes. The sensitivity of the cantilever beams to surface stress was found to be higher than the optical system could follow, which has led to a modified focus on processes that occur just at the electrode-electrolyte interface, e.g. the formation of the solid-electrolyte-interphase (SEI), as discussed in the future work section.

The NMTTDP contains test structure for the measurement of the mechanical, thermal, and electrical properties of nanoscale materials. Duirng the next three years we will continue to use this platform for the nanomechanical testing of metallic and semi-

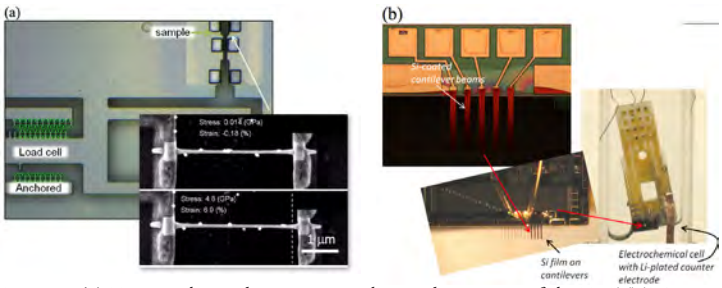
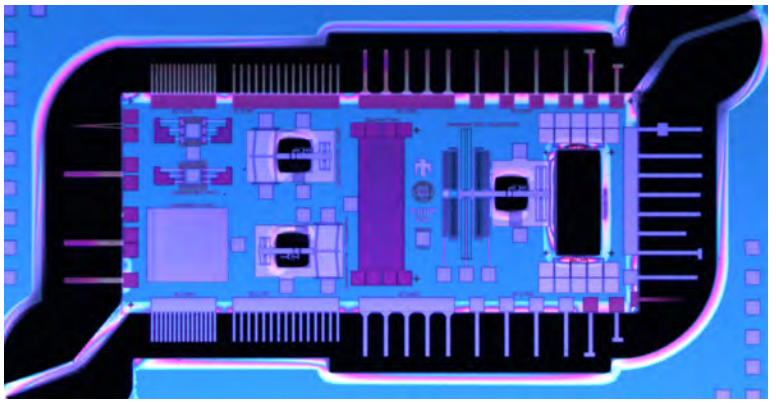
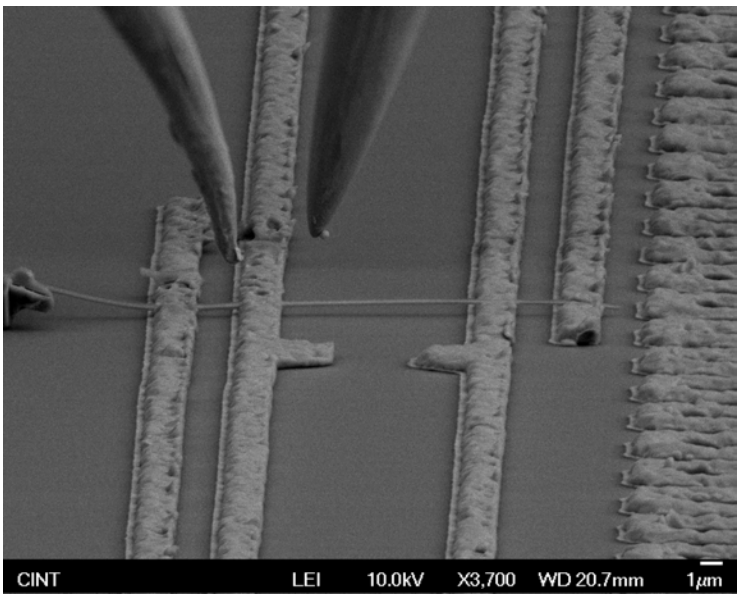


Figure 1.(a) Nanomechanical testing using the tensile test stage of the NMTTDP. A Pd nanowhisker is stressed to the point of fracture. The top inset image is the Pd nanowhisker in the unstressed state. The bottom inset image is the Pd nanowhisker with 4.8 GPa stress (6.9% strain) just prior to fracture. [From Prof. Gianola's group, U. Penn]. (b) Si-coated cantilever arrays on the NMTTDP used for measurement of stress generation during cycling in a Li-ion battery half cell. The image on the right shows the NMTTDP mounted on a chip carrier and immersed in battery electrolyte in a sealed cuvette for testing using laser light scattering. [In collaboration with Prof. Gulley, Dominican Univ.]



conducting nanowires, with a special focus on understanding plastic deformation mechanisms in monocrystalline FCC metal nanowhiskers and mono and polycrystalline BCC metal nanowires. Nanomechanical testing of semiconducting nanowires will focus on measurement of the electromechanical response of NWs, i.e. the effect of strain on electrical conductivity. We will also continue to use the cantilever beam arrays on the NMTTDP to measure surface stress in Li-ion battery electrode materials during electrochemical cycling with a special focus on understanding the formation and evolution of the solid-electrolyte-inter-



phase layer on silicon and on probing the chemical modification of passivating surface coatings applied to battery electrodes, such as ultra-thin aluminum oxide layers deposited by atomic layer deposition. In addition to nanomechanics measurements, the NMTTDP will be used to investigate the effect of strain on the optical and electronic structure of nanowires and two-dimensional semiconductors, such as bilayer graphene. These experiments will be performed in collaboration with Doorn and Htoon (CINT NPON thrust). We will also use the thermal analysis test structures on the NMTTDP to determine the thermal conductivity in semiconductor alloy and core-shell nanowires using a pulsed heating method. The goal of these studies is to understand the influence of alloying, nanostructuring, and doping on thermoelectric efficiency.

TEM Liquid Cell Discovery Platform

We have completed the successful fabrication and demonstration of a new CINT DP that provides a unique capability to perform experiments inside a transmission electron microscope using volatile liquids, such as aqueous solutions or battery electrolytes. This platform, the TEM Liquid Cell DP, uses two microfabricated chips, each having a thin silicon nitride window (~ 40 nm thick), that permits transmission of high energy electrons with little attenuation. The two chips are mated face-to-face to create a narrow a cavity, approximated 100 nm thick, see Fig. 2. Liquids are inserted in this cavity through two fill holes which are subsequently capped with epoxy to create a sealed liquid-filled chamber. Metal electrodes are also provided into the viewing region of the platform in order to permit the observation of electrochemical processes while imaging in the TEM. The platform has been tested with the assembly of LiFePO4 Li-ion battery cathode nanoparticles, using dielectrophoresis, and with filling and imaging through an ethylene carbonate based Li-ion battery electrolyte. Future work with this platform will focus on imaging the formation and evolution of the solid-electrolyte-interphase layer on Li-ion battery electrodes.

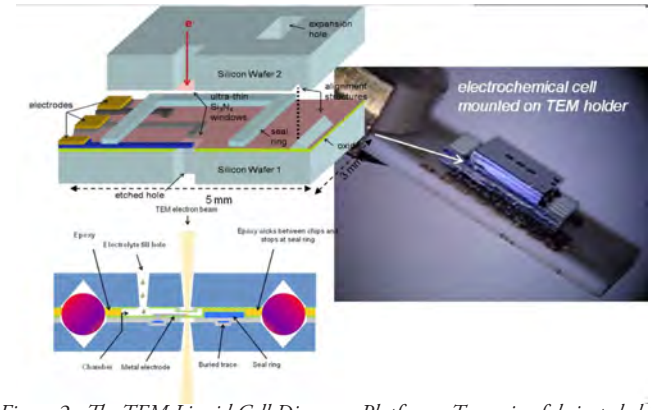


Figure 2. The TEM Liquid Cell Discovery Platform. Two microfabricated chips with electron transparent windows are mated face-to-face to create a thin cavity that is then filled with liquid and sealed. The image on the right shows the assembled platform on a TEM holder.

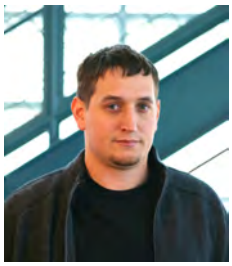
We will use the newly fabricated TEM Liquid Cell DP to investigate electrochemical mechanisms at solid electrode – liquid electrolyte interfaces. This work is complementary to the in situ TEM work involving open electrochemical cells using ionic liquid or solid electrolytes, as described in the NEM thrust activities. The goal of these studies is to image the formation and evolution of the solid-electrolyte-interphase layer on representative Li-ion battery nanoscale electrodes, including silicon and graphite anodes and LiFePO4 and LiMnxO2 cathodes, while these electrodes are immersed in ethylene carbonate-based Li-ion battery electrolytes. The sealed cell geometry of the TEM Liquid Cell DP permits future experiments that are aimed at understanding cell aging mechanisms. These studies will be performed by cycling sealed cells outside the TEM for periods ranging from days to weeks interspersed with periodic TEM imaging and analysis. This offers a view into long time scale degradation phenomena, an approach normally not possible in TEM electrochemical experiments. As an exploratory activity, we will also test imaging of the TEM Liquid Cell DP using aqueous solvents, with the goal of assessing the suitable of this platform for analysis of chemical synthesis or biology processes (in collaboration with the Soft, Bio, Composite Thrust).

Microfluidic Synthesis Discovery Platform

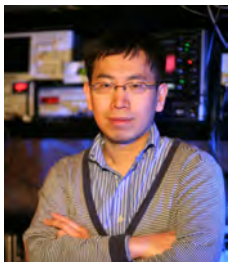
CINT has begun development of a new Microfluidic Synthesis Platform to advance both the science and practice of nanomaterials synthesis. The goal is to develop customized microfluidic chips, along with necessary temperature and fluidic controls, to allow improved control and in situ study and monitoring of nanomaterials synthesis. In particular, targets include greatly improving reproducibility of syntheses, on-chip synthesis of core-shell particles, as well as on-chip surface functionalization. These goals necessitate novel chip designs as well as advanced temperature controls, including multiple heating zones on a single chip. The supporting system is being assembled, and the now chip designs fabricated and tested in consultation with the user community, in particular with Professor Ping Liu (UT Arlington). In situ monitoring systems are currently in the planning stage but will be deployed in the upcoming year.

2011 CINT-funded Postdocs

To help ensure the continuing vitality of our internal science program at CINT we maintain a very active postdoctoral program funded through our Center resources. This program provides postdoctoral support for positions in each of our four Thrust areas as well as each of our three Integration Focus Activities. This support is a shared asset within the Center, and the postdoctoral associates who fill these positions help to further integration and collaboration within and between our Thrusts. We are pleased to provide a few vignettes from among our current corps of Center-funded postdoctoral researchers here. Our Center also benefits extensively from the intellectual input and participation as formal CINT Users of other postdoctoral researchers who are mentored by our CINT Scientists but funded through competitive postdoctoral fellowships at our respective host laboratories and other intra- and extramural research projects.



Jared Crochet- mentored by Steve Doorn
Jared investigated extrinsic factors that affect single-wall carbon nanotube light emission and absorption. At CINT he found that both excitons and free carriers could exist in compositionally engineered carbon nanotube aggregates and single dopant molecules could be imaged in real time as they interacted with nanotube surfaces.



Young Chul Jun - mentored by Igal Brener
Young Chul works on electrically tunable infrared metamaterials at CINT. He designs, fabricates, and characterizes active metamaterials based on semiconductor device structures, which may find applications in infrared sensing, thermal imaging, etc.

Allison Dickey - mentored by Mark Stevens
Allison uses simulations to determine the relationship between nanoparticle/protein diffusion and size in model membranes. She is also interested in examining how confinement affects the structural order of aqueous solutions.

Bill Mook - mentored by Nate Mara and Amit Misra
Bill is interested in the mechanical properties of materials at both the micro- and nanoscales. To investigate these properties he conducts mechanical tests (indentation, compression, tension, bending) inside of an electron microscope. This allows him to quantify properties such as hardness, elastic modulus, yield strength, flow stress, work hardening and fracture toughness of thin films, nanolaminates and other small structures.

Jason Haraldsen - mentored by Sasha Balatsky
Jason works on condensed matter theory in the areas of strongly correlated electron systems, multiferroics, and complex oxide interfaces. Other research areas include working with CINT users on data analysis through 3D visualization.

Kumar Palaniappan - mentored by Jennifer Hollingsworth
Kumar's project involves synthesis and surface manipulation of solution grown semiconductor nanowires (SCNWs) for applications in Photovoltaics and Thermoelectrics. He is also working on a novel apporach to fabricate semiconductor nanowires grown directly from the substrate called Flow Solution Liquid Solid (FSLS) method using a microfluidic reactor system.

Other 2011 CINT postdocs include: Yong-Shin Park mentored by Han Htoon, Ranjan Singh mentored by Hou-Tong Chen,Tom Harris mentored by John Sullivan, and Aditya Mohite mentored by Han Htoon.

Postdoc Highlight - Julio Martinez

Twelve years ago, Julio Martinez didn't know a word of English. Today, as a postdoctoral appointee at CINT, he is exploring the atomic and molecular world of thermoelectric and photoconductive nanowires and has become an expert at nanomanipulation.

His path to the world of nanowire research started when he moved from his native land of Buenos Aires, Argentina, to learn English in a Mississippi State University program. There he received his master's degree in chemical engineering and became aware of the nanotechnology field, so he traveled to the West Coast for an advanced degree.

It was when he pursued a Ph.D. in chemical engineering at the University of California-Davis that the field of bionanoelectronics "caught my eye," he said. The field examines the integration of modern electronic circuits with biological components using nanowires.

In graduate school, he focused his research on the integration of semiconductor nanowires and biomolecular motors, such as protein ion channels. Working with colleagues, his research resulted in a milestone for the bionanoelectronic field.

"At the time, people were doing some functional analysis on nanowires, but we showed that we can incorporate biological motors, such as ion pumps and ion channels, with nanowires," he said. Their research showed that the electrical field of the nanowire can open and close the channels, just as a biological cell would do. His dissertation proposal in this area garnered him the Lawrence Scholar Fellowship from Lawrence Livermore National Laboratory.

With a background heavy in materials and engineering, Martinez easily plugged into the field of electronic characterization and integration of nanowires, a field that brought him to CINT as a postdoctoral appointee three years ago.

At CINT, Martinez has concentrated his research on developing nanostructured materials for energy harvesting, primarily focusing on thermoelectric and photoconductive novel nanowire materials. In his work, he has come to better understand the factors that influence the thermoelectric properties of nanowires.

And he has discovered the mechanisms for the enhanced thermoelectric efficiency in boron doped silicon-germanium alloy nanowires. Currently, bulk SiGe alloys are being used for power generation, and SiGe has been proposed for spot cooling of microelectronics.

"As we get more miniaturization of the computer and computer chips, we need a device that can cool those devices in situ," he said. "Thermoelectric devices could be one of the solutions for the future."

During his postdoc position, Martinez has worked in the development and implementation of new capabilities at CINT. He implemented thermal and cryogenic capabilities for the study of nanomaterials, developed and tested the first thermoelectric-characterization platform for nanowires at Sandia National Laboratories, and developed the nano-welding method between nanowires and metal contacts. His work at CINT has a significant impact in the research community, and his work is currently being used by other research groups.

For the future, Martinez is looking forward to pursuing his career at either a national laboratory or a university so that he can continue cutting edge and novel science. For the time being though, he's enjoying his time in the western United States.

"I like working hard and making progress in my science, but I also enjoy taking my family to the beautiful mountains and the national parks that are so close to us," he said.

by Caroline Spaeth

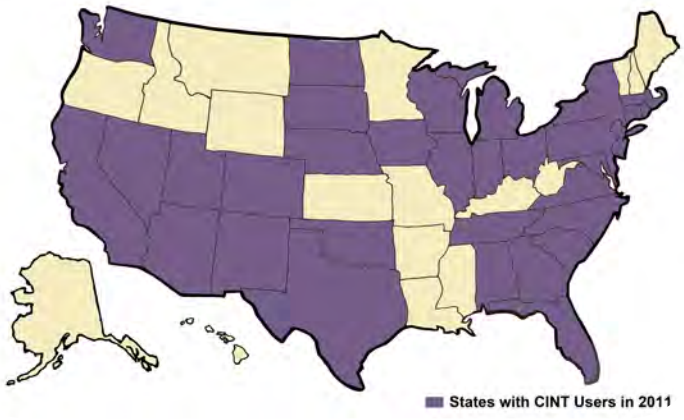
CINT User Program

The CINT user program is designed to provide the international scientific community access to Core and Gateway Facilities. User access can include use of capabilities in either or both of our Facilities as well as engagement of the CINT Scientist staff expertise. There are two modes of user access: General User access and Partner User access, each with variable scope and the ability to conduct nonproprietary or proprietary research.

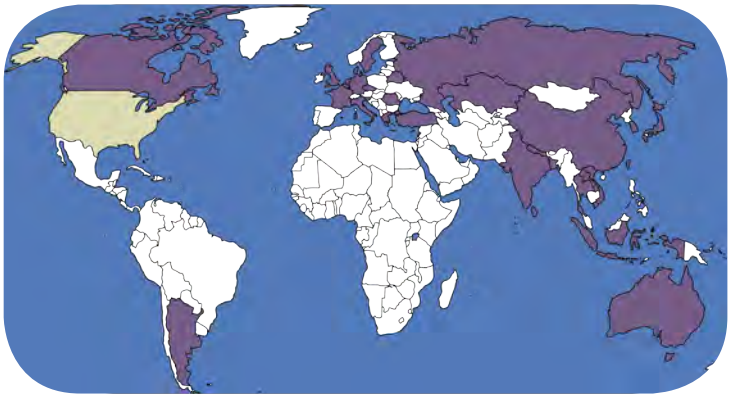
CINT users may conduct their approved research projects in collaboration with one or more CINT Scientists or may choose to access CINT capabilities independently. User proposals are evaluated on the merits of the science without preference for collaborative/independent access.

Users working independently will be properly trained and supervised by technical personnel. Some CINT capabilities cannot be operated independently for safety or complexity reasons.

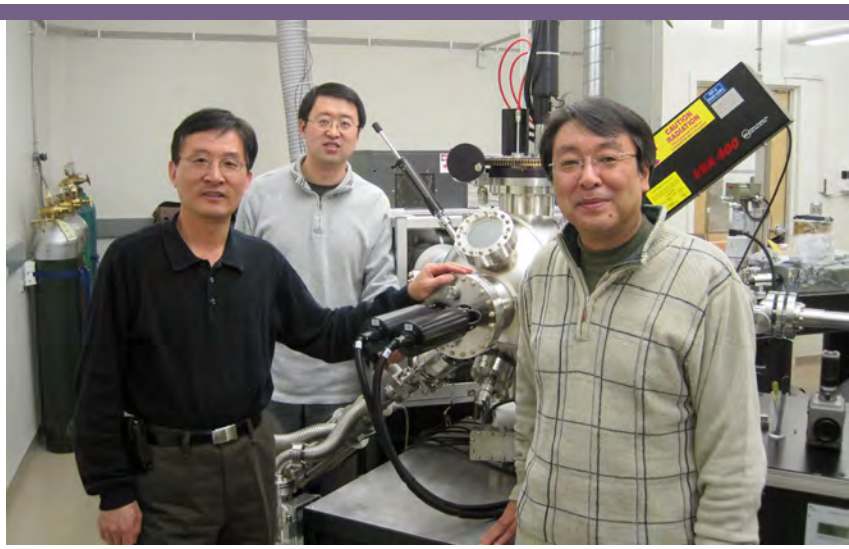
User proposals consist of a 2-page (maximum) pdf document that is uploaded via the website along with user information entered on-line. All user proposals undergo an initial feasibility/safety screening by CINT technical staff, and a technical peer-review conducted by external Proposal Review Panels that reflect the four CINT Scientific Thrusts. The CINT Management uses the Review Panel scores and comments to prioritize access to CINT.



CINT Users came from institutions in 33 different states.



In 2011, CINT had 138 foreign national users from 34 unique countries.



Left to right, CINT Scientist Quanxi Jia and postdoctoral researcher Li Yan with CINT User Jun Kono.

Users Executive Committee

The CINT Users Executive Committee (UEC) is an elected body of representatives that provides input from the user community to the CINT program management team, regarding facilities, operations, science, and quality of the on-site user environment. All UEC members are active CINT users, having either a current or very recently approved CINT user proposal. The current members are:

- Prof. Linda Peteanu, Chair, Carnegie Mellon University
- Dr. Ed Flynn, Senior Scientific, LLC.
- Prof. Guillame Gervais, McGill University
- Prof. Suneel Kodambaka,University of California, LA
- Prof. Joanna Millunchick, University of Michigan
- Prof. Dvora Perahia, Clemson University
- Prof. Elba Serrano New Mexico State University
- Dr. Eric Shaner, Sandia National Labs

The UEC is heavily involved in planning the technical portions of the CINT User Conferences each year. During the conference, the UEC meets privately and also hosts an informal open forum for current and prospective users to share information about, and provide feedback on, CINT operations and management. This has resulted in lively and constructive dialogue targeted not only towards operational improvements but also to a better understanding of DOE, BES and CINT policies.

To foster open communication between CINT and the User Community, the UEC has quarterly conference calls with members of the CINT management team. These provide a forum for the UEC and management to formulate new initiatives and develop a cooperative atmosphere in which to discuss and resolve user concerns.

In 2012, the UEC will co-organize the annual CINT User Conference and UEC members will work with CINT staff on two workshops. One will focus on the interface between biological particles and nanoparticles and the second will highlight recent advances in nano-mechanics. In addition, a special symposium is planned to honor the scientific achievements of Dr. Tom Picraux on the occasion of his retirement from CINT.

3D Tracking of Proteins - Jim Werner and Diane Lidke

Collaborations work best when both parties benefit. That continues to be the case with a now four-year collaboration between CINT scientist Jim Werner and University of New Mexico assistant professor Diane Lidke.

Werner, a physicist in CINT's Soft, Biological and Composite Nanomaterials Thrust, has been working with a team of CINT scientists in the last few years to develop a three-dimensional tracking microscope. The microscope system simultaneously samples four spots surrounding a molecule under scrutiny and tracks both its spatial and temporal dynamics.

What the microscope tracks is where Lidke comes in. Lidke, who has a Ph.D. in biophysics and teaches in UNM's Department of Pathology, is interested in applications of quantum dot nanoprobes and live cell imaging.

Through their work together, Werner and Lidke have used the instrument to follow 3D dynamics of key proteins involved in the human allergic response and associated biological signals. More recently, they used the microscope to follow 3D movement of individual protein molecules inside live cells.

"We have used optical microscopy in two dimensions. But we know that cells aren't flat; they have some 3D structure to them," Lidke said. "Working with Jim is really exciting because he has this special 3D tracking microscope, and by having this collaboration we're able to look at the motion of our proteins of interest in a way that we can't do here at UNM."

For Werner, the collaboration benefits his team's instrumentation work.

"I'm more interested in pushing the state of the art of this instrument and its capabilities, and Diane is interested in fundamental biological questions, so the collaboration works out pretty well," Werner said, adding that the combined work has led to stronger and more successful grant proposals.

Lidke's research in cell signaling focuses on the normal and diseased states of cells so they can compare the differences between the two conditions.

To facilitate the 3D molecular tracking, Lidke labels signaling molecules with quantum dots, tiny glowing nanocrystals. The photostability of quantum dots allows them to be used as a fluorescent tag or probe. Scientist Jennifer Hollingsworth in CINT's Nanophotonics and Optical Nanomaterials Thrust has provided Werner and Lidke with non-blinking quantum dots to improve consistent tracking and is also working with them to make the quantum dots more biologically compatible.

"A better probe will make your instrument better," Werner said. "So I'm definitely going to benefit from these new probes."

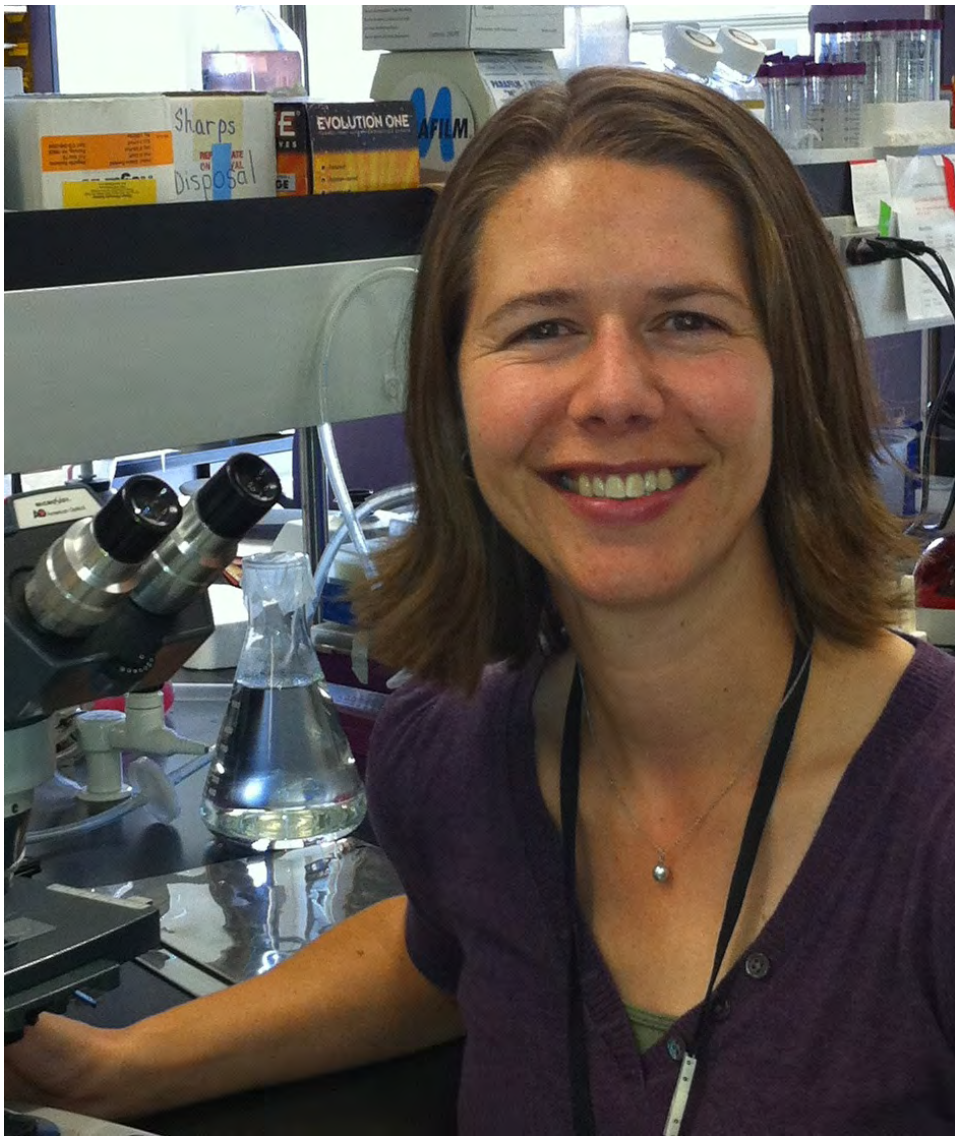
And so far, the improvements in the tracking and the instrument have continued to bolster advancements in the research. The two worked with others to publish a paper that demonstrated the method for time-resolved 3D molecular tracking in live cells using Werner's microscope.

The demonstrated method allows Lidke now to push the boundaries of her current research into protein behavior in cells under a variety of conditions, which could range from allergies to cancer.

"It allows us consider asking questions we haven't been able to ask before," she said. "We're just getting to the exciting applications."

by Caroline Spaeth

CINT User Diane Lidke at her lab at the University of New Mexico



CINT User Conference 2011

The Center for Integrated Nanotechnologies (CINT) held its 11th Annual Users Conference on September 14th-16th, 2011 at the Albuquerque Marriott Hotel in Albuquerque, New Mexico. There were 140 registered participants from 20 Universities, 3 Industries, and 3 Government Agencies and Laboratories.

Three plenary presentations opened up the Conference:
- Raymond Orbach the Director of The University of Texas at Austin's Energy Institute and former US DOE Undersecretary for Science, who gave a broad-reaching presentation on Our Sustainable Earth,
- Michael Flatté from The University of Iowa, who spoke on Solotronics: Manipulation, Control, and Application of a Solitary Dopant within a Semiconductor, and
- Ivan Schuller from The University of California at San Diego, who discussed NanoHybrids: Confinement, Proximity and Induced Phenomena.

Continuing with our tradition of science symposia around active areas of user projects and research at CINT, two parallel symposia were held during the event. Technical Symposium I: Single Element Addressability and Control from Soft to Hard Materials and Technical Symposium II: Probing Dynamic Nano Interfaces. A Poster Session with contributions from Users and CINT scientists was held, as well as an optional tour of the Core facility.

The Single Element Addressability and Control Symposium focused on how single element interrogation and control are important issues in nanomaterials integration and applications ranging from single molecule and nanoparticle tracking and spectroscopy to control and measurement of single dopants. Such capabilities will also be an essential aspect of advancing the emerging field of solotronics: optoelectronics based on single, independently addressable (optically, electronically, or magnetically) dopant or defect sites. To explore CINT's role in this arena, this symposium encompassed the following themes: Single molecule and nanoparticle spectroscopy, tracking, and control; Preparation of, and incorporation into, materials with single dopant sites; New functionality emerging from single defects and dopants; Imaging, spectroscopy and dynamics of single dopants; and correlated electrons and the emergence of new states inside a nominally "rigid" gap. These themes included discussions of top-down generation and bottom-up synthesis techniques, exploration of defects and dopants in graphene, topological insulators and superconductors; single optical or magnetic dopants in quantum dots; and dynamic probes of dopant migration at nanomaterials surfaces. The symposium also covered the ares of electronic and optical control and fingerptinting of single molecules on graphene, on carbon nanotubes and in the process of translocation through nanopores.

Speakers included:
- David Norris (ETH)
- Dan Gamellin (University of Washington)
- Han Htoon (CINT)
- Diane Lidke (University of New Mexico)
- Max DiVentra (University of California San Diego)
- Sasha Balatsky (CINT)
- Jared Crochet (Los Alamos National Laboratory)
- Laurent Cognet (University of Bordeaux / CNRS)
- Phil Collins (University of California, Irvine)
- Ed Bielejec (Sandia National Laboratories)
- Ezra Bussman (Sandia National Laboratories)

The second symposium, Probing Dynamic Nano Interfaces, focused on how nanoparticles, due to their unique size and shape dependence, exhibit significance enhanced tunable electro-optical and magnetic characteristics, together with an exceptional mechanical strength in comparison with bulk materials. However integration of nanoparticles into materials and devices without losing their properties pose a barrier to bridging the gap from scientific discovery to engineering innovation that will take advantage of the enhanced properties of the nano particles. Integration requires control of structure and dynamics at interfaces, which often requires development of new experimental methodologies. Structure and dynamics at soft nano-interfaces as resolved by different techniques, including optical methods, scattering techniques and computer simulations, were discussed as well.

Invited Speakers:
- Raymond Orbach (University of Texas, Austin)
- Eric Weeks (Emory University)
- Shengfeng Cheng (Sandia National Laboratories)
- Hongyou Fan (Sandia National Laboratories)

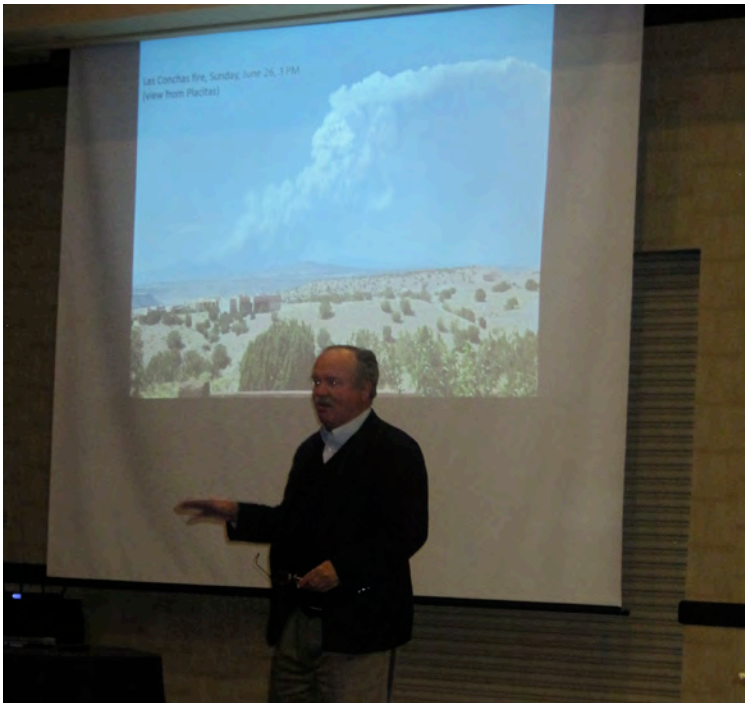
Dr. Raymond Orbach speaking at the 2011 CINT User Conference

- Andrew Price (Sandia National Laboratories)
- Ramanan Krishnamoorti (University of Houston)
- Wally Paxton (CINT)
- Anna Balazs (University of Pittsburgh)
- Jaroslaw Majewski (Los Alamos National Laboratory)
- Lisa Hall (Sandia National Laboratories)
- Alex Levine (University of California, Los Angeles)
- Jeff Brinker (Sandia National Laboratories & University of New Mexico)

The Conference was preceded by two highly attended events; a Solid-state lighting Science Energy Frontier research Center Conference (SSLS EFRC) and a focused Industrial Outreach Session.

The Solid-state lighting Science Energy Frontier research Center Conference (SSLS EFRC) covered topics on Novel Emitters and Light-Matter Interaction in Nanostructured Materials, and featured a plenary talk by Lars Samuelson, Director of the Nanometer Structure Consortium at Lund University. Additional speakers included John Schlager, NIST; Silvija Gradecak, MIT; Jennifer Hollingsworth, LANL; Leonid Butov, UC-San Diego; Vladimir Bulovic, MIT; and Stephane Kena-Cohen, Imperial College.

CINT's Industrial Outreach session entitled "A Practical Guide for working with CINT" attracted participants from over 20 small businesses. This workshop was specifically targeted to scientists and small business owners of technology companies in the private sector (industry, small business, start-ups, etc.). Speakers included a current CINT user from a small business (Mesa Tech International) and a representative from a local Venture Capital firm (Arch Venture Partners). The talks described various models for interacting with the Sandia and Los Alamos National Laboratories with a particular emphasis on intellectual property issues and navigating through "small business" funding opportunities. Representatives from the New Mexico Small Business Association and the Labs Tech Transfer offices were present to help answer questions about working with CINT. Several small businesses requested follow up meetings with CINT scientists as a result of the session.



Dr. Bob Parmenter the Preserve Scientist for the Valles Caldera Trust, along with Marie Rodriguez, the Natural Resources Manager of the Valles Caldera National Preserve, spoke at the conference banquet about the 2011 Las Conchas fire that threatened LANL property.

There were over 40 technical posters presented at the 2011 CINT User Conference.

Nanophotonics and Optical Nanomaterials Thrust

Igal Brener, Thrust Leader; Jennifer Hollingsworth, Acting Partner Science Leader

The Nanophotonics and Optical Nanomaterials thrust seeks to address the overall scientific challenge of understanding and controlling fundamental photonic, electronic and magnetic interactions in nanostructured optical materials fabricated using both chemical and physical synthesis. Major thrust research areas include: 1) Chemical and Physical Synthesis of Optical Low- Dimensional Nanophotonic Structures; 2) Optical Spectroscopy of Low-Dimensional Nanostructures; 3) Photonic Crystals, Metamaterials and Nanoplasmonics. This thrust interacts directly with the other three CINT scientific thrusts to leverage expertise in related fields such as theoretical analysis of nanostructures, soft biomaterials, ultrafast spectroscopy of hard and soft nanomaterials, and cleanroom semiconductor fabrication and processing. The scientific directions for this thrust will follow these three main categories and developments in these areas are expected to lead to rapid advances in light-capture applications (photovoltaics, photodetection, and radiation detection), light-emission applications (solid-state lighting, light-emitting diodes, lasers, etc.) and new understanding of electromagnetic phenomena and solid state excitations at the nanoscale.

Recent Accomplishments

In 2011 significant progress was made in a range of Thrust focus areas. Overall, these activities can be classified into four themes: (1) Spectroscopic investigations into the properties of novel 0D, 1D, and 2D optical and magnetic nanomaterials from the level of single nanostructures to ensemble behavior; (2) Development of new characterization tools; (3) Development of new optical nanomaterials; and (4) Materials integration toward emergent phenomena (metamaterials, coupled optical-plasmonic materials) and/or enhanced device-level performance.

Selected accomplishments in (1) include (a) demonstration of two single-NQD spectroscopy approaches to independently and directly measure the quantum yield of bi-exciton states (Q2X), including the revelation that near unity Q2X is possible in thick-shell ('giant') nanocrystal quantum dots (g-NQDs), (b) a systematic study of the pump-intensity- and shell-thickness-dependent evolution of photoluminescence blinking in core/shell nanocrystals, revealing that thick-shell NQDs are 'blinking-free' at all pump powers, (c) investigations of carrier dynamics in Si nanowires, including along-wire carrier transport, by ultrafast optical microscopy, (d) first ultrafast optical measurements on GaN/AlGaN core/shell nanowires, revealing the influence of the AlGaN shell on carrier relaxation, (e) demonstration of the coexistence of antiferromagnetic, ferromagnetic, and ferroelectric phases and the coupling between them in multiferroic TbMnO3 films using ultrafast optical pump-probe spectroscopy, (f) experimental demonstration that quantum charge fluctuations may underlie the giant magnetoelectric effect in multiferroic LuFe2O4, (g) first photoluminescence measurements on the multiferroic BiFeO3, and (h) further advances in Raman spectroscopy of carbon nanotubes (CNTs) that allowed us to establish that breakdown of the Condon approximation is observed for multiple phonon modes and to demonstrate for the first time demonstration strong Raman interference effects in CNTs. Progress in (2) that will enable future accomplishments in area (1) include (a) development of a novel single-NQD spectro-electrochemistry capability for controllably and reversibly injecting/extracting charges into/out-of individual optical nanomaterials while simultaneously monitoring changes in emission intensity and lifetime fluctuations, which has already been used to reveal mechanistic level understanding of NQD blinking behavior, and (b) implementation of a new near-IR photoluminescence excitation spectroscopy capability that has been integrated into a single-carbon nanotube (CNT) imaging system, which has thus far been applied to the study of CNT electronic doping at the single-tube and single-site levels. All of our spectroscopic investigations and integration efforts are supported by our activities in area (3), for which significant progress has also been made, including (a) completion of a comprehensive study of the effects of g-NQD reaction parameters on ultra-thick-shell growth and investigations into relationships between shell and particle structure and ensemble/single-NQD optical performance (including first demonstration of complete suppression of blinking by the thick-shell approach), (b) development of new synthetic routes to InP-based thick-shell NQDs and first demonstration of non-blinking behavior in the near-infrared, as well as suppressed photobleaching and long biexciton lifetimes (novel InP/CdS g-NQDs), (c) completion of mechanistic investigations into "flow" solution-liquid-solid semiconductor nanowire synthesis (a CINT technique) and demonstration of unprecedented axial heterostructuring enabled by this approach, and (d) development of novel method for the synthesis of in situ metal-contacted semiconductor nanowires that does not require polymer intermediates, which otherwise interfere with device integration. Lastly, from proof-of-concept devices to new methods for manipulating light-matter interactions, we have made the following progress in are (4): (a) integration of g-NQDs into two types of LEDs – direct-charge injection and down-conversion, demonstrating in both cases the transformational properties of thick-shell NQDs for light-emission applications (e.g., stability, solid-state performance, large Stokes shift for minimal self-reabsorption, etc.), (b) fabrication of the first highly fluorescent carbon nanotube/silica aerogel composite materials and films, where aerogels afford a solvent-free and surfactant-free environment for pursuit of nanotube photophysics in low-interaction environments including novel low-temperature behaviors not observed previously, (c) first demonstration of dielectric resonator metamaterial based on micron size cubes of tellurium on a BaF2 substrate with optical magnetism behavior in the mid-IR, (d) demonstrated semiconductor approaches for tuning infrared (~10 μm) metamaterials, and applying NPON Thrust activities to the bio-arena, (e) demonstrated a plasmonic sensor for malaria based on nanohole arrays and (f) revealed potential of advanced energy-transfer analyses to characterize nano-bio constructs in situ, as well as ability of biotemplates to facilitate ultra-efficient NQD-NQD and NQD-dye energy transfer.

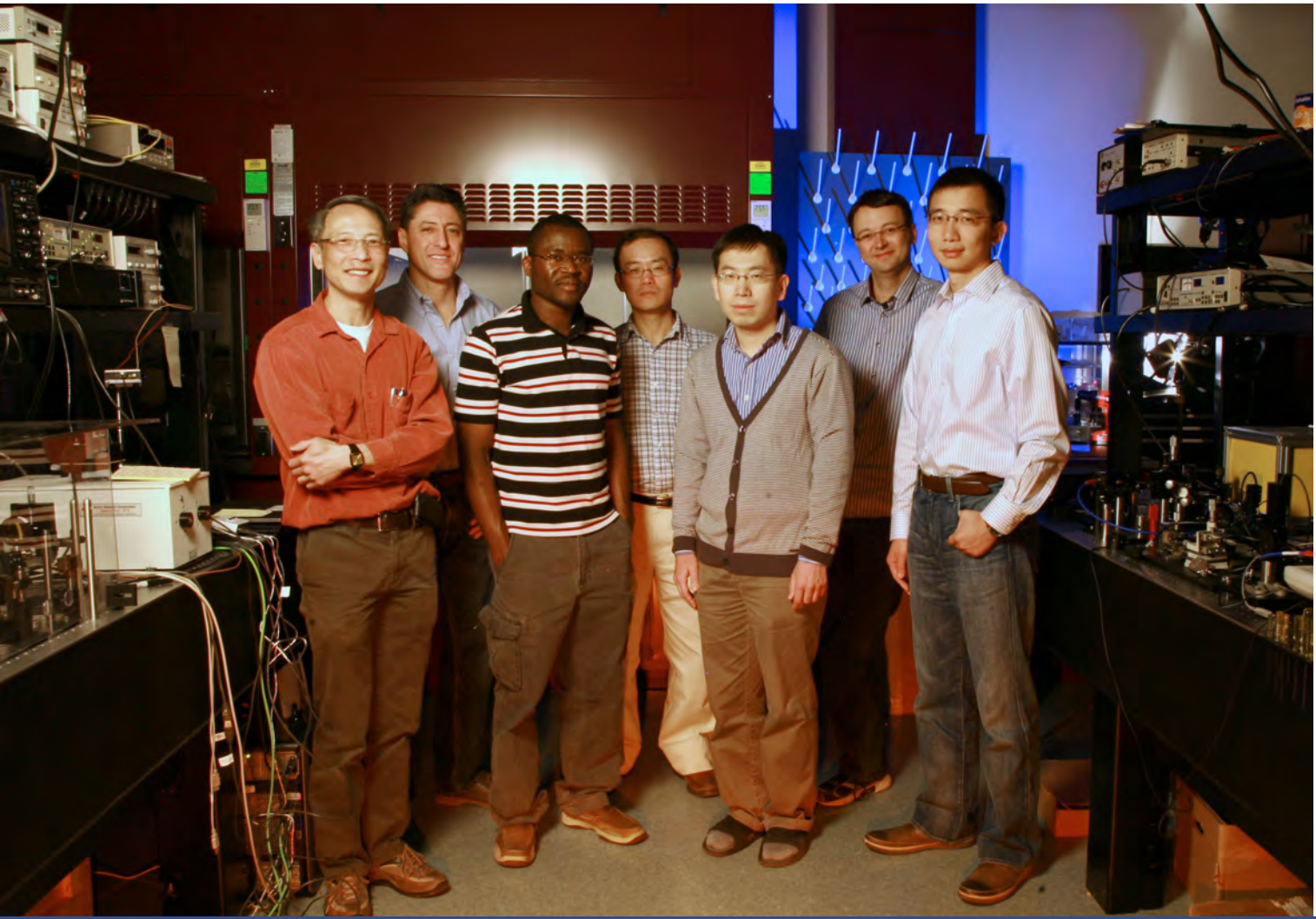
Future Directions

NPON Thrust activities in the coming year will clearly build on our recent successes, as well as extend into new directions. For example, exploiting the uniquely accessible multiexcitonic emission in g-NQDs, we will explore multiexciton-plasmon interactions, including development of an apertureless NSOM capability to perform 3D mapping of plasmon-exciton/multiexciton interactions. Similarly, we will investigate exciton-plasmon interactions

in less-explored CNT-metal complexes and use spectroelectrochemistry to study single CNTs. In the case of other 1D and even 2D structures, we will study nanowire heterostructures using ultrafast optical microscopy to shed light on their use in solar cells and nanoscale transistors, as well as using ultrafast optical and terahertz spectroscopy to unravel the interplay between different order parameters in magnetic/superconducting and ferroelectric/magnetic heterostructures. We can apply mid-infrared pump, terahertz-probe spectroscopy to the interaction between phonons and electrons in high-Tc superconductors, and we plan to develop a terahertz time-domain spectroscopy system in a strong magnetic field and apply it to studying the quantum Hall effect in graphene and two-dimensional electron gases. A new time-resolved PL system will be installed at the CINT Core, which will be used initially to study PL dynamics of semiconductor nanowires as a function of temperature. We will expand the work of coupled semiconductor heterostructures with metamaterials to include InGaAs and GaSb materials, parabolic quantum wells, etc. and combine nanowires in a 2D photonic crystal arrangement to study laser emission with the goal of reducing lasing threshold to a record low. In the area of CNTs, we will extend investigations into the origins of non-Condon behavior in nanotube Raman response to determine its extent in armchair structures and for high-energy excitations. We will use strain to realize tunability of the non-Condon response and Raman interference behavior.

We will enhance our single-tube near-IR photoluminescence capability by including a time-correlated single-photon counting capability, correlation spectroscopies, and addition of a tunable ps continuum excitation source. We will also pursue aerogel-CNT composites as optical cavities and for fundamental photophysical studies including probing of nanotube energy transfer behaviors and as new matrices for studying recently introduced empty nanotubes. Lastly, in addition to further fundamental explorations through advanced spectroscopic methods, our work in 0D optical nanomaterials will continue to include development of synthetic methods for novel functional NQDs, as well as new approaches for separating sub-ensembles of nanoparticles based on function that result, for example, from less-than fully homogeneous reaction conditions, including a new electrophoretic separation method. We also intend to develop new synthetic methods for fabrication of inverted nanoshell plasmonic-fluorophore coupled systems, especially infrared-emitting, toward intrinsic control of emitter radiative/nonradiative properties. Our existing non-blinking NQDs will be used in 3D particle tracking studies to facilitate fundamental understanding in cell membrane science and drug-tumor interactions. We will also purchase and perform initial experiments with a Nanoink, Inc. DPN 5000 nanolithography system to be installed at the CINT Gateway, including realization of nanoscale control over optical nanomaterial/metal nano-antenna integration.

Members of the NPON Thrust at the Core Facility.

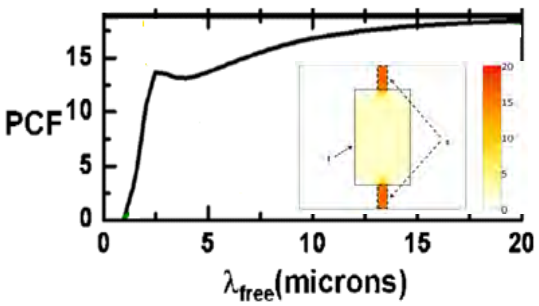


Nonresonant Broadband Funneling of Light via Ultrasubwavelength Channels

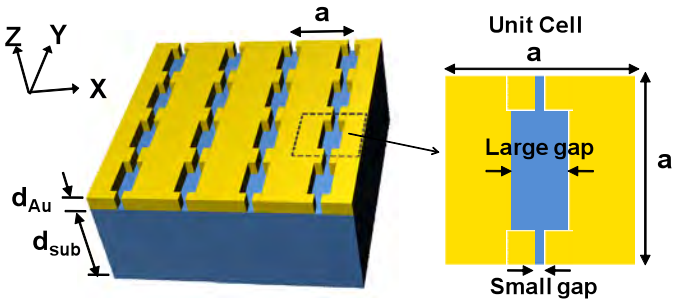
Accomplishment: The ability to confine and funnel light through extremely subwavelength volumes has significant implications for the control of light-matter interactions that affect key material properties such as absorption and emission rates, optical non-linearities and gain. An important goal has been to be able to achieve ultra-subwavelength light confinement across a wide spectral bandwidth and with sufficient transmission. Current approaches for achieving light confinement relies on the excitation of structural surface plasmon polaritons (SPP) in perforated nanostructured metal films, a phenomenon known as extraordinary optical transmission (EOT). EOT is a resonant phenomenon and therefore has a narrow spectral bandwidth. It also tends to have poor transmission.

In this work, performed in part under CINT user project led by Sandia scientist Ganesh Subramania in collaboration with Dr. Stavroula Foteinopoulou of University of Exeter, UK and CINT thrust leader Igal Brener, a new a paradigm to achieve utra-subwavelength and broadband light funneling is proposed. It consists of a 'double-grooved' aperture design comprising of periodic connected rectangular apertures of two different sizes engraved in thin gold film. In an illustrative test structure where the periodicity is 300nm with a large slit width of 100nm and small slit width of 15nm, it is shown that the incident light can be funneled into an area as small as (λ/500)2 across a broad wavelength range (λ ~ 3-20 μm) with high transmission (> 70 %). The electric field in the small gap region is enhanced by ~15-20X compared to the incident field. But most importantly, the fraction of the incident power that is funneled through the small gap is higher by the same factor than what one would expect from the area fraction occupied by the slit alone. In other words, 15-20 times more power funnels through an aperture whose area is 1/60th of the unit cell area. We quantify this enhanced power funneling by introducing a figure-of-merit called the "power confinement factor" (PCF). To explain and obtain a theoretical understanding of this behavior, collaborator Dr. Foteinopoulou along with computational simulations developed a quasi-static model based on charge response to the incident field that explains this behavior across most of the spectral regime. This model provides a simple intuitive rule to optimize the structure for high field enhancement, PCF and total transmission by tuning the relative dimensions of the small and the large slits as dictated by the specific applications without having to perform extensive simulations.

Significance: This new approach demonstrates for the first time a counter-example to a widespread notion that a resonant approach like the EOT is required to funnel light through subwavelength apertures with enhanced intensity. This design not only possesses but surpasses the capabilities achievable using EOT. The double-groove structure provides significantly higher transmission, enhanced power funneling and a broadband operation. The simplicity and robustness of this design makes it easy to implement thus, significantly impacting many areas of application such as mid-infrared detectors, molecular fingerprinting, optofluidics, non-linear devices and light sources.



Plot of PCF between 1-20 μm wavelength The inset shows the light intensity distribution within a unit cell and at 10 μm wavelength.



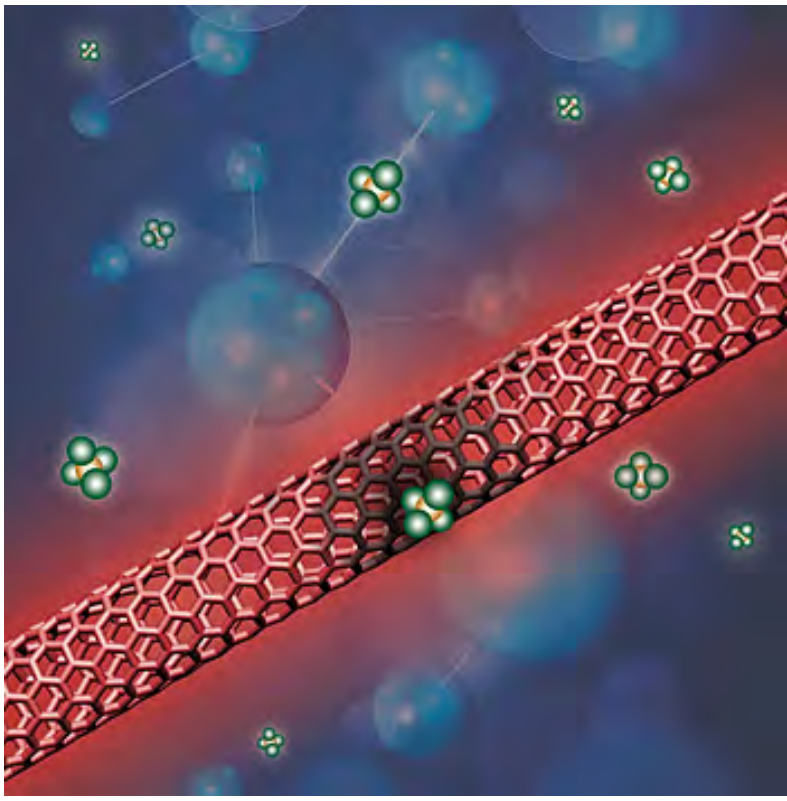
Left: Schematic of the double groove structure with periodicity 'a' on a Au film. Right: a single unit cell indicating the small and large gap.

Reference:
"Nonresonant Broadband Funneling of Light via Ultrasubwavelength Channels", Subramania, G., Foteinopoulou, S., and Brener. I, Phys. Rev. Lett. 107 (16), 163902 (2011).
CINT user project U2010B1064: "Electromagnetic Energy Transport through Sub-wavelength Channels and Localization"

CINT Scientist Igal Brener works with postdoctoral researcher Sheng Liu.

Los Alamos scientists detect and track single molecules with nanoscale carbon cylinders

LOS ALAMOS, New Mexico, January 10, 2012—Many physical and chemical processes necessary for biology and chemistry occur at the interface of water and solid surfaces. Researchers at The Center for Integrated Nanotechnologies publishing in Nature Nanotechnology have now shown that semiconducting carbon nanotubes—light emitting cylinders of pure carbon—have the potential to detect and track single molecules in water.



Artist's concept of nanotubes on the liquid surface. Image from Los Alamos National Laboratory.

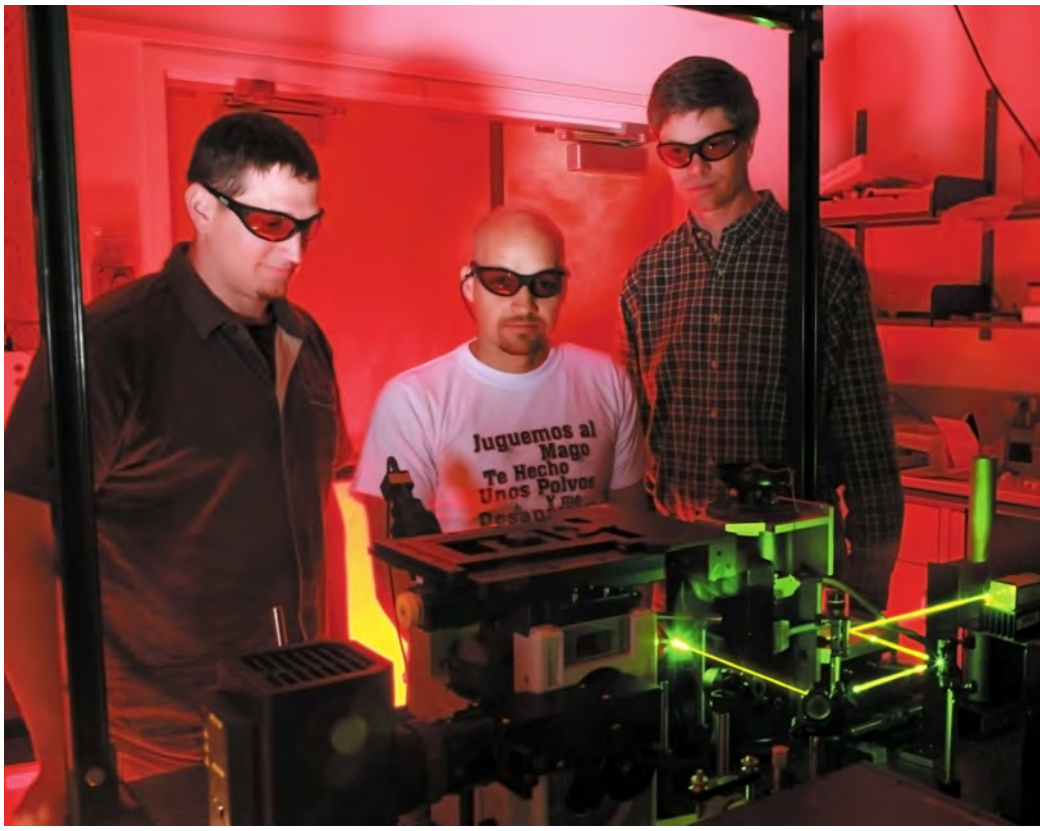
Using high-speed microscopic imaging, they found that nanotubes could both detect and track the motion of individual molecules as they bombard the surface at the water interface. Traditional techniques to investigate molecules on surfaces cannot be used in water because the study requires low-pressure atmospheres such as one finds in space. The team is hopeful that their work will lead to practical, nanotube-based, single-molecule detectors in aqueous biological and chemical environments.

Molecular motion and attachment to surfaces is important for driving chemistry that ranges from the production of ammonia on metal to the enzymatic oxidation of glucose. The attachment takes place through sporadic motion followed by a collision with the surface to which the molecule sticks. Molecules can then move along the surface where they can collide with other molecules and undergo chemical reactions.

In traditional "surface science" experiments these processes are imaged in a vacuum where other molecular species from the air cannot blur the image. In solutions such as water, there has been no way to do this directly. Consequently, researchers have been searching for a material that can be used in water to detect individual molecules for surface-science applications.

Inspired by this challenge a team of scientists (Jared Crochet, Juan Duque, Jim Werner, and Steve Doorn) at LANL's Center for Integrated Nanotechnologies explored using light-emitting carbon nanotubes as detectors. With techniques developed by others, the team used soap and water to stabilize the nanotubes where they could be imaged directly with a high-speed video camera. When illuminated with laser light these tubes shine brightly, like long glow sticks.

Left to right: CINT Postdoc Jared Crochet, User Juan Duque, & Scientist Steve Doorn



When the glowing nanotubes are exposed in water to different chemicals, the researchers saw that certain spots of the tube would briefly go dim as the molecules bombarded the surface. This allowed them to determine how effectively certain molecules would stick to the surface. The researchers were also able to track the motion of molecules as they moved along the surface. The team is now examining how chemical reactions proceed on nanotube surfaces to better understand chemistry at the water interface for biological and chemical applications.

Article from a LANL Press Release

Scientist highlight: Jen Hollingsworth

The Center for Integrated Nanotechnologies (MPA-CINT) offers scientists access to world-class facilities and advanced tools that enables nanoscience discoveries. However, it is not CINT's capabilities that make it special, said Jennifer Hollingsworth; instead, it's the national user facility's collaborative environment.

"You combine the capabilities and the researchers at CINT and you have breakthrough research happening here," said Hollingsworth. "It's a good model for doing interdisciplinary science." Collaboration and integration are central to CINT. Teaming with external users is at the core of the user facility's mission and developing the principles that govern the integration of nanoscale materials is at the heart of its vision.

Hollingsworth herself embodies the sort of cross-disciplinary expertise required in nanoscience. Originally trained as a classical inorganic chemist with a materials science inclination, she is now well versed in the science and language of her physicist and biologist collaborators. As a CINT scientist, she supports the center's nanophotonics and optical nanomaterials science thrust and is the Los Alamos lead for its nanowires integration focus area. Hollingsworth joined the Laboratory's Chemistry Division in 1999 as a Director's-funded Postdoctoral Fellow after earning her PhD in inorganic chemistry from Missouri's Washington University in St. Louis. "She is really enthusiastic and energetic so that makes her fun to work with," said CINT Chief Scientist Tom Picraux. "She is very important to CINT because she adds the chemical synthesis of nanomaterials aspect that we count on for our studies. She's also a good collaborator because she does her homework and understands things that are needed for the project."

CINT Scientist Jennifer Hollingsworth works alongside postdoctoral researcher Krishna Acharya.

A new class of nanocrystal quantum dots

As part of her CINT research, Hollingsworth recently collaborated with Laboratory scientists to develop a new class of nanocrystal quantum dots (NQDs) that benefit research ranging from bioimaging to solid-state lighting. NQDs are semiconductor nanoparticles with remarkable size-tunable optical properties, including the ability to efficiently emit light. Compared with molecular dye fluorophores, optically excited NQDs are more stable.

However, NQD applications have been limited due to a property known as fluorescence intermittency, or blinking. Under continuous illumination, single nanocrystal quantum dots turn "on" and "off" in an unpredictable fashion. Blinking limits the utility of conventional NQDs for applications requiring continuous and reliable emission of photons, such as single-particle tracking in advanced bioimaging and as single-photon light sources in quantum cryptography.

Hollingsworth and her team applied an ultrathick and structurally perfect shell of a higher bandgap semiconductor to the core NQD to create giant NQDs, which have suppressed blinking and remarkable photostability. The ability to follow the trajectory of single molecules as they perform their biological functions is an important goal for advanced bioimaging.

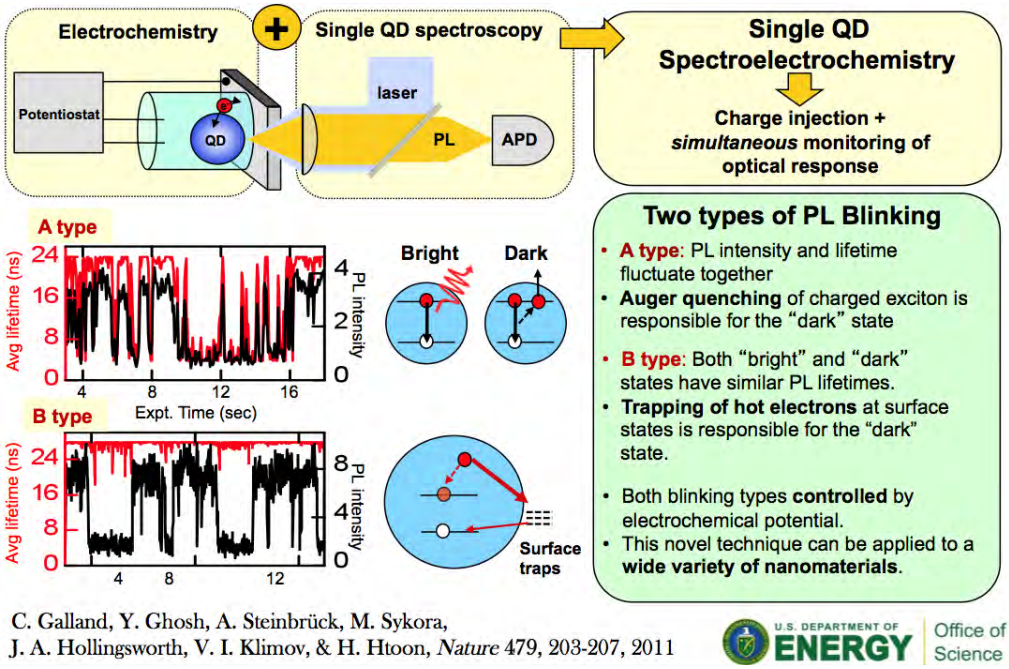
"Without her, the project would not have been possible," said collaborator Han Htoon, of Physical Chemistry and Applied Spectroscopy, who has worked with Hollingsworth for 10 years. "She and her postdocs created the inorganic shell that helped stop the blinking. Her expertise in this area is invaluable."

Since this discovery, Hollingsworth has begun collaborating with external researchers interested in capitalizing on the new properties of these nanomaterials and enhancing them by combining them with other nanoscale structures, such as plasmonic nanoparticles. The work, which supports the Laboratory's national energy security efforts, recently received a patent.

Hollingsworth and Htoon are also co-principal investigators on a project exploring the use of giant NQDs for high-efficiency solid-state lighting. Their work has received a Single- Investigator and Small-Group Research (SISGR) project grant from the Department of Energy's Office of Science, Basic Energy Science.

Los Alamos researchers unravel the mystery of quantum dot blinking

LOS ALAMOS, New Mexico, November 9, 2011—Research by Los Alamos scientists published today in the journal Nature documents significant progress in understanding the phenomenon of quantum-dot blinking. Their findings should enhance the ability of biologists to track single particles, enable technologists to create novel light-emitting diodes and single-photon sources, and boost efforts of energy researchers to develop new types of highly efficient solar cells.



C. Galland, Y. Ghosh, A. Steinbrück, M. Sykora, J. A. Hollingsworth, V. I. Klimov, & H. Htoon, *Nature* 479, 203-207, 2011

U.S. DEPARTMENT OF ENERGY | Office of Science

Most exciting is that the Los Alamos researchers have shown that blinking can be controlled and even completely suppressed electrochemically. As the Nature article describes, the group developed a novel spectro-electrochemical experiment that allowed them to controllably charge and discharge a single quantum dot while monitoring its blinking behavior. These experiments facilitated the discovery of two distinct blinking mechanisms. "Our work is an important step in the development of nanostructures with stable, blinking-free properties for applications from light-emitting diodes and single-photon sources to solar cells," said Victor Klimov, LANL scientist and director of the Center for Advanced Solar Photophysics (CASP).

Quantum dots are particles between 1 and 10 nanometers in diameter. A nanometer is only one billionth of a meter across, or about 1/3000th the diameter of a human hair. At these tiny dimensions, the rules of quantum physics allow scientists to produce particles with finely tunable, size-dependent electronic and optical properties. Together with the fact that they can be fabricated by means of facile wet-chemistry techniques, their quantum nature makes these dots attractive materials for a wide range of applications.

Nanocrystal quantum dots have been on the research scene for decades. The color they produce when excited by light absorption or electrical current can be precisely tuned from the infrared through the visible to the ultraviolet spectra, and they are cheap and easy to make.

Set against these advantages is a drawback—quantum-dot optical properties can randomly vary over time. Perhaps, the most dramatic manifestation of this variation is quantum-dot "blinking." Additionally, if energized by electrical current or light, they are characterized by an effect known as Auger recombination that both competes with light emission in light-emitting diodes and reduces current output in solar cells. Both blinking and Auger recombination reduce the efficiency of quantum dots, and controlling them has been the focus of intense research.

To probe the mechanism responsible for blinking, Christophe Galland, postdoctoral researcher in CASP, along with collaborators from the Center for Integrated Nanotechnologies (CINT) and CASP developed a novel spectro-electrochemical experiment that allowed them to controllably charge and discharge a single quantum dot while monitoring its blinking behavior. It is this work that is described in the Nature article. Its main result is the discovery of two distinct blinking mechanisms.

The first is consistent with the traditional concept of quantum-dot blinking, that is, the random electrical charging and discharging of the core of the dot. In this model, a charged state is "dark" due to highly efficient nonradiative Auger recombination.

The second mechanism was a surprise; the majority of quantum dots blink due to the filling and emptying of a surface defect "trap" on the dot. If not occupied, this trap intercepts a "hot" electron that would otherwise produce photon emission, thus causing a blink. With further research into the photophysical properties of quantum dots, the scientists hope to provide a comprehensive theoretical model of this phenomenon.

"The new single nanocrystal spectro-electrochemistry technique developed here could readily be extended to study the effect of charging in a wide array of nanostructures, including carbon nanotubes and nanowires," said Han Htoon, a CINT staff scientist who took part in the research. "I believe that it will become an important new capability for CINT."

Experiments were conducted at CINT, a U.S. Department of Energy Office of Science User Facility and Nanoscale Science Research Center, and CASP an Energy Frontier Research Center funded by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences. This work was also sponsored by the National Institutes of Health, NIH-NIGMS grant 1R01GM084702–01 (Htoon, Sykora, Hollingsworth, P.I.) that has the core aim of developing novel non-blinking quantum dots as molecular probes. This work was also sponsored by the Los Alamos National Laboratory Directed Research and Development (LDRD) program.
Article from a LANL Press Release.

Nanoscale Electronics and Mechanics Thrust

Quanxi Jia, Thrust Leader; Michael Lilly, Partner Science Leader

This thrust is focused on understanding and controlling electrical and mechanical properties arising from confinement on the nanoscale, interactions within nanostructures, and the integration of heterogeneous nanostructures for much improved and/or novel functionalities. Reduced dimensions as well as the influence of surfaces and interfaces can give rise to emergent functionalities not found in micro- and macro-scale systems. For electronic and mechanical systems, important integration issues involve energy transfer across interfaces, the role of defects in nanostructured materials, and interactions between nanoscale building blocks in integrated structures. These scientific issues arise in both electrical and mechanical nanosystems as we bring nanostructures together to implement specific functions, combine different materials to manipulate electrical or mechanical behaviors, and/or control the defect landscapes in given nanostructured materials for desired structural and functional properties.

CINT Technologist Kevin Baldwin makes samples on the Physical Vapor Deposition System.

Recent Accomplishments

Our accomplishments in FY11 are reflected in a wide range of topical areas including nanowires and nanowire heterostructures, high-mobility 2D based III-V materials and 1D quantum devices, nanomanipulation and integration of nanostructures, mechanical responses in nanostructured metals, novel nanobatattery assembly and testing platforms, effects of surface/interface on the functionalities of complex materials, and discovery platforms.

Selected accomplishments in nanowires include (a) the demonstration of extremely small transition regions in nanowire axial heterojunctions grown by the standard liquid phase catalyst method (vapor-liquid-solid technique); (b) successful fabrication of silicon-germanium heterostructures with an abruptness of less than 10 nm using in situ Au-Ga alloying, compared to previous transition regions which were ≥ the nanowire diameter (~40 to 80 nm); and (c) demonstration of the exclusive contribution of nanowire surface to the minority carrier transport and recombination through studies of the nanowire diameter dependence. Major achievements in research on high-mobility 2D based materials and devices include (a) the establishment of capabilities to grow 2D hole-gas structures; (b)the fabrication of devices with closely spaced double quantum wires for studies of Coulomb blockade; and (c) the measurement of charge sensing in double quantum dot in Si MOS devices. Efforts in nanomanipulation and integration of nanostructures have led to (a) the development of thermoelectric measurement platforms to characterize the thermal properties of SiGe alloy nanowires as a function of alloy composition and nanowire diameter to extract alloy scattering and surface scattering contributions to thermal properties; (b) successful measurement of the energy levels of individual PbS quantum dots directly using scanning tunneling spectroscopy (STM); and (c) the discovery that the confined-charge wave functions in quantum dots break the parity selection rules for the electronic transitions. In studies of mechanical response in nanostructured metals, we have discovered that the mechanical properties of nanoporous metals depend on not only the relative density, ligament size and morphology, but also on the surface topology and structure. In the front of novel nanobattery assembly and testing platforms, one of the most significant breakthroughs is the development of novel nanobattery assembly and testing platform inside a transmission electron microscope (TEM), which allows a direct study of the structural evolution of individual nanowire or nanoparticle electrodes with near-atomic resolution in real time. The results provide important battery operation and degradation mechanisms that can guide the development of high performance batteries. The investigation of the effect of surface/interface on the functionalities of complex materials has led to noteworthy inventions of highly resistive strongly ferromagnetic strained films and vertical interface strained ferroelectric thick films. Our different discovery platforms work offer powerful tools to measure the thermal conductivity and electrical response and structural changes following electrochemical lihtiation.

Future Directions

In the coming year our nanowire research will establish the origin of planar defect formation in nanowires during growth, demonstrate the use of catalyst alloying to eliminate kinking in silicon nanowires during CVD growth, and illustrate radial nanopillar epitaxial growth and the formation of nanopillar radial p-i-n solar cells. The study of high-mobility 2D based materials and quantum devices will target gated 1D and 0D hole gas structures, grow InAs 2D electron gas to make engineered topological materials, fabricate hybrid quantum dot/donor devices for silicon quantum computing, and use electrostatic quantum dots to measure important transport properties of these devices. In the area of nanomanipulation and integration of nanostructures, we will use STM lithography to fabricate atomically-precise single qubits that can be integrated with conventional lithographic techniques for electronic measurements. Research on the mechanical and physical properties of nanostructured materials will focus on in-situ study of the mechanical and electrical responses of materials such as nanocomposites, nanowires, nanopillars, and thin films. We will also explore the effect of mechanical strain on the functionalities of epitaxial nanocomposite films, and bring new Magellan HRSEM on line for users to begin collecting data. Exploration of energy storage materials will center on the measurement of electrochemical signals of individual NWs and nanoparticles. We expect to correlate these with the in-situ microstructure evolution to reveal the intrinsic electrochemistry of nanomaterials. In the front of development of discovery platforms, we will concentrate on the design and fabrication of in situ TEM liquid cell to observe dynamic changes in the anode surface during electrochemical cycling.

Enhanced superconducting properties through integration of NbC with highly aligned CNT forest

Accomplishment: We have successfully integrated superconducting NbC with highly aligned carbon nanotube (CNT) forests using a chemical solution approach.1 Fig. 1 shows the schematic drawing of the processing steps to form the CNT-NbC composites. The formation of superconducting NbC coating on the CNT forests does not destroy the microstructure of CNTs. Importantly, NbC shows much improved superconducting properties such as higher irreversibility field and upper critical field (the highest reported for the bulk NbC). Furthermore, the superconducting properties of the CNT-NbC composite become anisotropic compared with pure NbC. Fig. 3 show shows the upper critical fields when the field is parallel and perpendicular to the aligned CNT forest, respectively. In other words, the highly oriented CNTs embedded in superconducting NbC can function as defects and effectively enhance the superconducting properties of the NbC.

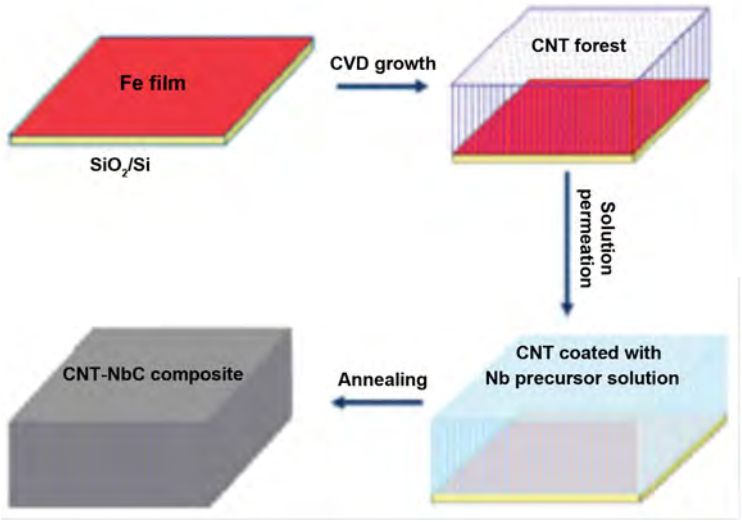


Figure 1. Schematic processing steps for the synthesis of CNT-NbC composites.

Challenge: The growth of ceramic-like NbC with desired functionalities has been a big challenge because a reaction temperature above 1000 °C is generally required. Such a high processing temperature leaves no playground to manipulate the microstructure and/or defect landscape in NbC and to control the functionalities desired for specific applications.

Significance: The formation of CNT and superconductor composites makes it possible to produce new and/or improved functionalities that the individual material does not possess. Highly oriented CNTs embedded in superconducting NbC matrix can function as defects and effectively enhance the superconducting properties of the NbC.

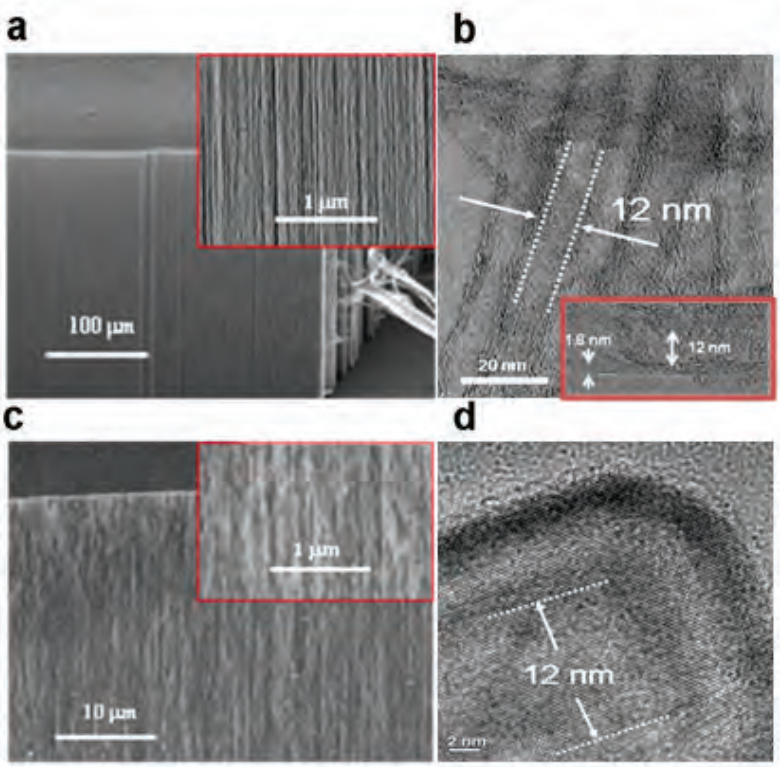


Figure 2. Morphology and microstructure of the prepared CNT forest and CNT:NbC composite. a) SEM image of a highly aligned CNT forest, b) HRTEM image of CNTs, c) SEM image of as-synthesized CNT:NbC composite, and d) HRTEM image of NbC coated CNT. Insets show the magnified SEM image of CNT forest (a), the high-resolution electron microscopy image of the as-grown multi-wall CNTs (b), and the magnified SEM image CNT:NbC composite (c), respectively.

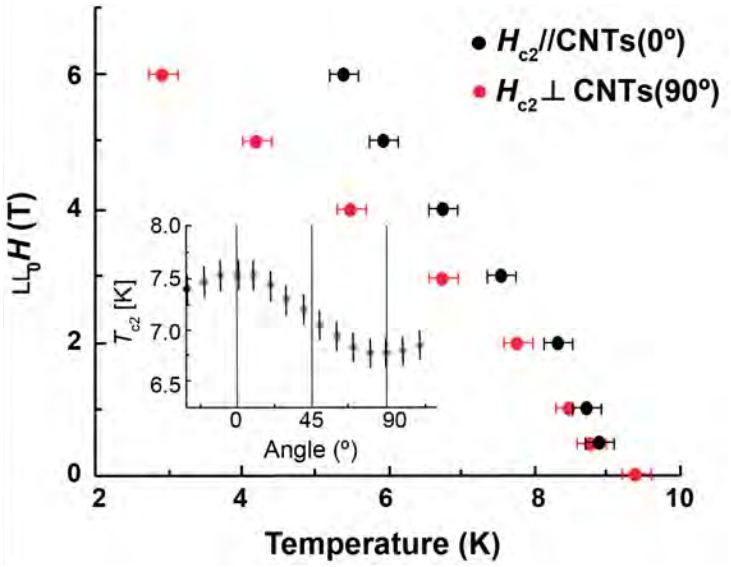


Figure 3. Anisotropic properties of the upper critical magnetic field of a CNT-NbC composite. Inset shows the angular dependence of the temperature at which ρ/ρn = 80% at an applied field of 3T, where 0° and 90° correspond to the field parallel and normal to the CNT growth direction, respectively.

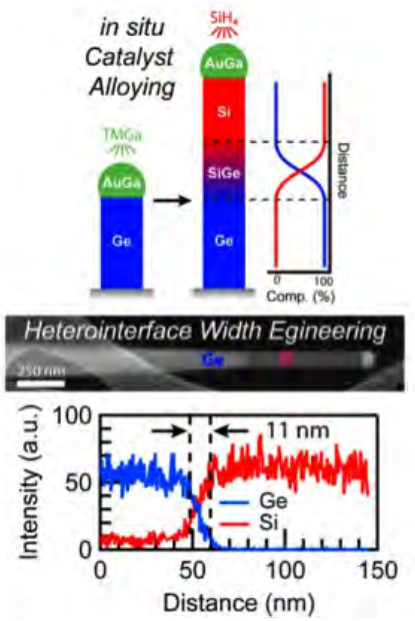
References:

1. Q. X. Jia, T. M. McCleskey, A. K. Burrell, Y. Lin, G. Collis, H. Wang, A. D. Q. Li, and S. R. Foltyn, "Polymer-assisted deposition of metal-oxide films," Nat. Mater. 3, 529 (2004).
2. G.F. Zou, H.M. Luo, S. Baily, Y.Y. Zhang, N.F. Haberkorn, J. Xiong, E. Bauer, T.M. McCleskey, A K. Burrell, L. Civale, Y.T. Zhu, J.L. MacManus-Driscoll, and Q.X. Jia, "Highly aligned carbon nanotube forests cotaed by superconducting NbC" Nat. Commun. 2, 428 (2011).

CINT Contact: Quanxi Jia

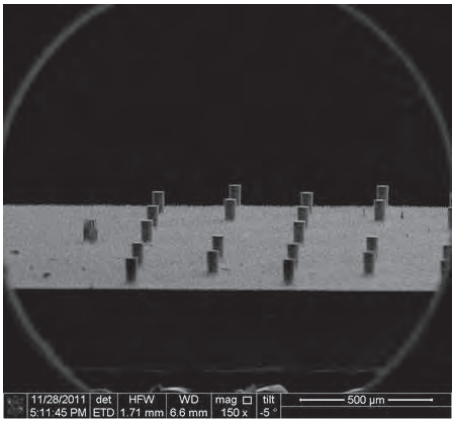
Controlling the interface width in Si/Ge nanowire heterojunctions

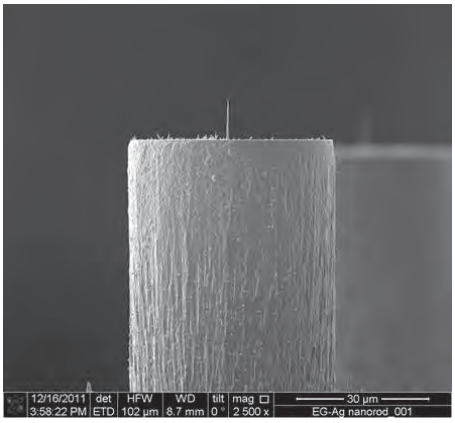
Accomplishment: High quality semiconductor nanowire growth requires the use of a liquid catalyst in a process called vapor-liquid-solid (VLS) growth. One limitation of the VLS growth approach has been an inability to create sharp nanowire interfaces. The reason for the lack of interface abruptness is that a substantial amount of growth solute atoms are dissolve into the liquid Au catalyst which is typically used. Thus when changing growth species, for example from Ge to Si, there is a long transition region as Ge atoms are slowly depleted from the liquid by growth and replaced by Si atoms. The present work reports for the first time the systematic increase in heterointerface sharpness by using an alloy catalyst. We demonstrate this result for Si/Ge axial nanowires where the composition of a AuGa alloy catalyst is varied in situ using the precursor trimethylgallium. The key concept is that for VLS nanowire growth the transition region width is dictated by the rate of solute depletion from the catalyst, which in turn is proportional to the solute solubility within the catalyst. Our approach to controlling the Au(1-x)Ga(x) catalyst alloy composition in situ provides a means to adjust the semiconductor solubility within the catalyst alloy and thus tune the heterojunction width. Specifically, we show a 4-times decrease in the heterointerface width for 60 nm diameter Ge-Si nanowires grown from pure Au (44 nm width) compared to interfaces grown from a Au(0.66)Ga(0.34) catalyst alloy (11 nm width). We also developed a growth model which accurately simulates heterointerface widths as a function of solute solubility in alloy catalysts.

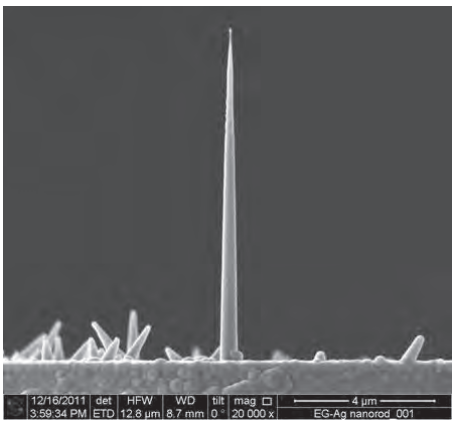


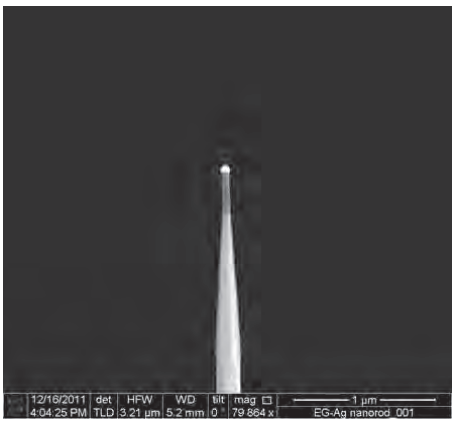
Abrupt interfaces by AuGa catalyst alloying.

Significance: The importance of the control of interface sharpness lies in the ability to precisely tune the electronic transport properties by modulating the composition and/or dopant type to create novel high-performance devices. Compared to compositionally uniform nanowires, axial heterostructured and modulation doped semiconductor nanowires have a much wider relevance for electronic, photovoltaic, and thermoelectric device applications. For high subthreshold slope nanowire devices such as tunnel and avalanche field effect transistors, the performance is directly related to the junction abruptness. However, for group IV nanowires grown by the Au-catalyzed VLS mechanism, junction abruptness is limited in magnitude to the order of the nanowire diameter as described above. Thus, establishing a method to create more abrupt axial heterojunctions, while maintaining VLS growth, is important to further exploit the inherent benefits of nanowires. Currently we are extending this concept to increase the sharpness of axial dopant profiles in Si, Ge, Si/Ge p-n junction nanowires using atom tomography dopant profiling.









A series of images showing a single nanowire grown out of a micropost. Images from CINT User Danny Perea.

Reference:
Controlling Heterojunction Abruptness in VLS-Grown Semiconductor Nanowires via in situ Catalyst Alloying, Daniel Perea, Nan Li, Robert M. Dickerson, A. Misra, and S. Tom Picraux, Nano Lett. 11, 3117 (2011).

CINT Contact:Tom Picraux

Voltage increases up to 25% observed in closely packed nanowires

Unexpected voltage increases of up to 25 percent in two barely separated nanowires have been observed at the Center for Integrated Nanotechnologies. Designers of next-generation devices using nanowires to deliver electric currents — including telephones, handheld computers, batteries and certain solar arrays — may need to make allowances for such surprise boosts.

"People have been working on nanowires for 20 years," says CINT researcher Mike Lilly. "At first, you study such wires individually or all together, but eventually you want a systematic way of studying the integration of nanowires into nanocircuitry. That's what's happening now. It's important to know how nanowires interact with each other rather than with regular wires."

Though the gallium-arsenide nanowire structures used by Lilly's team are fragile, nanowires in general have very practical characteristics — they may crack less than their bigger cousins, they're cheaper to produce and they offer better electronic control. For years, the best available test method required researchers to put a charged piece of material called a gate between two nanowires on a single shelf. The gate, flooded with electrons, acted as a barrier: It maintained the integrity, in effect, of the wires on either side of it by repelling any electrons attempting to escape across it. But the smallest wire separation allowed by the gate was 80 nanometers. Nanowires in future devices will be packed together much more closely, so a much smaller gap was necessary for testing.

The current test design has the brilliance of simplicity. What Lilly and co-workers at McGill University in Montreal envisioned was to put the nanowires one above the other, rather than side by side, by separating them with a few atomic layers of extremely pure, home-grown crystal. This allowed them to test nanowires separated vertically by only 15 nanometers — about the distance next-generation devices are expected to require. And because each wire sits on its own independent platform, each can be independently fed and controlled by electrical inputs varied by the researchers.

While applications for technical devices interest Lilly, it's the characteristics of nanowires as a problem in one-dimensional (1-D) basic science that fascinates him. A 1-D wire is not your common, thick-waisted, 3-D household wire, which allows current to move horizontally, vertically, and forward; nor is it your smaller, flattened micron-sized 2-D wires in typical electronic devices that allow electrons to move forward and across but not up and down. In 1-D wires, the electrons can only move in one direction: forward, like prisoners coming to lunch, one behind the other. "In the long run, our test device will allow us to probe how 1-D conductors are different from 2-D and 3-D conductors," Lilly said. "They are expected to be very different, but there are relatively few experimental techniques that have been used to study the 1-D ground state."

One reason for the difference is the Coulomb force, responsible for what is termed the Coulomb "drag" effect, regardless of whether the force hastens or retards currents. Operating between wires, the force is inversely proportional to the square of the distance; that is, in ordinary microelectronics, the force is practically unnoticeable, but at nanodistances, the force is large enough that electrons in one wire can "feel" the individual electrons moving in another placed nearby.

Mike Lilly holding up the nanocircuitry test device.

The drag means that the first wire needs more energy because the Coulomb force creates, in effect, increased resistance. "The amount is very small," said Lilly, "and we can't measure it. What we can measure is the voltage of the other wire." There are no straightforward answers as to why the Coulomb force creates negative or positive drag, but it does.

What's known is that "enough electrons get knocked along that they provide positive source at one wire end, negative at the other," Lilly said. A voltage builds up in the opposite direction to keep electrons in place," thus increasing drag. The so-called Fermi sea — a 3-D concept used to predict the average energy of electrons in metal — should totally break down in 1-D wires, which instead should form a Luttinger liquid, Lilly said. A Luttinger liquid is a theoretical model that describes the interactions of electrons in a 1-D conductor. To better understand the Luttinger liquid is Lilly's underlying motive for the experiment. (Enrico Fermi was a leading theoretical physicist of the 20th century who played an important role in the development of the atomic bomb. Joaquin Luttinger was a 20th century physicist known for his theories of how electrons interact in one-dimensional metals.)

Having an interest on many levels proved useful because making the test device "took us a very long time," he said. "It's not impossible to do in other labs, but CINT has crystal-growing capabilities, a microfabrication facility and support for fundamental research from the Department of Energy's Office of Basic Energy Sciences (BES). The BES core program is interested in new science and new discoveries, like the work we're doing in trying to understand what is going on when you're working with very small systems."

Device fabrication was conducted under a user project at the Center for Integrated Nanotechnologies, a DOE Office of Science national user facility jointly run by Sandia and Los Alamos national laboratories. The device design and measurement were completed under the DOE Office of Science BES/Division of Materials Science and Engineering research program.

The work required the crystal-growing expertise of CINT researcher John Reno, the fabrication and measurement skills of McGill doctoral student Dominique Laroche and elements of previous work by Sandia researcher Jerry Simmons.

- Neal Singer, as a SNL press release

Soft, Biological and Composite Nanomaterials Thrust

Stephen Doorn, Acting Thrust Leader; George Bachand, Partner Science Leader

The Soft, Biological and Composite Nanomaterials Thrust focuses on solution-based nanomaterials, and targets improved understanding of how to integrate disparate classes of materials to produce functional results. Inspiration is drawn from a long-term grand challenge in nanoscale materials research, which is to be able to mimic the exquisite structures and functions that Nature produces through the synthesis, assembly, reconfiguration and exploitation of disparate components. Activities of the Thrust are directed toward key scientific areas: (1) Controlling interfaces and interactions between disparate classes of materials across multiple length scales; (2) Developing and applying new characterization tools for studying soft, biological and composite systems on multiple length and time scales; and (3) Exploring the roles of disorder and dynamics in controlling the performance of functional soft, biological and composite materials. Within this framework, topics include synthesis of multi-component nanoscale building blocks, assembly of components using both active and passive assembly methods, development of instrumentation for characterization of complex, disordered and dynamic composite materials, the study of dynamic and reconfigurable surfaces and interfaces, the incorporation of soft or biological materials into micro-scale device architectures, and the development of membrane-based composite materials.

Recent Accomplishments

In the past year, significant advances have been made in each of our three science themes through both internal CINT science and collaborative projects with CINT Users. (1) Controlling interfaces and interactions. Highlights in this area include several aspects of metal nanostructure development including novel magnetic nanoparticles, which a CINT user has applied to breast cancer detection and shown an order of magnitude sensitivity enhancement over current approaches. Our gold and silver nanoparticle development has incorporated bio-inspired evolutionary approaches to create novel structures and fluorescent clusters with extended spectral responses and improved solution, photophysical and biological stability. New interfacial chemistry has been developed to direct the formation of neuronal networks on silicon surfaces, as well as for attaching hybrid nanostructures to molecular shuttles to drive directed assembly of user-developed fluorescent/ magnetic nanoparticle hybrids into ordered structures. As part of our goals for developing new polymer-based membrane architectures, we have also demonstrated the ability to generate biomimetic monolayer and bilayer membranes from amphiphilic block co-polymer micelles. (2) Development and Application of New characterization tools. We have used fluorescence microscopy imaging and electrophysiology measurements to probe neuronal activity in surface-assembled networks. We have also developed time-resolved super resolution approaches to single-molecule imaging, which a CINT user has applied to understanding cellulose activity on crystalline cellulose fibers. Use of nanoparticle optical probes is also being demonstrated by CINT-developed 3D tracking of quantum dot labeled proteins inside of cells. Fluorescence correlation spectroscopy of DNA-templated silver nanoclusters enabled the determination of cluster radii, brightness and blinking dynamics. Pairing of our unique characterization tools and synthetic capabilities earned CINT researchers an R&D 100 award for "NanoCluster Beacons: Shedding Light on Specific Nucleic-Acid Targets." (3) Disorder and dynamics in controlling integrated materials functionality. A key objective has been demonstrating an ability to control synthetic membrane response to environmental conditions including changes in pH and through interactions with nanoparticles and substrate functionality. In particular, we have demonstrated how the structure of nanoporous metals can be used to impact the dynamic response of supported lipid membranes, and have shown how variation of synthesis parameters define the fluid behavior of phospholipid-silica thin film composites and result in robust application platforms. Potential for controlling the aggregation and morphology of constituent polymers has been demonstrated in our first ever mapping and successful modeling of the nanoscale phase behavior of a mixed polymer brush system. The responsiveness of our membrane systems enabled us to also control their use for nanoparticle organization. Two recent examples include ZrCl4 driven organization of gold nanoparticles in supported lipid bilayers, and control over the aggregation state of porphyrin assemblies in lipid membranes.

Future Directions

Moving forward we will continue our efforts at enabling the bio-inspired integration science of soft nanomaterial systems. (1) Controlling interfaces and interactions. Research in this area will continue to focus on developing the fundamental building blocks for composite nanoassemblies. Examples include new synthetic approaches to magnetite nanoparticles to improve reproducibility and size control (and will exploit development of the CINT Microfluidics Discovery Platform), and development of libraries of in vivo polymers using biological combinatorics. New strategies for complex materials assembly will be developed, including adding functionality to polymersome assemblies through incorporation of asymmetric biological macromolecules and devising artificial light-harvesting antenna assemblies based on a 3-component energy transfer system. Efforts will also include further engineering of surface patterning for functional neuronal assemblies and developing the capability for active manipulation (e.g., via dielectrophoresis) of biomolecular shuttles for directed nanoparticle assembly. Our nanoparticle self-assembly studies will also be moved into the new area of DNA-mediated assembly and functionality of carbon nanotube ladder structures. (2) New characterization tools. Here our efforts will include the development of magnetic, SERS-based, and new approaches to confocal fluorescence microscopy (including rotating disk methods) for probing protein motor function and functionality of bio-hybrid assemblies. 3D tracking capability will be enhanced by incorporating CINT-developed non-blinking quantum dot probes and adding spinning disk capability to provide contextual information. New capabilities for evaluating spectral and diffusion characteristics of single nanoparticles and enzymes in fluid environments will be also established. Single-molecule imaging of cellulose activity will be extended to evaluate the molecular level mechanisms of cellulose breakdown and synergistic activity between endo-exo and exo-exo cellulases. Powerful advanced fluores-

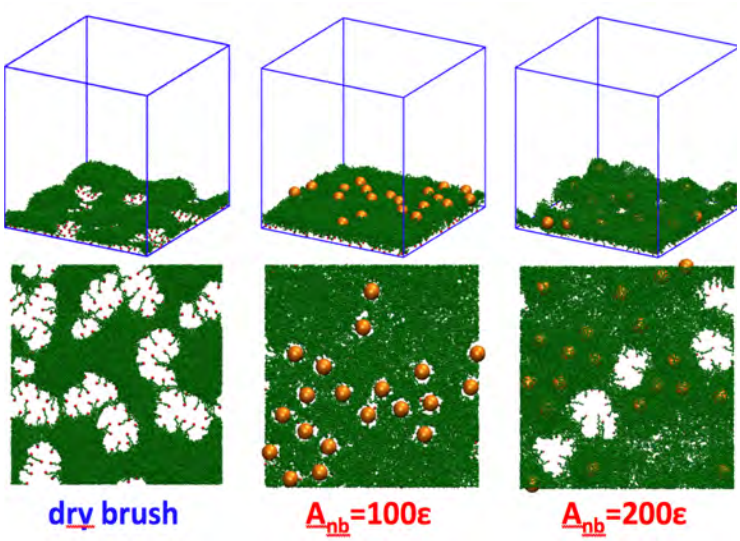
cence correlation methods will also be incorporated into our single-element capabilities, including scanning volume and pulsed interleaved excitation FCS to enable detailed size and shape analysis of our silver nanoclusters. (3) Disorder and dynamics in controlling integrated materials functionality. In this area, we will continue to exploit our new capabilities for creating polymersome and polymer brush assemblies by probing novel substrate interactions, including behaviors at non-planar and graphene substrates. Additionally, environmentally responsive polymer membranes will be generated through chemical functionalization strategies and design of interactions at nanoporous substrates. Pursuit of complex functionality will also include study of light-harvesting and biogenesis in model photosynthetic bacterium.

CINT postdoc, Jeff Crisp working at a hood.

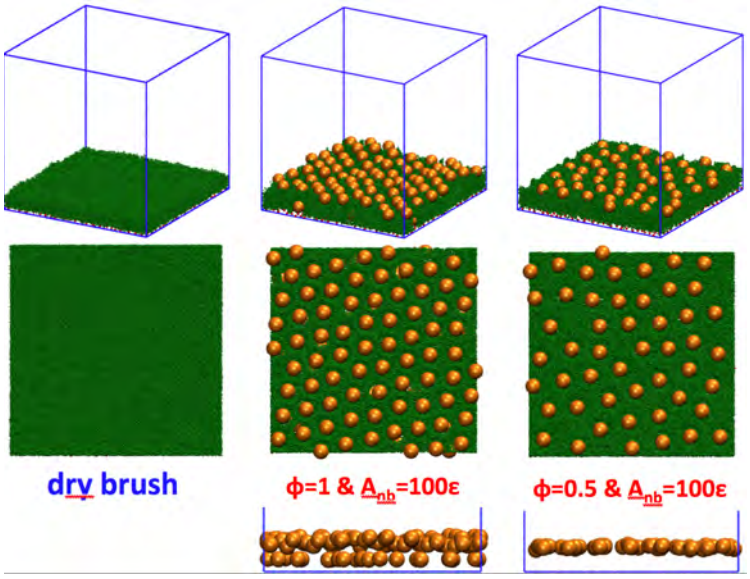
Nanocomposite encapsulation of biological samples for long-term storage and transport

A research team led by CINT investigators is developing methods for encapsulating biological samples for long-term storage and transport using inexpensive nanocomposite materials that can be kept at room temperature in an effort funded by the National Institutes of Health. This research stems as a result of a CINT user project, work done as part of a CINT Integration Focus Area (IFA) in Membrane Nanocomposites; and long-standing CINT expertise. This is a unique effort with members of CINT-LANL, CINT-SNL and CINT users participating in an externally funded activity

The original CINT user project was an effort pioneered by CINT users, Dr. Gabriel P Lopez (UNM, Duke) and Dr. Gautam Gupta (former UNM graduate student, current LANL TSM) and CINT scientists, Dr. Gabriel A. Montaño and former CINT scientist, Dr. Andrew P. Shreve (current UNM professor), aimed at developing biocompatible methods for silicate encapsulation of supramolecular assemblies. The research developed in this effort set the groundwork for developing the long-term storage methods that are being further developed in the current NIH effort. Simultaneously, research in the CINT IFA began looking at responsive polymer-based composite nanomaterials, based heavily upon a long-history of research by Dr. Dale Huber (CINT-SNL) and recent efforts by the Montaño lab in biomimetic polymer membrane design. The responsive polymers are being investigated as a means to create a "pseudo cell-wall" around the biological material of interest prior to silicate processing. This is thought by the team to be a key and necessary development in making silicate encapsulation strategies suitable for a wide-range of typically labile, biological materials of interest.



Solvent Evaporation: Low brush density and low NP density (Φ =0.2). Partially adsorbed nanoparticles make the brush more uniform.



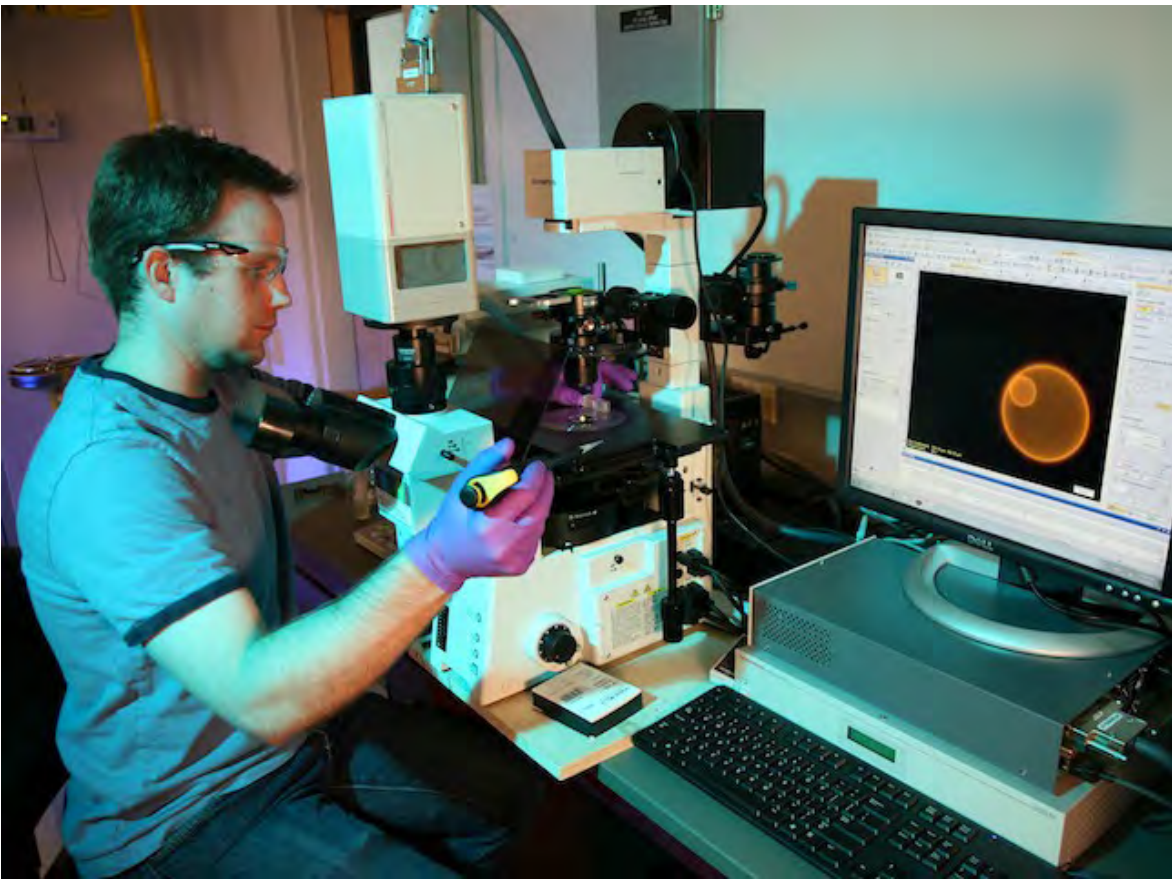
Solvent Evaporation: High brush density and high/medium NP density

The research team is currently pursuing development of a combination of polymer/silicate hybrid chemistries to create nanocomposite encapsulation materials capable of capture/release and long-term storage of samples of interest to the NIH National Children's Study (NCS). It is the goal of the CINT-led research team to develop inexpensive methods for storage of NCS samples thereby eliminating millions of dollars in cost using current state-of-the-art storage methods. Technologies developed in this project have a wide-range of potential beyond the currently funded effort and it is the hope of the CINT team to develop new research areas based upon this technology, in energy and security technologies in particular.

Participating Team Members: Gabriel A Montano (PI), Gautam Gupta, Andrew M. Dattelbaum (LANL); George D. Bachand (co-PI), Dale L. Huber, Edward Moczydlowski (SNL); Gabriel P. Lopez (co-PI), Andrew P. Shreve (UNM)

CINT Contacts: Gabe Montano and George Bachand

Wally Paxton - CINT Scientist highlight



Ever since his discovery of the first autonomous non-biological nanomotor in graduate school, Wally Paxton's science has been in motion.

Not only has Paxton's research been focused on motion—in particular, the motion of molecular and nanoscale machines—but his research has moved and evolved throughout his academic and technical experience.

Paxton is the newest staff member at CINT, based at the Core facility in the Soft Biological and Composite Nanomaterials Thrust. He was at Penn State working on his doctorate in chemistry eight years ago when his work on the first-ever demonstration of moving catalytic nanoparticles helped him embark on his career in nanotechnology. The demonstration hinged on understanding how to get mechanical motion out of chemical energy on a very small scale.

"This was pretty revolutionary, I think, because it had been proposed that you could move small objects by this mechanism—which we eventually figured out—but nobody actually demonstrated it," Paxton said. "This was the first demonstration of self-electrophoretic motion."

The paper he published with colleagues on the subject in 2004 has since been cited more than 200 times. The work impelled him into research on this energy transduction mechanism for autonomous motion.

In the meantime, he worked as a postdoctoral researcher at Pacific Northwest National Laboratory, but it was his next position at Northwestern University under Professor Fraser Stoddart that advanced his interests and his research.

"I was looking at ways to connect molecular machines to surfaces, and Stoddart is really well known for making molecular machines, molecules that will do certain things with certain stimuli" in order to get a mechanical actuation of the molecule, Paxton said. Drawing on his knowledge of Click chemistry, he delved into strategies of attaching molecules to an interface or surface. At Northwestern, he developed a scanning probe lithographic method of modifying organic monolayers.

Coming to CINT helped Paxton advance his interests even further, by researching the use of soft materials as a matrix for integrating molecular machines at the nanoscale.

"Wally was a wonderful find for us as a organization. I think he fits very well with our mission at CINT in developing new types of materials and assemblies at the nanoscale," said Gabe Montano, who manages the Programmable Membrane-based Nanocomposites Integration Focus Area at CINT's Core facility.

"He's interested in a lot of asymmetrical assemblies that mimic biological processes. And we use a lot of chemistry approaches to mimic these systems," Montano said. "His fabulous training and research background overlaps nicely with our membrane integration focus area."

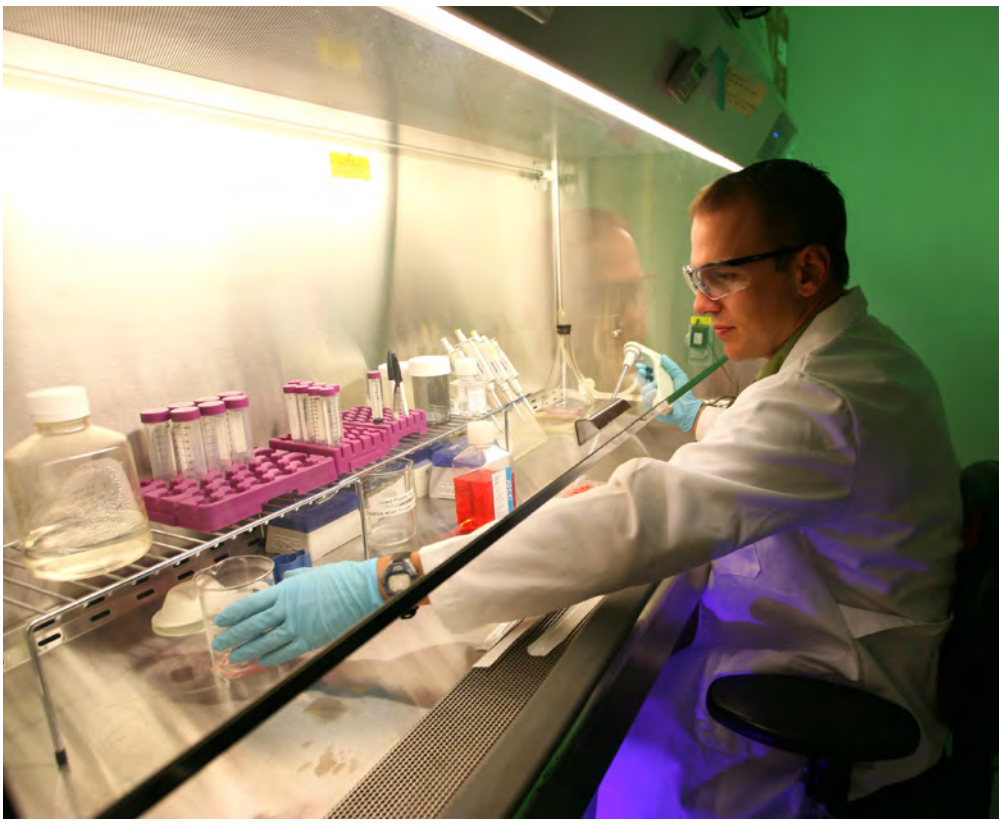
At CINT, Paxton is specializing in surface modification and characterization, with an eye toward creating self-assembled structures from soft materials. In his current research, he is looking at the integration of natural and synthetic functional molecules into biomimetic materials.

The collaborative environment at the facility has allowed him to collaborate with former colleagues and brought his research almost full circle—yet progressing to a smaller, more advanced nanoscale.

"I'm taking the same principles [of converting chemical energy to mechanical energy] on micron-sized structures and demonstrating that it still holds true on these much smaller scales," he said.

–Caroline Spaeth, LANL staff writer

Directing cellular morphogenesis and polarization using nanoscale chemical and topological cues



Scientific Accomplishments: The ability to grow a wide range of eukaryotic cells ex vivo is well-established and has spurred considerable interest in reconstructing artificial tissues and organs in a "cell-by-cell" manner. While successful constructs such as the artificial urinary bladder have been realized, development of more complex tissues and organs is limited by the inability to regulate and mediate interactions between different cells types. For example, reconstruction of neural tissue to treat traumatic brain injuries has been limited by the inability to controllably direct synaptic formation among individual neurons. Engineering two-dimensional neural networks using micro- and nano-fabrication techniques has been pursued for a number of years. Networks with pre-defined functionality, however, have remained elusive based on difficulties associated with organizing individual cell morphology and directing synaptic connections between neurons.

Our idea was to develop a dual guidance cue strategy to direct the in vitro morphogenetic maturity and synaptic formation among neurons using a combination of chemical and topo-graphical interfaces on engineered substrates. In collaboration with CINT User Conrad James at Sandia National Laboratories, a multi-step fabrication scheme was developed to produce chemically bifunctional and topographically defined surfaces for the organization of in vitro neuronal networks. We hypothesized that the different chemical functionalities (i.e., hydrophobic vs. cationic/hydrophilic) would direct cell adhesion and neural process development, while the topographic features would direct polarization and process morphogenesis.

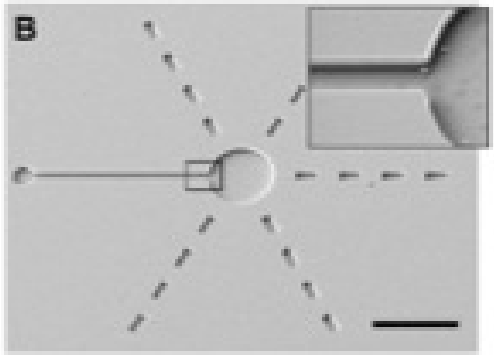
Dissociated hippocampal pyramidal neurons grown on fabricated substrates experienced directed cytoarchitectural polarization. Charged, hydrophilic surfaces directed adhesion of cell bodies and outgrowth of neural processes, whereas hydrophobic surfaces resisted cell attachment. Moreover, neural processes formed quickly on continuous lines and were delayed on interrupted lines. Outgrowth of this first process on the continuous lines leads to polarization of the cell and maturation of the process into an axon, whereas the delayed processes mature into dendrites.

Significance: Our work provides a proof-of principle that nanoscale patterning of chemical and topographic cues can control the morphogenesis and polarization on ex vivo cells cultured on artificial substrates. In particular, the ability to regulate cell physiology and maturity using chemically bifunctional nano-interfaces provides a novel path for developing more complex, artificial tissues and organs. A key challenge moving forward involves the application of our dual guidance cue strategy to three-dimensional architectures that will more closely mimic those found in living organisms.

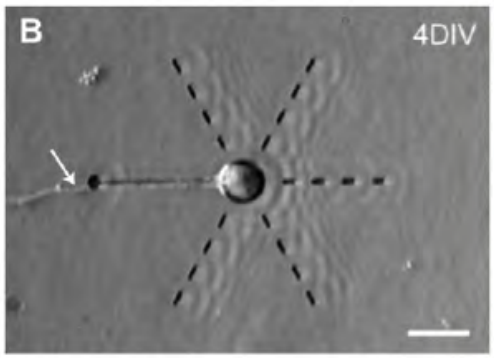
Reference:

"Combined chemical and topographical guidance cues for directing cytoarchitectural polarization in primary neurons", Greene, A.C., Washburn, C.M., Bachand, G.D., and C.D. James. Biomaterials 2011, 32, 8860-8869.

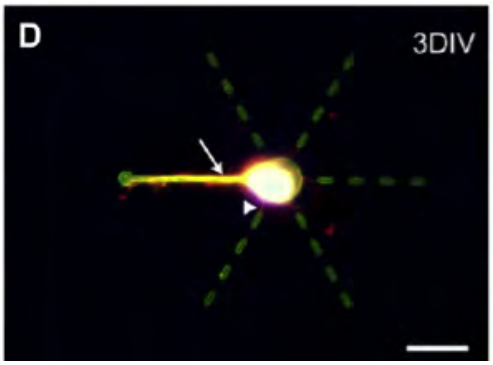
CINT Contact: George Bachand



Scanning electron micrograph of a test surface.



Phase contrast micrograph showing adhesion of a hippocampal neuron to the centralnode and outgrowth of a neural process.



Epifluorescence micrograph showing outgrowth of the first neural process following a continuous line topographically defined on the surface.

Theory and Simulation of Nanoscale Phenomena Thrust

Normand Modine, Thrust Leader: Alexander Balatsky, Partner Science Leader

The Theory and Simulation of Nanoscale Phenomena Thrust focuses on identifying the fundamental concepts that control the unique behavior of integrated materials and systems with nanoscale structure. As the relative strengths of various interactions change with length scale, competition between interactions can lead to spontaneous self-organization at characteristic length scales. In integrated nanosystems, these intrinsic length scales can couple to naturally occurring or artificially imposed nanoscale inhomogeneity leading to the coexistence of different types of ordering and/or emergent phenomena. The various components of an integrated nanosystem each have their own intrinsic properties. This provides freedom to control and optimize system behavior. Conversely, successful nanoscale integration requires control over the interactions between components, which must be weak enough to maintain the unique properties of the nanoscale components, but strong enough that the components interact in order to achieve new properties and functionality. Improved understanding of how the interactions in nanosystems can be controlled through integration and how novel behavior emerges as a result of integration will help optimize particular functionality and even achieve multifunctional and/or responsive materials and systems. Therefore, this thrust aims to understand the role of novel and competing interactions in nanoscale integration. This effort is organized into three science directions that together form the basis for integration at the nanoscale: (i) Nanoparticles in Complex Environments, (ii) Excitation and Transport in Nanostructured Systems, and (iii) Nanodomain/Nanostructure Interactions.

Recent Accomplishments

Work in the past year in collaboration with our user community has lead to new computational capabilities as well as significant progress in each of our three science directions. New tools include a novel Non-Adiabatic Excited State Molecular Dynamics (NA-ESMD) framework for modeling excited state dynamics and radiationless relaxation in large molecular systems and the extention of the Exciton Scattering Model for modeling electron-phonon coupling processes in organic materials. In addition, we continued to develop methods based on the time-dependent density functional theory to determine the fundamental properties controlling electronic heat transport at the nanoscale. We applied the CINT Visualization system to improve our understanding of nanoplasmons in graphene and the three dimensional structure of Fermi surfaces. In studies focused on nanoparticles in complex environments, a significant portion of our effort investigated the effects of environment on the interaction between particles. We used modeling based on classical fluid theory to calculate interaction energies between polymer-coated nanorods in a polymer matrix and demonstrate good qualitative agreement with experiments. Likewise, applying molecular dynamics simulations, we reproduced the measured force-extension data of single molecule single-strand DNA, including the scaling as a function of salt concentration and the unexplained logarithmic scaling at high forces. We also compared the shearing interactions between polymer-grafted surfaces for the cases of polyelectrolyte and neutral polymer coatings. We investigated the effect of environment on the assembly of particles by modeling 2nm alkanethiol coated nanoparticles at the water/vapor interface. In initial steps toward understanding how particle interactions might produce new properties in integrated systems, we applied molecular dynamics simulations to probe the molecular conformation of conjugated polymers confined to optically active nanoparticles and to determine the mechanical strength of self-healing and welded polymer films as a function of the degree of interdiffusion across the interface. In the area of excitation and transport in nanostructured systems, highlights include the development of a theory of electronic tunneling through DNA bases on graphene and the calculation of the essentially exact nonequilibrium fully quantum dynamics of an electron-phonon coupled nanowire (Holstein polaron) driven by a strong external electric field. The NA-ESND package discussed above was applied to model photoinduced conformational dynamics in conjugated polyfluorenes and energy transfer in light-harvesting dendrimers. Nanodomain/nanostructure interactions were investigated for both soft and hard systems. Self-consistent field theory calculations of the phase behavior of mixed polymer brushes, both in bulk and confined geometries, demonstrated that confinement can lead to long-range order in the nanoscale phase separation. The sequence of phases obtained as a function of the polymer volume fraction agreed with experiment. For semiconductor surfaces, we applied tools previously developed at CINT to simulate the coexistence of reconstructions on InGaAs and GaAsBi alloys at finite temperature including a previously unexplained triple period phase experimentally observed on GaAs. We explained the onset of superconducting order at oxide interfaces as a result of charge transfer, and for epitaxial multiferroic TbMnO3 films, we simulated the coupled magnetic phases and modeled ultrafast optical pump-probe spectroscopy experiments.

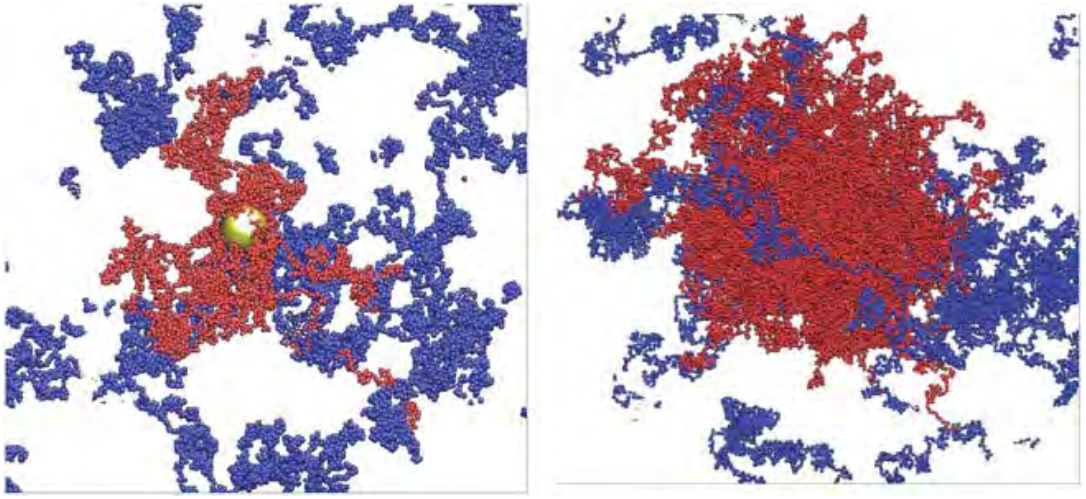


Image from CINT User Project publication in Soft Matter 7 (2011) 1418-1425: Snapshot of a nanoparticle of radius R =4σ for (a) Σ = 0.04 and (b) Σ = 0.32 chains/σ². Most of the melt chains (blue) have been removed to visualize the grafted chains (red). CINT Contact Gary Grest.

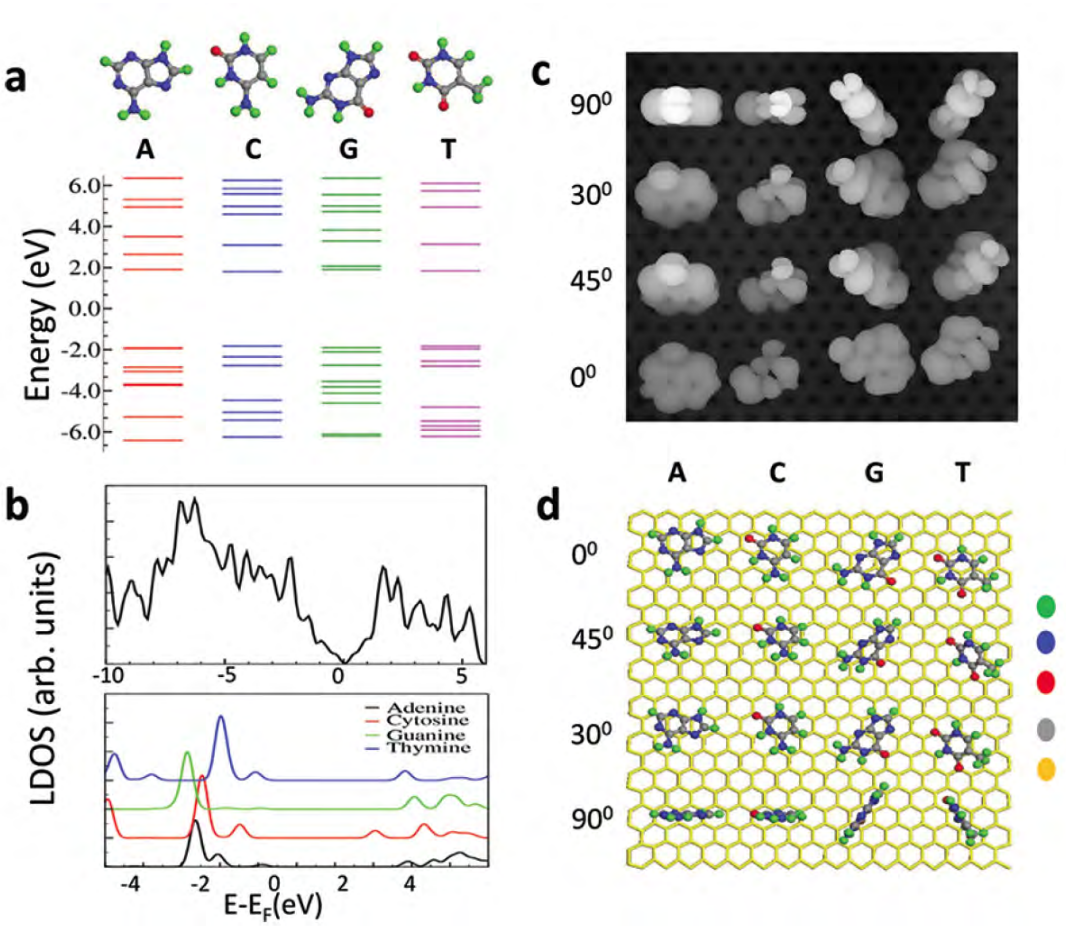
Future Directions

In the coming year our efforts to understand nanoparticles in complex environments will include extending calculations of the forces between polymer-coated nanorods to systems in which the polymer brush coating is different than the homopolymer matrix as well as investigating the interactions of polymer brushes with nanoparticles. This work will align with the Programmable Membrane Based Nanocomposites IFA. We will also examine longer chains of single strand DNA an attempt to reach the neutral scaling regime. In order to further investigate the assembly of particles, we will simulate the structure and mechanical properties of dodecanethiol coated Au nanoparticle at the water/vapor interface. We will extend studies of conjugated polymers confined to optically active nanoparticles to ionizable carboxylate and amine terminated side chains with varying degrees of ionization, and we will model the effect of nanoparticles on the mechanical strength of immiscible polymer films. In addition, we will perform atomistic molecular dynamics simulations of a set of poly(ethylene-co-acrylic acid) ionomers neutralized with various cations to better understand nanoscale aggregation in these systems and its effect on ion dynamics. In the theme of excitation and transport, we will develop theory for a variety of integrated nanosystems involving graphene including inelastic tunneling into graphene with and without adsorbed nanostructures, novel electronic states in quantum corrals on graphene, and the local electronic signatures of a DNA base in a graphene nanopore. We will extend the NA-ESMD package to be able to model excited state dynamics within a Quantum Mechanics/Molecular Mechanics (QM/MM) hybrid framework, and we will apply the NA-ESMD package to model excited state dynamics in semiconductor quantum dots. We will also apply the Exciton Scattering Model to model energy transport and electron transfer in organic molecular networks and apply previously developed TDDFT tools to model the nonlinear optical response in semiconductor quantum dots. We will also model nonlinear ultrafast optical pump-probe response of correlated systems from first principles using model Hamiltonians. Within the nanodomain/nanostructure interactions science direction, we will add strain interactions to our models of semiconductor surface reconstruction and further develop our models of phase coexistence and competing orders at interfaces. We will also develop the capability of modeling ultrafast optical and terahertz spectroscopic probes of heterostructures, including YBCO superconductors on ferromagnetic LSMO colossal magnetoresistance films.

Postdoc Jason Haraldsen demonstrates the 3-D visualization capability at CINT

Electronic Fingerprints of DNA Bases on Graphene

Accomplishment: In this letter, the use of graphene is proposed as a deposition substrate for macromolecular sequencing. Both the Dirac linear dispersion of electronic states in graphene and its robust mechanical properties serve to make it a superior substrate compared to metals. The authors have calculated the tunneling conductance and local density of states (LDOS) for the specific case of single DNA bases at various orientations on the surface and have shown that the different nucleotides have significantly different LDOS peaks (fingerprints), allowing differentiation via local tunneling conductance. The calculated nitrogen atom LDOS for A, T, C, and G bases show distinct peaks that vary depending on configuration. However, a planar orientation of DNA bases with respect to the graphene surface is the most stable, since it favors π−π stacking between the base and aromatic carbons in graphene. It is found that guanine provides the largest peak at a negative bias at −1.3 eV. Peaks for the other bases at higher energies have features at positive and negative scanning tunneling microscopy (STM) bias and provide fingerprints that allow unique identification. The calculated LDOS fingerprints can help guide scanning tunneling spectroscopy (STS) as an approach to identify DNA bases, and likely other biomolecules on graphene surfaces.



(a) Molecular energy levels of each isolated DNA base molecule. (b) Upper panel shows LDOS of carbon atom in pure graphene and lower panel shows nitrogen peak LDOS in isolated DNA bases. (c) Integrated (−3.0 eV to EF = 0) partial charge density of DNA bases on graphene plane. Base types are organized in columns and angles between base-ring and graphene plane are varied along rows as indicated. This simulation of STM topography is done using HIVE-STM code. (d) Molecular orientations of DNA bases corresponding to the images in panel c are displayed.

Challenge: The ability to sequence DNA quickly and affordably is one of the great challenges in this era. The determination of the precise sequence of the four nucleotides [adenine (A), cytosine (C), guanine (G), and thymine (T)] in DNA molecules is an important goal for both fundamental research interests as well as large number of applications in biomedical research, biotechnology, drug delivery, and biomaterial growth.

Significance: This work develops a detailed understanding of the interactions and adsorption between graphene and biomolecules using an approach goes beyond the structural analysis of such hybrid systems. In this letter, the possibilities of using STM and STS for the determination and sequencing of DNA on substrate helps provide an opportunity for electronic identifications of all bases via the tunneling conductance from a local probe.

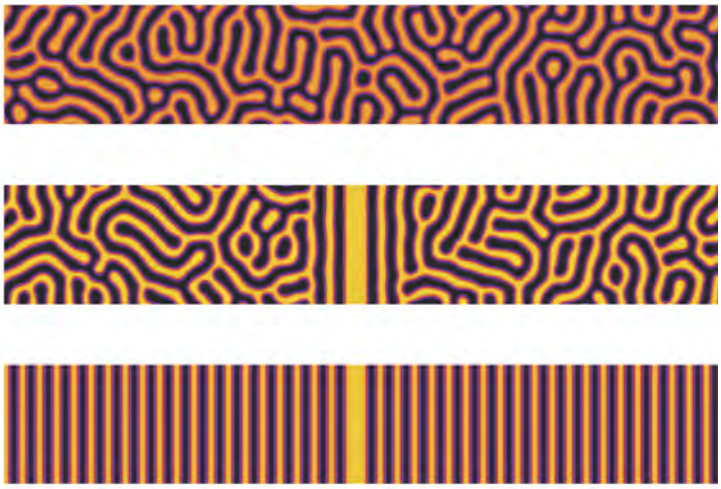
Reference:
T. Ahmed, S. Kilina, T. Das, J. T. Haraldsen, J. J. Rehr, and A. V. Balatsky, "Electronic Fingerprints of DNA Bases on Graphene," NanoLetters 12, 927 (2012).

CINT Contact: Sasha Balatsky

Potential New Nanolithography Tool from Directed Assembly of Mixed Polymer Brushes

Scientific Accomplishments: Top-down lithography is a well-established industrial technology that allows for the patterning of geometrical designs with nanometer-level precision and accuracy. Though conventional lithography has achieved the continual shrinkage of surface features, it is widely believed that fundamental limitations will soon be reached. These limitations could be overcome by combining molecular self-assembly with lithographic techniques in a process known as templated self-assembly. Most work in this area to date has focused on the use of self-assembling block copolymers. An alternative polymer system is a mixture of two different homopolymers that are covalently bonded to a substrate to produce a polymer "brush". The two different polymers will prefer to phase separate from each other, but because of their covalent bond to the substrate, only micro-phase separation is possible, resulting in nanoscale self-assembled patterns. Mixed brushes have various advantages over diblock copolymers; in particular they could be grown on three-dimensional substrates and on a wider variety of substrates.

Our idea was to use boundary interactions to orient these nanoscale assemblies into long range ordered patterns. Through a two-step polymerization scheme, micron-scale mixed polymer brush regions bordered by a region of pure polymer could be produced. We anticipate that the interaction with the pure polymer would direct the phase separation parallel to this interface by drawing the compatible polymer chains to the interface, forming the first nanoscale domain in the phase separation pattern.



Top view of the density A polymer in a symmetric mixed polymer brush. Top image: bulk polymer brush; middle image: polymer brush constrained by a pure brush region, that is quenched from high to low temperature quickly; bottom image: a confined polymer brush that has been slowly annealed.

To demonstrate that this ordering mechanism in mixed polymer brushes is possible, we carried out theoretical simulations with CINT Users Su-Mi Hur and Glenn Fredrickson at the University of California, Santa Barbara. We calculated the morphology of a mixed polymer brush consisting of two polymers (A and B) of the same length, both grafted to a hard substrate, using self-consistent field theory. When the brush is not confined laterally, a disordered pattern forms, consisting of regions rich in either polymer A or B. However, when a pure brush region of polymer A is introduced, it templates the assembly of domains of polymer A next to the pure brush region. Slowly annealing the system leads to a regular pattern of nanoscale stripes. The calculations also show that the pattern is robust to perturbations, such as roughness in the pure brush region.

Density of polymer A in a mixed brush near a rough region of pure polymer A (right in both images). Well-ordered stripes persist even with line edge roughness.

Significance: These calculations demonstrate a proof-of principle, that templating a mixed polymer brush can lead to well-ordered domains that display long range order. In principle one could make the patterns in any desirable shape or geometry. The size of the pattern features is determined by the polymer molecular weight, which is tunable by synthesis. In general, the synthesis of mixed polymer brushes is simple and uses inexpensive reagents. Once demonstrated experimentally, this new technique for nanolithography could have profound implications on a number of technologies that utilize high-density patterned surfaces.

Reference:

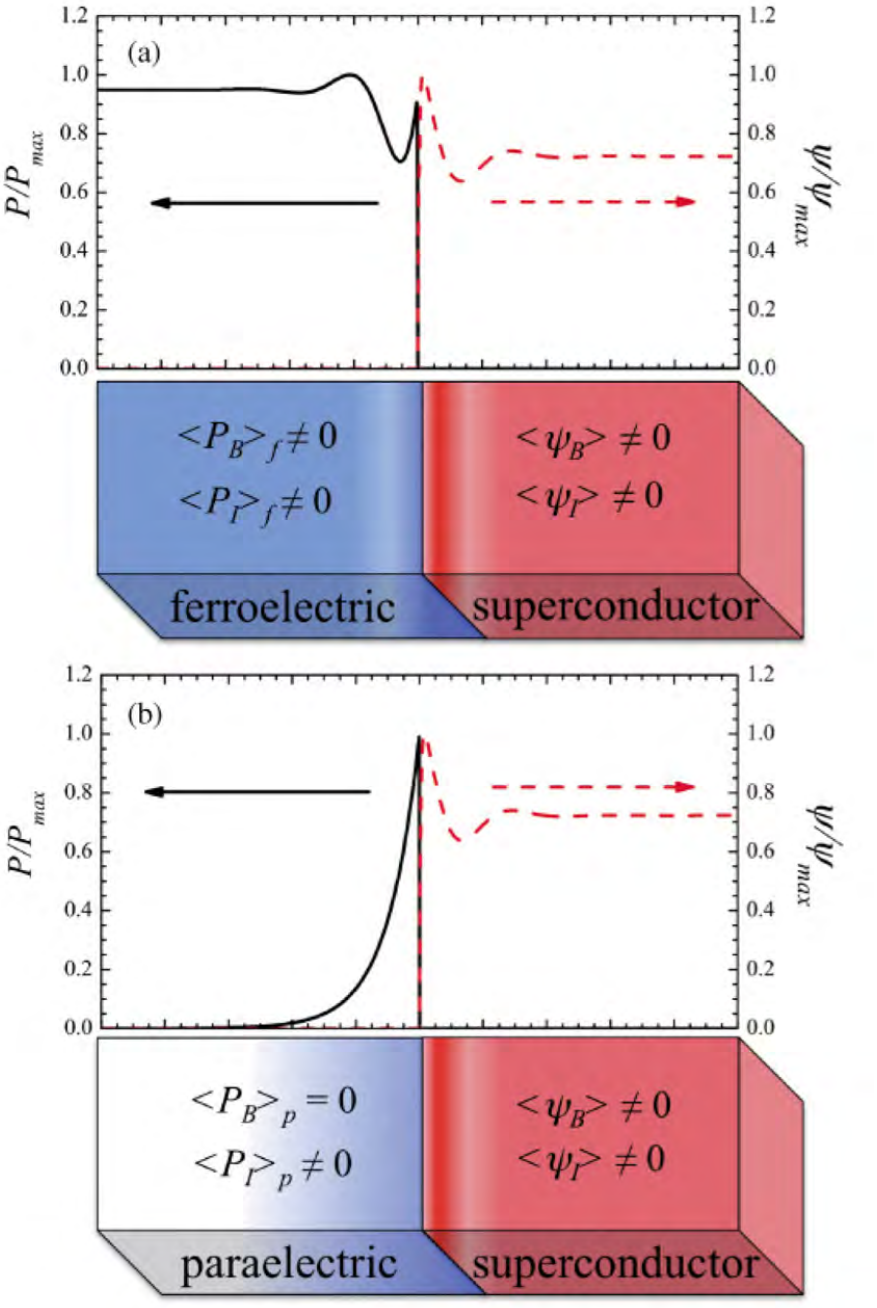
"Self-consistent field simulations of self- and directed-assembly in a mixed polymer brush", S.M. Hur, A. L. Frischknecht, D. L. Huber, and G. H. Fredrickson. Soft Matter 2011, 7, 8776-8788.

CINT Contacts: Amalie Frischknecht and Dale Huber.

Induced polarization at a paraelectric/ superconducting interface

Accomplishment: Through an examination of the modified electronic states at the interface between superconducting and ferro(para)electric heterostructures, it was discovered that electric polarization P and superconducting ψ order parameters can be significantly modified by a coupling that is linear in P, and brought about by explicit symmetry breaking at the interface. Using an effective action and a Ginzburg-Landau formalism, it is predicted that an interaction term linear in the electric polarization will modify the both order parameters at the interface, and will produce a modulation of the ferroelectric polarization and superconducting order parameters. Futhermore, it is shown that a paraelectric/superconductor interaction will produce an interface-induced polarization.

Challenge: The understanding of the electronic states produced at complex oxide interfaces has been a grand challenge since the discovery of that the interaction between LaAlO3 and SrTiO3 produces an interfacial two-dimensional (2D) electron gas that is superconducting at low temperatures. While this occurs at much lower temperatures than high-Tc superconductors, this finding shows the importance of theoretical investigations of the interfacial interactions between the competing states, as well as the induced coupling produced by symmetry breaking, which can provide information that is critical to the understanding of these complex phenomena.



(a) A FE (blue, left) and SC (red, right) interface. Here, we illustrate the modulation of ψz and Pz. (b) The interface of a PE (blue, left) and superconductor (red, right) The plot demonstrates the decaying interface-induced electric polarization, while the SC order parameter has a modulation at the interface.

Significance: Due a linear coupling at the paraelectric/superconducting interface, the prediction of modified electronic states details the importance of symmetry breaking at the interface. This work clearly shows that the interface states can be vastly different than the bulk states, and provides an avenue for future experimental projects on the investigation of these states.

Reference:

J. T. Haraldsen, S. A. Trugman, A. V. Balatsky, "Induced polarization at a paraelectric/ superconducting interface," Phys. Rev. B 84, 020103(R) (2011).

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Awards

Andrew Dattelbaum
- Winner of Postdoctoral Distinguished Mentor Award at LANL - 2012

Steve Doorn
- Winner of the LANL Fellows Prize for Research - 2012

Amalie Frishknecht
- Appointed to Editorial Advisory Board forMacromolecules and ACS Mictoletters - 2012

Gary Grest
- Selected as Editor of Physical Review E - 2011

Quanxi Jia
- Selected as American Physical Society Fellow - 2011
- Winner of Postdoctoral Distinguished Mentor Award at LANL - 2011
- Selected as American Association for the Advancement of Science Fellow - 2012

Nan Li
- Winner of Postdoctoral Distinguished Performance Award at LANL - 2012

Nate Mara
- Winner of the TMS Young Leaders Professional Development Award - 2012

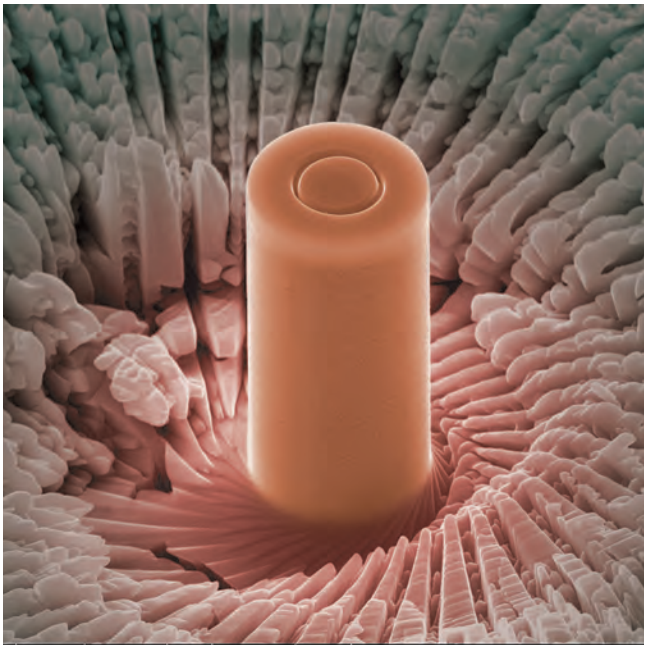
Jennifer Martinez
- Winner of Postdoctoral Distinguished Mentor Award at LANL - 2012

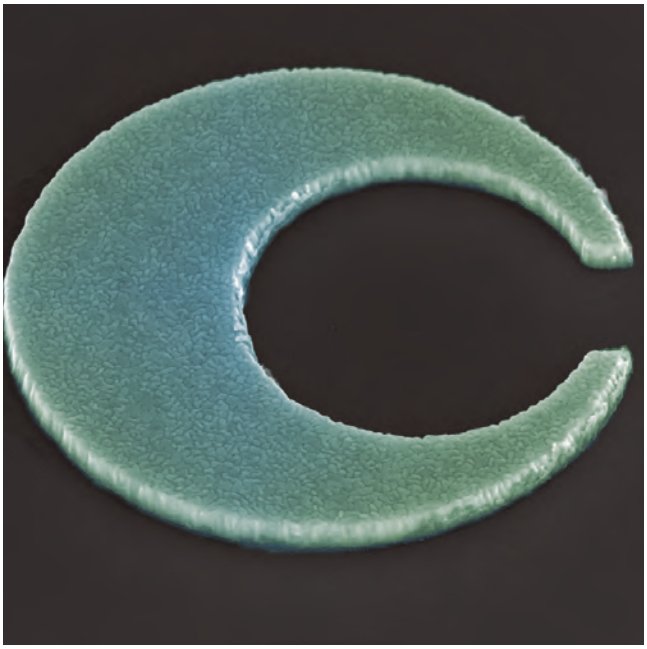
Amit Misra
- Selected as an ASM International Fellow - 2011
- Selected as a Los Alamos National Laboratory Fellow - 2012

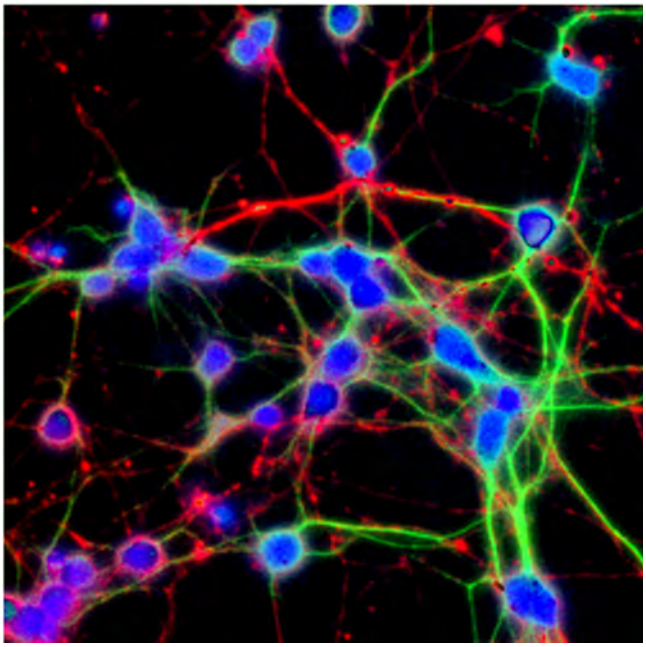
Tom Picraux
- Winner of Postdoctoral Distinguished Mentor Award at LANL - 2012

Neal Shinn
- Trustee of the American Vacuum Society - 2011

Jim Werner
- R&D 100 Award (with Hsin-Chih (Tim) Yeh, Jaswinder Sharma, & Jen Martinez) - 2011
- Distinguished Patent Award at LANL (with Peter Goodwin, & Andy Shreve) - 2011
- Winner of Postdoctoral Distinguished Mentor Award at LANL - 2011







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