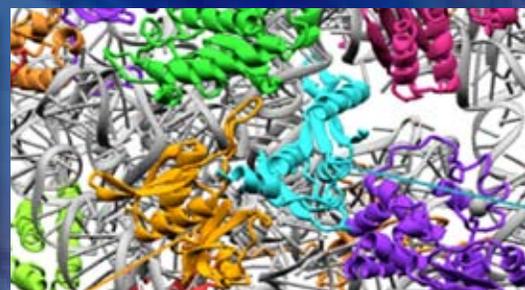


LDRD

2009 Annual Report

Laboratory Directed Research & Development Program Activities



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Acknowledgments

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Introduction

Each year, Brookhaven National Laboratory (BNL) is required to provide a program description and overview of its Laboratory Directed Research and Development Program (LDRD) to the Department of Energy in accordance with DOE Order 413.2B dated April 19, 2006. This report provides a detailed look at the scientific and technical activities for each of the LDRD projects funded by BNL in FY2009, as required. In FY2009, the BNL LDRD Program funded 57 projects, 6 of which were new starts, at a total cost of \$11,671,567. Approximately 25% of the total funds was invested in a focused FY2009 LDRD call for proposals, and the remaining ~75% was awarded to openly competed LDRD projects.

The investments that BNL makes in its LDRD program largely support the Laboratory's strategic goals as outlined in the BNL Laboratory Plan. BNL has five Laboratory Initiatives, Photon Sciences, QCD Matter, Energy, Physics of the Universe, and Bio/Climate and Environmental Sciences. These major initiatives support the growth and evolution of the major business lines (i.e. mission areas) of the Laboratory. In addition, there are three smaller initiatives that support growth and program development in targeted areas, i.e. Biological Imaging, Computation, and Detectors for National Security. Approximately 88% of BNL LDRD funds supported one of the major or targeted initiatives. Of this, about 58% supported the five major initiatives and about 30% supported the smaller initiatives. About 12% was invested in other innovative research and development activities. In total, these LDRD investments supported 105 postdoctoral researchers and graduates students in whole or in part. In FY2009, new LDRD investments (5 of the 6 new projects started) largely supported the BNL initiative in Energy; \$3.465M supported projects started in FY2009, of which \$2.974M funded the focused call for proposals in Energy R&D (see Figure 1, below).

This Project Activities Report represents the future of BNL science; it is an impressive body of exploratory work that investigates many scientific and technical directions in support of the DOE and BNL Missions. We hope that you enjoy it.

FY2009 LDRD Project Investments in BNL Scientific Initiative Areas

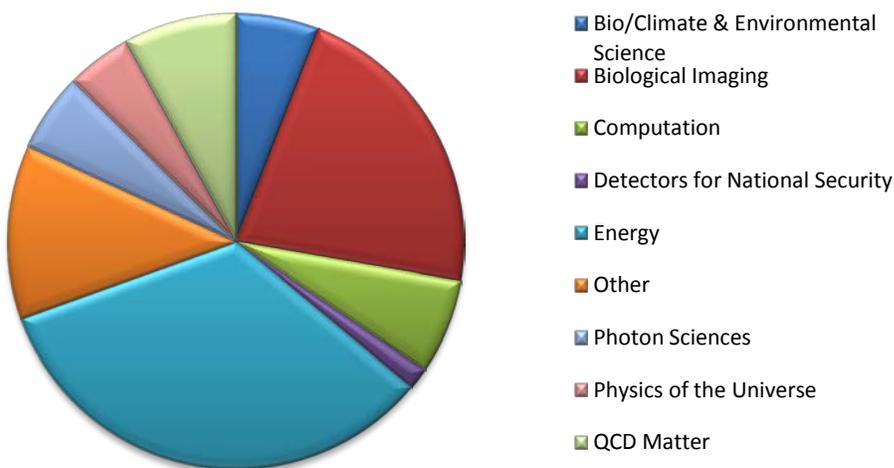


Figure 1. FY2009 BNL LDRD Spending by Initiative

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT
2009 PROJECT SUMMARIES

QCD Thermodynamics at Non-Zero Temperature and Density

LDRD Project 07-001

Frithjof Karsch

PURPOSE:

The objective of the project is to improve our understanding of the QCD phase diagram through a systematic study of phase transitions in an extended parameter space defined by the quark mass, the temperature and the baryon chemical potential. The aim is to enhance control over the baryon density or chemical potential dependence of the QCD transition and improve current studies of the chiral critical point in the QCD phase diagram. The project provides important input to the preparation of experimental programs (low energy runs at RHIC and the CBM experiment at FAIR) that aim at a study of QCD at high baryon number density.

APPROACH:

It is expected that the QCD phase diagram changes qualitatively when going from vanishing baryon chemical potential to values of the order of a few hundred MeV. Model calculations suggest that a line of first order phase transitions emerges at non-zero baryon chemical potential starting at a critical point (2nd order phase transition point). Similarly the transition changes from a continuous crossover to a first order phase transition when the quark mass is reduced to sufficiently small values. We use Taylor expansion techniques to analyze the phase diagram of QCD and study the connection between transitions that exist at small quark masses and those conjectured to exist at non-zero quark chemical potential. For this purpose we developed a program that automatizes the calculation of higher order Taylor expansion coefficients. This allows us to perform calculations at higher orders in the expansion and will improve our knowledge of finite density QCD considerably.

The numerical calculations are performed in the context of studies of QCD Thermodynamics performed by the RIKEN/BNL-Bielefeld-Columbia Collaboration on the QCDOC and BG/L computers at BNL as well as on the apeNEXT computer at Bielefeld University, Germany. The collaboration involves about 15 members from Bielefeld University (Prof. E. Laermann et al.), Columbia University (Prof. N.H. Christ, Prof. R.D. Mawhinney, M. Cheng), the GSI-Darmstadt, Germany, where former members of our group (C. Schmidt, W. Soeldner) are now based, and our BNL based Lattice Group. S. Ejiri also participates in the WHOT collaboration, which performs studies of finite temperature and density QCD with so-called Wilson fermions.

TECHNICAL PROGRESS AND RESULTS:

During most of FY2009 we completed our analysis of the influence of light Goldstone modes on the thermodynamics in the chiral limit. This led to a new analysis of scaling properties of the chiral phase transition as it is expressed in terms of the so-called magnetic equation of state. In this calculation we managed to reduce systematic errors significantly compared to earlier calculations. We continued to combine this study with our Taylor expansion calculations in order to extract the dependence of the chiral phase transition line on the baryon chemical potential. This will lead to a determination of the leading, quadratic curvature term that characterizes the shape of the transition line in the chiral limit.

The structure of the Taylor expansion coefficients has been used to suggest experimentally accessible observables (higher moments of conserved charges) that allow to detect the transition from hadronic matter to the quark gluon plasma phase.

Most of our numerical studies have been performed with improved staggered fermions. However, some studies also have been performed with improved Wilson fermions. First studies have also been performed within domain wall fermions. This will in the future allow us to get better control over the influence of chiral symmetry restoration on the deconfining properties of the QCD phase transition.

SPECIFIC ACCOMPLISHMENTS:

This project resulted in three publications that appeared in Physical Review D and Physical Review letters, and one publication submitted to Physical Review D. They present new results on the structure of the QCD phase diagram, universal aspects of the QCD phase transition and the fluctuation of conserved charges at the phase boundaries. These results have been reported at several conferences, including this year's lattice conference and the Quark Matter conference. They are published or are going to be published in 6 conference reports.

Lattice QCD Simulations on BlueGene/L

LDRD Project 07-002

Frithjof Karsch

PURPOSE:

The objective of the project is to build up a computational environment with highly optimized programs and libraries that allows us to perform efficient QCD thermodynamics simulations on BG/L computers. This requires us to port the Columbia Physics System (CPS) software package, which forms the basis for the comfortable computing environment used on the RIKEN/BNL and DOE owned QCDOC computers, also to BlueGene/L. CPS will be used to run QCD thermodynamics projects efficiently on BlueGene/L.

APPROACH:

The BlueGene/L architecture has many features in common with the QCDOC computers installed at BNL. The basic parallel computing paradigm thus can easily be mapped onto the BlueGene/L machines. However, on QCDOC central parts of the computing programs have been coded in Assembler to reach satisfactory efficiency. These parts of lattice QCD programs require an individual treatment on different computer architectures and need to be ported to BlueGene/L. Moreover, recent advances in lattice simulation and integration schemes (RHMC algorithm, Omelyan integration, quotient force terms) as well as the development of refined fermion discretization schemes with improved flavor symmetry (stout action, domain wall fermions) require the development of new programs. These have to be optimized for new computers such as BlueGene/L and have to be integrated into a common library environment; the CPS software package will be used by our BNL based Lattice Group in joint research projects with the lattice group at Columbia University as well as research groups at LLNL and LANL.

TECHNICAL PROGRESS AND RESULTS:

During 2008 and 2009 we have used our software which has been developed for projects on BlueGene/L and P computers in large scale projects on QCD thermodynamics.

The QCD thermodynamics project on BlueGene/L computers is to a large extent part of the so-called hot QCD Collaboration, a consortium of lattice gauge theory groups in the US. The goal of this collaboration is to extend existing studies of QCD thermodynamics by performing simulations with parameters that are even closer to the continuum limit. This will improve control over systematic errors in the continuum extrapolation and will improve results obtained for the QCD equation of state and transition temperature. Apart from this we performed calculations of the equation of state with physical values of the light quark masses and a physical value of the strange quark mass. These projects are part of the RBC-Bielefeld research project, which also uses computing resources on the BNL QCDOC computers and the apeNEXT computer in Bielefeld. We started to optimize our programs for the use on even larger lattices of size that allow calculations with smaller discretization errors. For this project our group received dedicated computational resources during the test phase of a new, 1 Petaflops, BlueGene/P installation at the John von Neumann Centre in Juelich, Germany. A large fraction of this resource could be used for three months in 2009 (July-September). Following this initial phase all data have been transferred to Brookhaven and the project been continued on the BlueGene/L of the New York Center for Computational Sciences at BNL.

SPECIFIC ACCOMPLISHMENTS:

This project resulted in 4 publications that will or have already been published in Physical Review D and Nuclear Physics A. Results of this project have been reported at several conferences, including Quark Matter 2009 in Knoxville, Tennessee, and the Lattice conference in Beijing, China. These results are published or are going to be published in 7 conference reports.

Proof-of-Principle Laser System for ILC Positron Source

LDRD Project 07-004

Igor Pogorelsky

PURPOSE:

Inverse Compton scattering between counter-propagating laser- and electron-beams is one of the prime candidates for generating intense γ -rays for diverse applications, including polarized positron- and muon sources for lepton-lepton colliders. Production of a high-current positron beam requires a multi-kHz picosecond laser of multi-kW average power that is far beyond present-day industry capabilities. We propose to circumvent this constraint by capitalizing on the fact that the bulk of the Compton γ -ray energy is consumed from the electron beam, while the attenuation of the laser is negligible. This provides the possibility to “recycle” laser energy for multiple Compton interactions thus relaxing the laser requirements. The goal of this project is to demonstrate the feasibility of this approach and thus its potential toward applications for future colliders and laser synchrotron light sources for multi-disciplinary needs.

APPROACH:

A precursor to this project was the ATF Compton scattering experiment. Using a mid-IR picosecond CO₂ gas laser that produces 10 times more photons per Joule of laser energy than shorter-wavelength solid-state lasers, we demonstrated a record-high x-ray yield that meets the ILC requirements for a single laser/e-beam interaction. Notably, contemporary lasers are not powerful enough to maintain the required high x-ray flux at a high multi-kHz repetition rate. The essence of the proposed approach is to increase the repetition rate of the γ -ray source (up to 100 times!) above the laser repetition rate limit by placing the laser/e-beam interaction point (IP) inside a regenerative laser ring cavity as is illustrated in Fig.1. This allows multiple laser/e-beam interactions on every laser shot. A laser amplifier placed inside the cavity will compensate for round-trip optical losses in a circulating laser pulse. At the same time, due to the restricted CO₂ gas laser amplifier bandwidth, the circulating pulse becomes distorted and aggravates the laser/e-beam interaction efficiency. To overcome this problem we proposed and implemented a novel isotopically enriched CO₂ gas mixture that allows for the amplification of a picosecond laser pulse without distortion.

Development, simulation and experimental testing of such a regenerative CO₂ laser cavity constitute the main part of this project. Along with Igor Pogorelsky (PI, Scientist), other leading contributors to this project are Vitaly Yakimenko (Scientist, Head of the ATF) and Mikhail Polyanskiy (Post-Doctoral Research Associate).

TECHNICAL PROGRESS AND RESULTS:

In the course of the project, several important milestones have been accomplished:

- Experimental demonstration of the possibility of incorporating the Compton optical setup (a pair of confocal, off-axis parabolic mirrors with a hole for transmitting the e-beam and γ -rays) into a regenerative laser cavity and circulating a train of picosecond laser pulses through such a Compton IP;
- Development and testing of the method of injecting a picosecond laser pulse into the amplifier cavity using an optically controlled semiconductor switch;
- Development of a comprehensive computer model of a regenerative picosecond CO₂ laser amplifier;

- Demonstrated by simulations how CO₂ isotopes improve the time structure of laser pulses circulating in a Compton cavity;
- Installed an isotope-recovery cryogenic gas handling system;
- Experimental demonstration of a picosecond laser pulse amplification in the multi-isotope CO₂ amplifier.

Fig. 2 and 3 illustrate the last two milestones accomplished during the 3rd year of the project. We developed and installed a cryogenic gas manifold that allows freezing out and reusing expensive isotopic gas components when the laser amplifier needs to be refilled or opened for maintenance. We subsequently demonstrated that the laser operating with the isotopic mixture CO₂¹⁶:CO₂¹⁶O¹⁸:CO₂¹⁸ does not distort the pulse as is shown in Fig.3 (f).

This LDRD project culminated with a White Paper “High-flux Inverse Compton Scattering for Applications in High-Energy Physics, Medicine, Industry and National Security” which has been submitted to the DOE Panel on Accelerators for America’s Future.

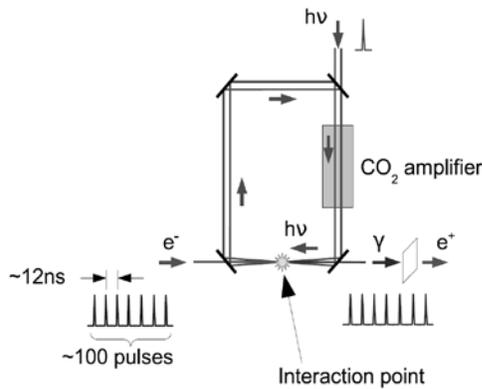


Figure 1. Principle diagram of intra-cavity, high-repetition Compton source.

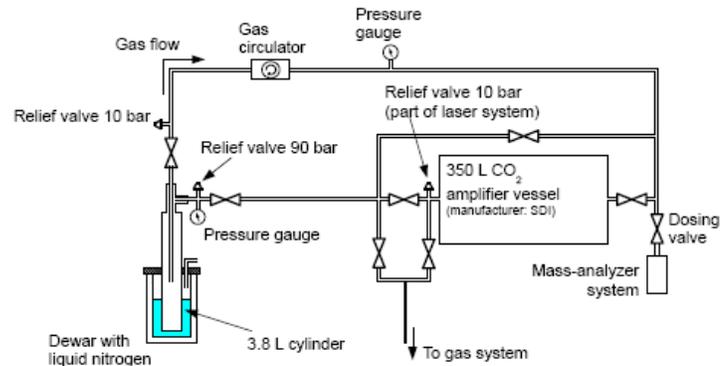


Figure 2. Cryogenic isotope handling gas system installed at the regenerative laser amplifier.

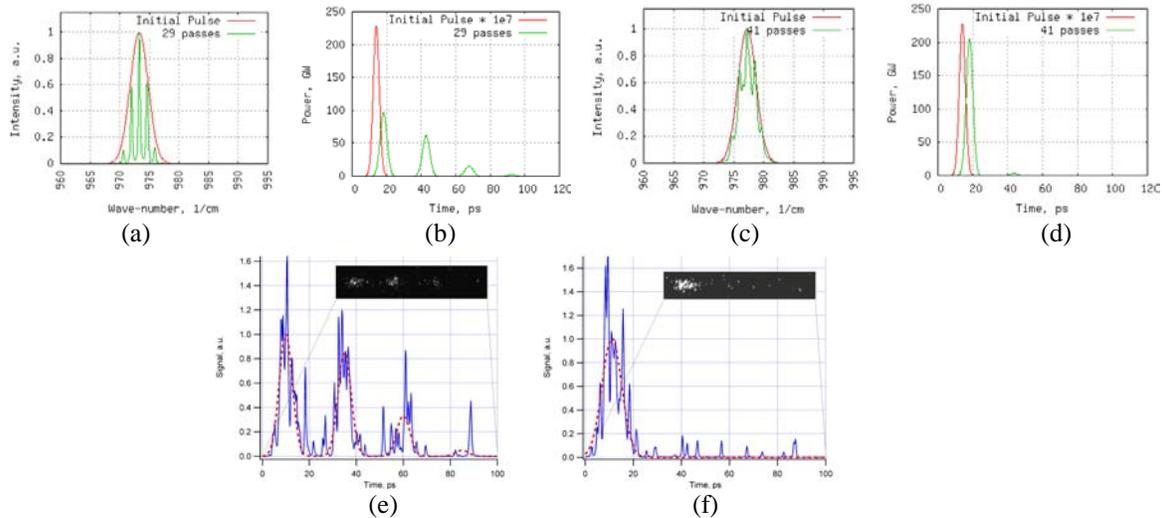


Figure 3. Spectral distortion of a circulating 5-ps laser pulse by a laser amplifier and the corresponding time structure: (a) and (b) simulated for a regular 10-atm laser gas composition, (c) and (d) simulated for the 10-atm multi-isotope laser; (e) experimental result (streak camera trace) for a 5-ps laser pulse amplified in a 10-atm regenerative CO₂ laser filled with regular gas; (f) same for the laser with isotopic gas mixture.

Sensitive Searches for CP-violation in Hadronic Systems

LDRD Project 07-005

Yannis Semertzidis

PURPOSE:

For the purpose of a high precision storage ring electric dipole moment (EDM) experiment we had to develop a hadronic polarimeter with the following characteristics: 1) Have high efficiency (ϵ) and high analyzing power (A), with the product $\epsilon \times A^2$ being the relevant statistical quantity a.k.a. figure of merit (FOM). 2) Have a low systematic error. As the level of the EDM signal is at the parts per million (ppm) and therefore the systematic error needs to be below that. Precision measurements such as the EDM experiment are sensitive to systematic errors which can easily mask the signal we wish to observe.

APPROACH:

The proposed experiment would utilize counter-rotating longitudinally polarized proton beams simultaneously stored in a dedicated ring with purely electrostatic bending. The electric field strength and ring bending radius would be chosen to select a “magic” energy which would cancel horizontal beam spin precession with respect to the momentum vector associated with the proton’s anomalous magnetic moment. In these experiments, we seek to demonstrate that by this approach, it is possible to control systematic errors at the level necessary.

The project team works in collaboration with an internationally renowned team of researchers. Most of the experimental work was done using polarized beams stored at COSY (Jülich/Germany). Our collaborations include Edward Stephenson from IUCF, a world-renowned expert in this field, and Professor Gerco Onderwater from KVI/The Netherlands. We hired Dr. Astrid Imig using LDRD funds, and other BNL researchers include William Morse, Donald Lazarus, Vasily Dzhordzhadze and Yannis Semertzidis. We utilized numerous runs at the COSY facility to investigate several different ways of probing the polarization state of the stored beam. The COSY ring and the EDDA detector modified to serve as a polarimeter is shown in Figure 1. Results with the uncorrected and corrected data are shown in Figure 2. The corrected data for rate and geometry effects are shown to be consistent with zero placing a very strict limit on the systematic errors.

TECHNICAL PROGRESS AND RESULTS:

We have concluded that by far the best way is to use nuclear elastic scattering off solid carbon target. The target is the limiting aperture in the ring and we extract the beam by driving slowly on it using various methods, one of which (proven to be the best so far) by adding white noise in the vertical phase space of the beam. The status of this project and the technical progress was reviewed at BNL for Dec 7 & 8, 2009 (see <https://www.bnl.gov/edm/review/>). The intense testing plan put together by the polarimeter team worked extremely well. The results of the runs showed that the polarimeter systematic errors are <0.1 ppm, much below the sensitivity of the experiment. The results of this test are currently written up for publication. The committee report (see https://www.bnl.gov/edm/review/files/pdf/pEDM_Review_Report_sv_123009.pdf) was positive about this polarimeter work, and recognized the results to date as being important start toward the development of a high precision storage-ring electric dipole experiment, though much work remains to be done.

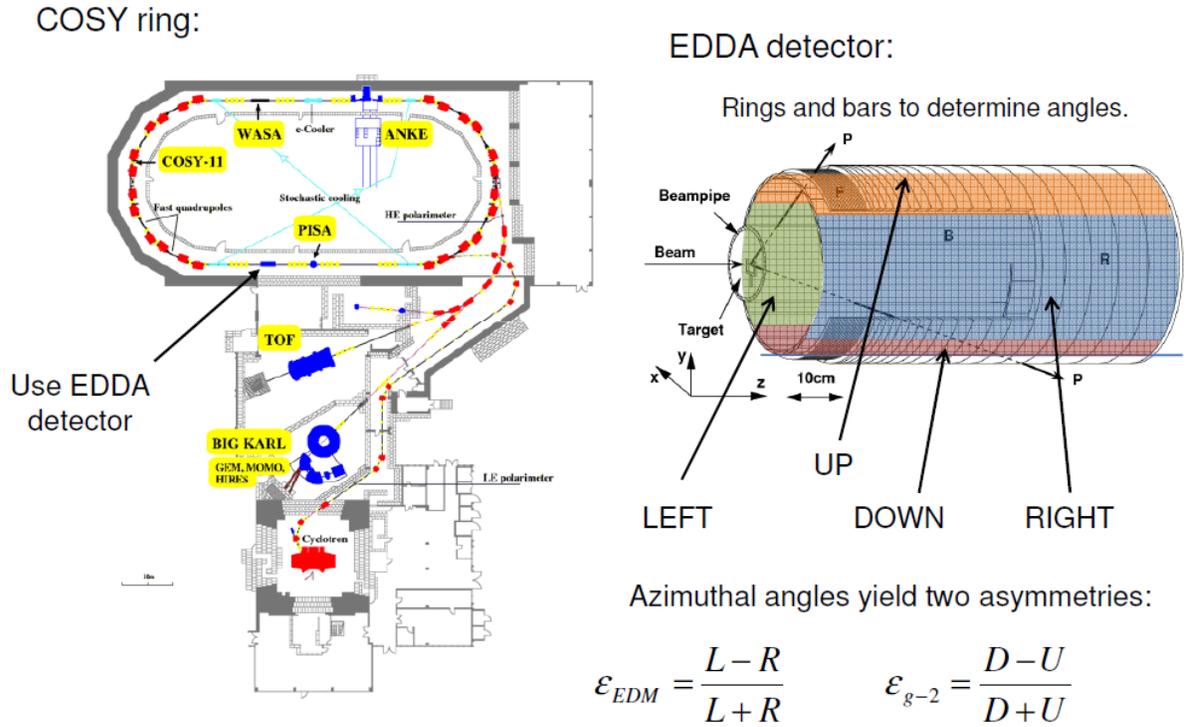


Figure 1. The COSY ring (left) at Jülich/Germany with 185 m circumference and the EDDA detector with ~1m length used as the polarimeter are shown here.

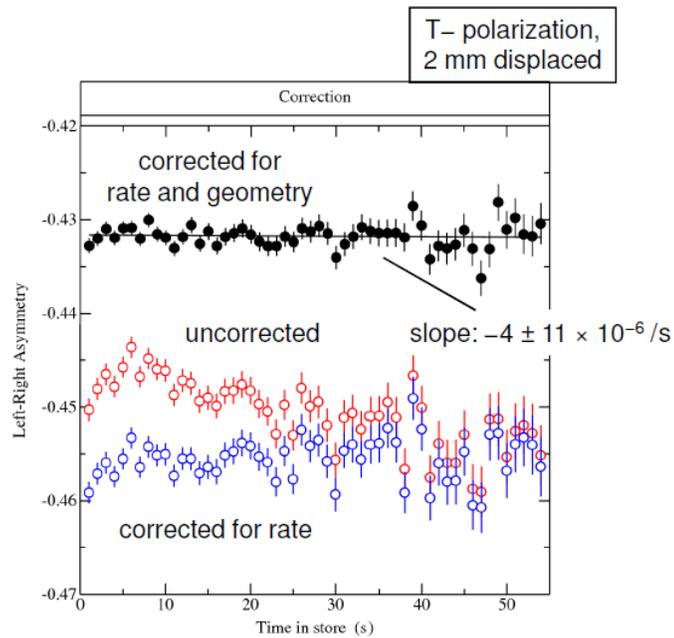


Figure 2. The polarimeter systematic errors are shown to be well under control when corrected for rate and geometry effects.

Feasibility and Design Studies for a Detector for e+p, e+A, p+p, p+A, and A+A Collisions at BNL

LDRD Project 07-006

Thomas Ullrich

PURPOSE:

A future Electron-Ion Collider (EIC) embodies the vision of the field of High Energy Nuclear Physics for reaching the next QCD frontier: the study of gluons which bind all atomic nuclei. Such a facility, which provides high-luminosity collisions at center-of-mass energies from 30-100 GeV with polarized electron and nuclear beams may be sited at either BNL or JLAB.

The aim of this LDRD project was two-fold. One goal was to strengthen the physics case for a future EIC, by conducting studies to demonstrate the feasibility of a broad range of measurements with high physics impact. From these studies, requirements on the machine (beam energies and luminosities) and on detector design will be evolved.

The second goal was to translate these requirements into a design for a realistic EIC detector concept (acceptance and particle identification capabilities). To achieve this, physics simulations were performed to optimize the design. The case of e+A physics is especially challenging in a collider environment, as the experimental layout must allow for the detection and reconstruction of the scattered low-energy electron.

The outcome of this LDRD was to provide a first rough detector design that would serve as the baseline for further studies within the official EIC Task Force at BNL that was formed in spring 2009.

APPROACH:

The physics aspects at an EIC (especially eA) are sufficiently different from those of existing facilities that detector concepts and approaches have to be developed almost from scratch. Therefore, the generation of simulated e+p and e+A collisions is essential. By using existing e+p generators at EIC energies we were able to make progress in understanding the basic detector requirements. Now that this has been accomplished, we will, in the near future, modify these generators to also work for e+A collisions.

TECHNICAL PROGRESS AND RESULTS:

In the past year, a large step forward has been taken in this project with the setting up of the EIC Task force at BNL. Working with colleagues from the EIC Task Force, we have developed a framework in which to run multiple e+p generators (PEPSI, RAPGAP and PYTHIA) in both DIS and diffractive mode and with/without radiative corrections as appropriate. The output from these simulations is stored in a common format, thus simplifying the interface to the detector simulation package. This code and the referring detailed documentation are available on the web for any member of the EIC collaboration to use.

We used the above mentioned physics generators to study various key measurements of the EIC program and examined in great detail the phase space (spatial and momentum) dependence of the produced particles thus defining the requirements for an EIC detector. During the summer of 2009, we mentored 3 undergraduate students from Stony Brook on the SULI scheme who joined the effort. Working in collaboration with the C-AD department, who are designing the interaction region to our requirements (as shown in Fig. 1); we were able to come up with a detector design that encompasses the majority of the most important physics. This concept was imple-

mented in a GEANT3 framework called ESIM. It allows to optimize the various detector components and study their response to various physics measurements.

The backbone of each detector concept is the design of the magnetic field. We have settled on a solenoidal field in the central detector which is complemented by strong dipole fields in the forward/backward region, thus allowing us to detect scattered electrons to angles as low as 1° off of the beam axis. The detector has almost 4π electromagnetic calorimeter coverage augmented by hadronic calorimetry, especially in the central region. High precision tracking and particle identification out to 4-5 GeV/c are considered necessary to conduct the key measurements. Figure 2 shows a rendering of this detector with tracks from a PYTHIA event: The track going to the upper right is the outgoing proton interacting with the hadronic calorimeter creating a shower of particles. The track going to the bottom left is the outgoing electron, interacting in the electromagnetic calorimeter, creating a shower of particles.

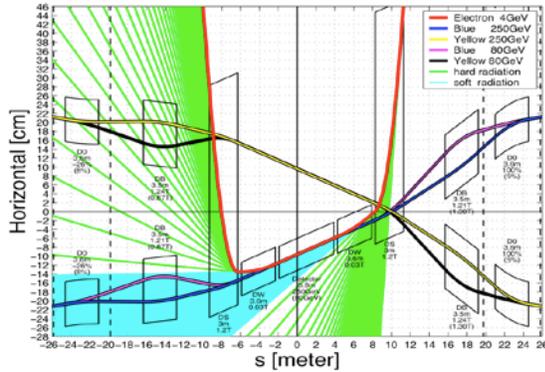


Fig 1. The IR region being proposed for eRHIC, showing the detector, beampipes and radiation.

Within the created framework one is now able to easily modify the various components and the magnetic field to further optimize performance and cost.

One of the important measurements to make is that of diffractive collisions, which gives us the best handle on the measurement of the gluon distribution. However, due to their nature, they are difficult to detect as either they produce a vector meson with the ion going down the beamline, or they produce a number of particles with a gap in rapidity-space between the ion and the particles. We evaluated the trade-off between identification efficiency of diffractive events and their purity, i.e., the level of contamination with non-diffractive background events. Studies using the RAPGAP and PYTHIA event generators show that a hermetic detector to fully characterize the event, with specific emphasis on the forward region is absolutely mandatory, although the requirements on momentum resolution and PID in the forward region are moderate (for these kind of events).

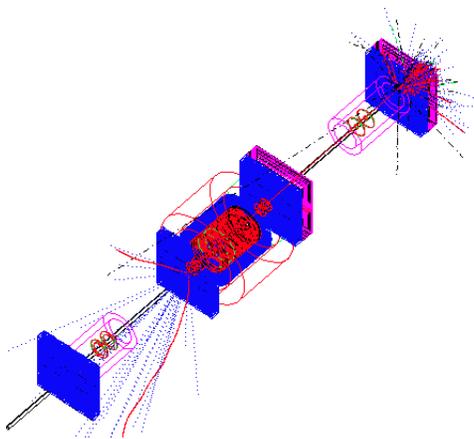


Fig 2. A GEANT3 model of a possible detector for eRHIC with particle tracks generated from PYTHIA.

Recent work has focused on a low-energy electron option for EIC at BNL (MeRHIC). Studies are underway to see how the changed event kinematics due to the lower electron beam energy impact the current detector design. At the same time how the reduced center-of-mass energy affects the sensitivity to various key measurements is also being investigated in detail.

A Novel and Compact Muon Telescope Detector for QCD Lab

LDRD Project 07-007

Zhangbu Xu

PURPOSE:

We propose R&D on a large-area and cost-effective muon telescope detector (MTD) for RHIC and for next generation detectors at a future QCD Lab from the state-of-the-art multi-gap resistive plate chamber (MRPC) with large module and long strips. Conventional muon detectors rely heavily on tracking stations while this new R&D project proposes to use good timing and coarse spatial resolutions to identify muons with momentum of a few GeV/c. This R&D project focuses on studying the capability of muon identification based on timing resolution from the MRPC detector with large module, long strips and fast electronics for online trigger. We have carried out a timing resolution study at the FermiLab test beam facility (T963) and in the prototype in the real environment at STAR in Au+Au, p+p and d+Au collisions in year 2007-2008. We installed a new prototype equipped with the Time of Flight (TOF) electronics for p+p and Au+Au collisions at RHIC in run 2008-2010. This allows us to assess the detector time resolution and its trigger and particle identification capability. A large-area muon detector around center of mass at RHIC will be crucial for advancing our knowledge of the Quark-Gluon Plasma (QGP). It directly addresses many of the open questions and long-term goals proposed in 4 RHIC white papers published in Nuclear Physics A **757** (2005). Since muons do not participate in strong interactions, they provide penetrating probes to the strongly interacting Quark-Gluon Plasma.

APPROACH:

A compact detector identifying muons of momentum at a few GeV/c should achieve hadron rejection of a few hundreds and allow us to investigate dimuon pair from virtual (heavy) photon decays, QGP thermal radiation, possible correlations of quarks and gluons as resonances in QGP, initial lepton production, and heavy flavor (charm quark and bottom quark). In addition to an effective trigger and cleaner signal-to-background ratio, electron-muon correlation can be used to distinguish lepton pair production and heavy quark decays.

The basic technology, but with small pads, has been proposed in STAR and PHENIX at RHIC and ALICE at the Large Hadron Collider (LHC) as Time-of-Flight Detectors. This R&D project focuses on studying timing and spatial resolution from the MRPC detector with large module, long strips and fast electronics for online trigger to achieve necessary muon identification and hadron background rejection.

Components for the prototype and contributions from other collaborators:

1. *Long MRPC modules: Prof. Cheng Li, and Dr. Yongjie Sun (USTC/China), Prof. Yi Wang and Dr. Xiaobin Wang (Tsinghua University/China)*
2. *Front-end electronics and gas box: Drs. Bill Llope and Geary Eppley (Rice)*
3. *Trigger electronics and logics: Dr. Jack Engelage (UC Berkeley, Space Lab)*
4. *Simulations: Guoji Lin (Yale University)*

5. T963 test beam: Dick Majka, Nikolai Simernov, Guoji Lin (Yale University), Yi Wang and Xiaobin Wang (Tsinghua Univeristy/China), Zhangbu Xu (BNL)
6. Prototype in STAR for 2007—2010 and data analysis: Lijuan Ruan, Patricia Fachini (BNL), L. Li (UT Austin) and Y. Zhou (USTC)
7. Test setup at BNL physics building: L.J. Ruan, X.B. Wang, Z.B. Xu and Y. Zhou

TECHNICAL PROGRESS AND RESULTS:

In earlier years, we have successfully produced 4 Long MRPC modules in China. The results from cosmic ray and beam tests using prototype front-end electronics show good timing resolution (less than 70 ps), high efficiency (>95%) and good spatial resolution (<1cm). This satisfies the needs for a large-area muon detector. Modules installed behind the STAR magnet have successfully taken triggered data in Au+Au, d+Au and p+p collisions, and offline tracking of particles from Time-Projection Chamber (TPC) is able to match with hits from Long MRPC. The muon identification and background rejection capabilities have been obtained. In the current fiscal year:

1. Modules installed behind the STAR magnet with new TOF electronics have successfully taken triggered data in p+p collisions, and offline tracking of particles from the TPC is able to match with hits from Long MRPC.
2. Simulations on heavy flavor programs including J/psi, Upsilon and electron-muon correlations have been carried. The results indicate that with full-coverage of the muon telescope detector at STAR, all the above measurements are promising and have a clear advantage over electron channels.

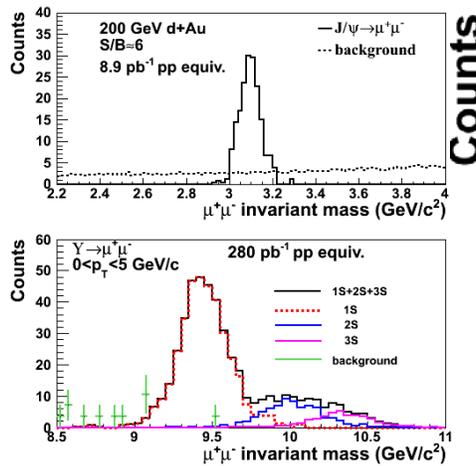


Fig.1 With full MTD acceptance, simulations on J/psi and Upsilon. The signal over background ratio for J/psi is expected to be 6 in d+Au and 2 in central Au+Au. Upsilon measurement is expected to be background free.

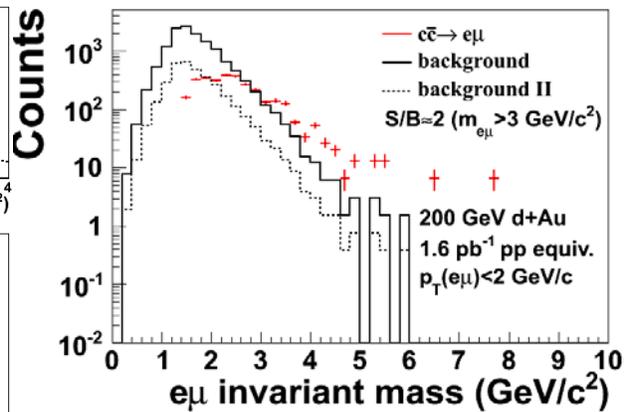


Fig.2 Simulations on electron muon correlation from charm decay. The signal over background ratio is about 2 with transverse momentum of the pair less than 2 GeV/c and invariant mass of the pair larger than 3 GeV/c².

Future Work and Milestones:

1. Assess time resolution, hadron rejection, and muon identification using p+p collisions taken in year 2009 and obtain data in Au+Au collisions at STAR in 2009-2010.
2. Assess the level 0 trigger capabilities with full coverage of the MTD at STAR at RHIC II.
3. Proposal for full-coverage MTD for STAR has been submitted and is to be approved.

Design Optimization of a Reactor Neutrino Experiment

LDRD Project 07-010

David E. Jaffe, Steve Kettell and Laurence Littenberg

PURPOSE:

We propose use of Geant4-based simulation to evaluate and optimize proposed elements of the Daya Bay Reactor Neutrino Experiment including options for a muon veto system and tracker. A portion of the funding is to be used for simulation and software workshops (one per year). Success of the studies will contribute in part to the approval of the Daya Bay Reactor Neutrino Experiment by the Office of Science of the DOE.

APPROACH:

The Daya Bay experiment offered the opportunity for Brookhaven to become a leader in the reactor neutrino effort that strives to measure the currently unknown neutrino mixing parameter $\sin^2 2\theta_{13}$. The muon veto system is essential in order for the Daya Bay experiment to reach its design sensitivity. Careful evaluation and optimization is needed to ensure that the cosmogenic background can be sufficiently well-suppressed and that the remaining background can be reliably estimated. Extensive use of Geant4-based simulation, validated by comparison with relevant data, is employed to evaluate muon veto system designs and background estimations. Many of the studies have been done in collaboration with Hongshang (Kevin) Zhang, a postdoc hired with resources of this LDRD.

TECHNICAL PROGRESS AND RESULTS:

The simulation and design work provided by this LDRD led to approval of the Daya Bay Reactor Neutrino Experiment by the DOE. The experiment is currently in the construction phase.

Kevin Zhang used his expertise to assess how changes in the design of the muon veto system, necessitated by changes in the expected PMT performance and/or coverage as well as interaction with other systems, would affect the overall performance of the muon veto system. The results have been used to decide to refurbish PMTs from the Macro experiment for re-use in Daya Bay.

Extensive modifications and improvements were also made to the simulation and analysis software by Kevin Zhang to study muon-induced backgrounds. The results largely confirmed previous estimates using other techniques.

Development of Laser Beam Shaper for Low Emittance Electron Beams

LDRD Project 07-019

Triveni Rao and Thomas Tsang

PURPOSE:

Typically photocathode drive laser output is characterized to be Gaussian in transverse and longitudinal dimensions. However, applications such as high brightness electron injectors require non Gaussian shapes to minimize the emittance of the electron beam. For example, a high-current ERL, such as the one being built at BNL, requires a flat-top transverse and longitudinal profile with pulse duration of ~60 ps for low charge (<1.4 nC) and ~120 ps for high charge (>5 nC) operations. This project is directed towards evaluating different techniques for modifying the beam profile, selecting the ones suitable for the ERL operation, and designing, constructing and testing the selected beam shaper.

APPROACH:

The laser pulse needs to be shaped in both the time (longitudinal) and the space (transverse) domains. The initial beam shaping is aimed at generating a rectangular beam profile. Although a number of techniques can be used to shape the laser beam, after evaluating various techniques theoretically and experimentally, a Gaussian-to-flat-top refractive spatial beam shaping device, Newport ZB-128X is selected for spatial shaping. This passive device is identified to be the most suitable in terms of technical feasibility, simplicity, and reliability for use in a high average power laser system. For longitudinal shaping, pulse stacking using birefringent crystals is chosen since it is relatively simple and provides stable pulse shaping. Although it has limited parametric flexibility, for well known input laser parameters, it is possible to achieve the required longitudinal profile with this technique.

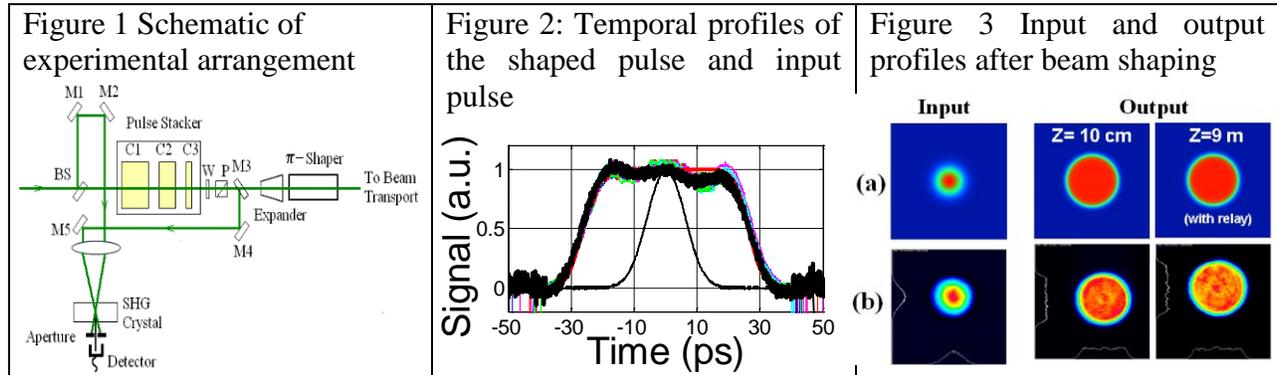
A passively mode-locked Nd-vanadate laser oscillator (Time-Bandwidth Cheetah-X) is presently used for testing the refractive beam shaper module. The parameters of this laser resemble closely the one planned to be used for the ERL experiments. It delivers s-polarized laser pulses at 532 nm wavelength with average power of 2.5 Watts at a repetition rate of 81.25 MHz. The pulse duration was measured to be 10 ps FWHM by using an autocorrelator. The beam waist diameter was measured to be 1.3 mm with an ellipticity of ~0.97 and a beam divergence of ~0.15 mrad using a CCD camera (DataRay USB TaperCamD20-15). This camera has a tapered pixel array size of 15.8x15.8 mm, sufficient for the examination of uniquely large spatial beam shapes. A home-built repetitively scanning auto/cross-correlator is employed to measure the laser pulse width before and after the beam shapers.

TECHNICAL PROGRESS AND RESULTS:

In the first year of the project, the spatial profile of the laser beam was converted from a Gaussian to a flat top using passive refractive optics. Subsequent work focused on shaping the temporal profile, evaluating the optimal sequencing of components, establishing the tolerances and transporting the beam over long distance by relay imaging to maintain the modified shape.

The experimental setup is shown in Fig. 1. The laser beam was first split into two using a 50% beam splitter, passed through two delay lines (arms) and then re-combined and focused on a type II second harmonic crystal (KDP) for auto and cross-correlation measurements. In one arm of the cross-correlator, a stack of three YVO4 birefringent crystals C1, C2, and C3 in decreasing crystal

thickness of 24 mm, 12 mm and 6 mm respectively is positioned. By appropriately aligning the orientations of the crystals, a near flat-top pulse profile with FWHM duration of ~ 53 ps was obtained. It has a rise and fall time of ~ 10 ps as dictated by the initial pulse width. The intensity modulation over the flat-top region is calculated to be $\sim 9\%$ (rms). Figure 2 depicts the experimental cross-correlations, the corresponding de-convoluted laser pulse shape, and the theoretically calculated pulse shape for a static phase of $\pi/2$ between all interfering pulses. The experimental cross-correlation agrees reasonably well with theoretical calculations. The temporal shaper and the spatial shaper were then stacked together, the output beam was transported over 9 m by Keplerian relay imaging. Figure 3 shows the beam profiles of input beam, output beam at 10 cm from the beam shaper and the output beam at 9 m from the beam shaper after relay imaging, along with expected profiles based on simulations using the computer code ZEMAX. At a distance of 10 cm away from the π -shaper and at 9 m distance with image relay system, the intensity modulations in the measured spatial beam profile are calculated to be $\sim 7\%$ (rms) and $\sim 10\%$ (rms) respectively over the plateau region. The optical transmission of the π -shaper is measured to be $\sim 92\%$. The tolerance on the angular misalignment (or tilt) and laser beam de-center (or beam lateral offset) relative to the axis of π -shaper are ~ 0.5 mrad and ~ 20 μm respectively. Similarly, the tolerance on the input beam size is ~ 60 μm at the optimum beam waist diameter of 4.7 mm.



The results of this work have been published in Physical Review Special Topics: Accelerators and Beams.

The future work will be directed towards shaping the ultraviolet (UV) beam of the ERL laser. The choice of the crystals and their dimensions is expected to change for the UV beam. Furthermore, although the laser parameters of the ERL and the TBWP lasers are similar, they are not identical, requiring additional modifications to the beam shapers.

The techniques developed in this project will be useful in a number of applications. The laser beam shaping is an enabling technology that is needed for any high current low emittance electron beam source, especially RHIC II, eRHIC, ILC and future light sources.

Surface Engineered and Core-Shell Nanowires: Nanoscale Building Blocks for Third Generation Photovoltaics

LDRD Project 07-023

Peter Sutter, Eli Sutter and Nicholas Camillone, III

PURPOSE:

Nanostructures, in which reduced spatial dimensionality and quantum confinement modify the intrinsic electronic and optoelectronic properties of a given material, have a significant but as yet unrealized potential for performance improvements in photovoltaic (PV) devices. Semiconductor nanowires (NWs) are self-assembled nanomaterials that are particularly well suited for future PV applications, as they combine inexpensive fabrication with possible performance enhancements due to confinement effects and efficient light absorption and carrier collection. In this project, we explore the synthesis, electronic, and optoelectronic properties of semiconductor NWs with controlled surface termination and of core-shell NW structures. The results will help establish a fundamental scientific basis for evaluating possible NW-based third-generation PV devices.

APPROACH:

We use *in-situ* transmission electron microscopy (TEM) to study the formation of NW heterostructures and to establish the fundamental factors governing their synthesis. We further combine the synthesis of novel NW-based architectures, such as surface-passivated and core-shell NWs, with electrical transport and photo-transport measurements on individual NWs. These measurements take advantage of the unique instrumentation available at the Center for Functional Nanomaterials (CFN), including nanofabrication facilities, electron microscopes, a UHV Nanoprobe, a variable-temperature photocurrent microscope and facilities for high-resolution electron-beam induced current measurements.

TECHNICAL PROGRESS AND RESULTS:

As in the previous two years, this project has involved activities in NW synthesis and processing, combined with measurements of single NW electrical and opto-electronic properties. Examples of key results obtained in the third year of funding are given below.

A - One-step synthesis of Ge-SiO₂ Core-Shell nanowires

Nanowire heterostructures in which a semiconducting core is surrounded by a dielectric shell are of key interest for NW field-effect transistors (FETs) and could be used to tailor the surface passivation and reduce charge traps in NW-based PV devices. The broad application of such core-shell structures is hindered by the complex processing typically required to sequentially synthesize both a high-quality core and shell. We have demonstrated the realization of a one-step process with moderate thermal budget that yields single-crystalline Ge NWs encapsulated in SiO₂ shells, which can serve as high-quality gate oxides or passivation layers. We established the

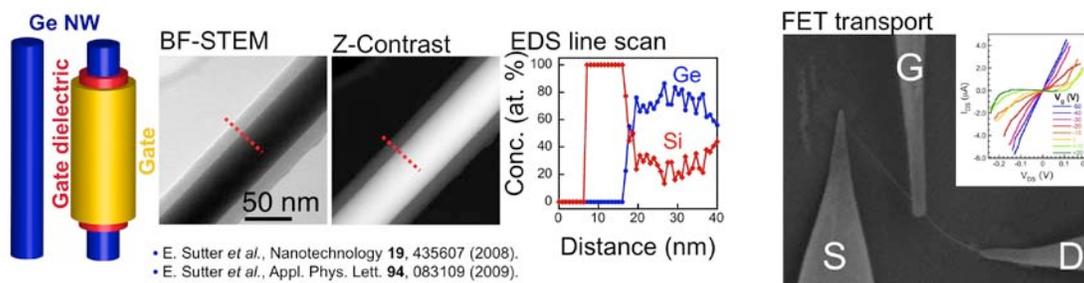


FIG. 1 Structure and chemical composition, and electrical properties of Ge-SiO₂ core-shell NWs.

mechanisms that give rise to the formation of the semiconductor-dielectric core-shell structures – a root-growth different from the conventional NW growth process. To demonstrate the high materials quality achieved, we reported initial electrical measurements on single Ge-SiO₂ FET devices.

B – Mechanisms of controlled doping during nanowire synthesis

Semiconductor NWs can be prepared in high-yield vapor-liquid-solid (VLS) processes with remarkably reproducible structure and electronic properties, but the successful realization of high performance devices requires the implementation of controlled doping over a large concentration range, which has proven to be a significant challenge. We have demonstrated successful Sb-doping of Ge NWs during their synthesis by thermal evaporation using a combination of Ge powder for growth and Sb powder for doping. *In-situ* annealing experiments in a transmission electron microscope (TEM) have been used to identify the mechanisms of doping during NW growth. These experiments established that a liquid ternary Au-Sb-Ge alloy constitutes the active phase of the VLS seed drop at high temperatures, which governs the growth of the one-dimensional Ge NW and its doping by Sb. The determination of the phase behavior of complex multicomponent nano-alloy drops, as achieved here, paves the way for rational doping strategies in NW growth.

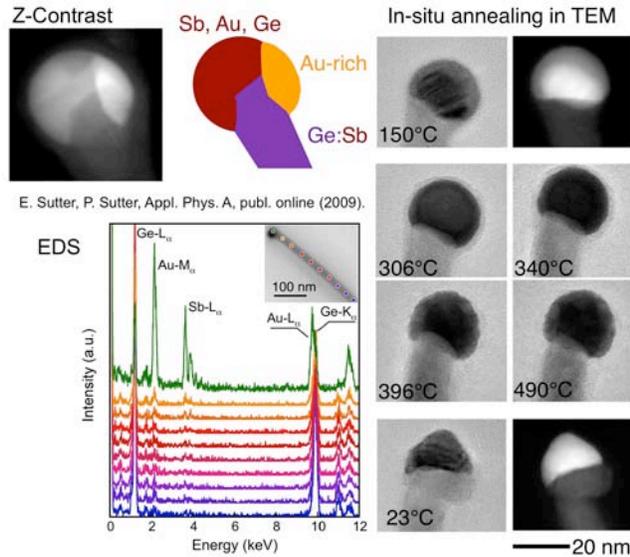


FIG. 2 Investigation of doping mechanisms in Ge NW growth.

C – Single nanowire optoelectronic properties: Electron beam induced current measurements

A major factor affecting NW device performance is the sensitivity to surface effects, e.g. band bending and recombination at surface trap states. To understand such effects we have developed microscopic techniques for spatially resolved measurements on single NWs: photocurrent microscopy and electron beam induced current mapping (EBIC, fig. 3), in which an electron beam scanned across the device excites electron-hole pairs. The resulting current is recorded as a spatial map containing information on electric fields and minority carrier diffusion lengths. Two types of NWs, Ge and Si, have been studied. Ge NWs typically show individual hot spots, likely associated with localized structural changes. EBIC in Si NW is concentrated near the NW center. We find dramatic differences in the charge trap density between Ge and Si: the signal in Si NWs is well-localized, whereas a diffuse halo – due to current from trap states with long discharging times – stretches across the entire Ge EBIC map. Future measurements will concentrate on measuring diffusion lengths and potential profiles in doped NWs, and will explore surface passivation in core-shell NWs.

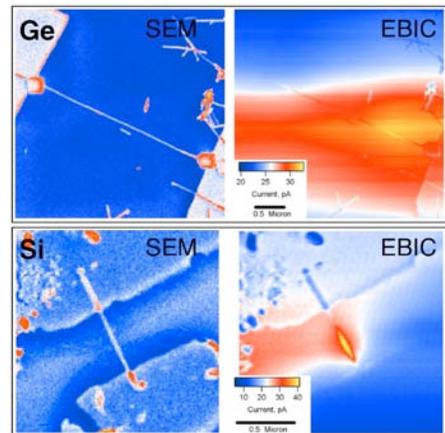


FIG. 3 EBIC maps of single Ge and Si NWs.

Precision Assembly of Nano-Objects – Approaching Artificial Photosynthesis

LDRD Project 07-025

William Sherman

PURPOSE:

Recent studies have revealed that the efficient functioning of natural photosynthesis systems depends critically on the precise arrangement of molecular antennae and reaction centers on a biomolecular scaffold. The overarching goal of this project is to develop techniques that will allow nano-engineers to construct and manipulate opto-electronically active materials with a level of precision approaching that found in these natural systems. We have focused on the assembly of metallic NanoParticles (NPs) because of their well known tunable opto-electronic properties. We are using biomolecular scaffolds (primarily DNA) to direct formation, which have three key virtues: they assemble in parallel, they can form nanomechanical devices, and they form a wide variety of highly precise structures with feature sizes ranging from the 0.34 nm space between stacked base pairs up beyond the ~50 nm persistence length of a double helix. The natural continuation of this work is to create more precise and more complex structures, and to scaffold a broader variety of NPs and other guests such as fullerenes and organic dyes. A more important follow-up will be the study and optimization of electron and energy transfer between scaffolded guests. Precision arrangements of NPs have been used to make low power computer processors, sub-wavelength yet efficient carriers of photonic signals, and SERS substrates, among a broad variety of other areas that could prove fruitful for future investigation.

APPROACH:

Strands of DNA naturally wind up into a uni-axial or ‘linear’ double helix. They can also fold up into ‘branched’ structures, wherein a single strand can wind through and connect several double helices, and sets of such strands can form very complex assemblies. These structures are far more versatile tools for nano-scale assembly than linear DNA. However stabilization of the branched structures in solution typically requires ~10 mM concentration of divalent cations, usually Mg^{2+} . These divalent counterions, cause rapid aggregation of NPs, which has presented a barrier to the use of branched DNA scaffolds for NPs. A good, broadly-applicable solution to this problem is a key step toward unlocking the potential of branched DNA scaffolds.

In collaboration with Oleg Gang at the CFN, we have worked on developing a composite coating of DNA and zwitterions that allows nanoparticles to remain suspended in a solution with 10 mM Mg^{2+} , while also allowing them to attach to DNA scaffolds. We have developed a DNA scaffold that has regularly spaced small clusters of three binding sites. Each nanoparticle has multiple strands of DNA covalently attached to it (this is a very important element of our design, since it eliminates the expensive necessity of fractionating off NPs with exactly one strand of DNA on them). The strands of DNA on the NPs can bind to the clusters of binding sites on the scaffold and are held precisely in place with constrained position and orientation.

TECHNICAL PROGRESS AND RESULTS:

Several smaller side projects were supported by this LDRD, but the most exciting results of 2009 were clearly in the main program. Much of the groundwork for this project was accomplished in 2008. We had assembled the branched DNA scaffold and observed it forming well via Atomic Force Microscopy (AFM). We had also done preliminary tests of the zwitterion/DNA coating for the gold NPs and verified that they don’t aggregate rapidly in the relevant buffers.

The central achievement of 2009 was solving the last hurdles to get the nanoparticles optimally

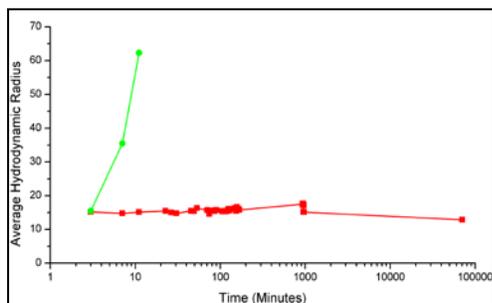


Figure 1 Dynamic Light Scattering reveals increasing size in minutes caused by aggregation of conventionally prepared 5nm gold NPs (green). Similar NPs with zwitterion/DNA coating (red) don't aggregate for over 7 weeks.

mounted onto the DNA scaffolds. The first part of the experiment was characterizing the effectiveness of the zwitterions/DNA coatings at preventing nanoparticle aggregation. Fig. 1 shows Dynamic Light Scattering (DLS) studies showing the size of the nanoparticles or aggregates in solution, and revealed that while conventionally prepared NPs aggregate significantly in less than 10 minutes, the NPs with the zwitterions/DNA coatings did not aggregate for over 7 weeks. Subsequent studies showed that the coating only prevented aggregation of 5 nm gold NPs for a couple of hours when the concentration of Mg^{2+} was 15 mM.

It proved difficult to image the arrays with the NPs on them via AFM. It also proved difficult to get those arrays to stick to TEM grids. However, we found that

the NPs scaffolded on DNA arrays prepared on mica substrates as usual for AFM, could be imaged effectively via Scanning Electron Microscopy (SEM), as shown in Fig. 2 C and D. The

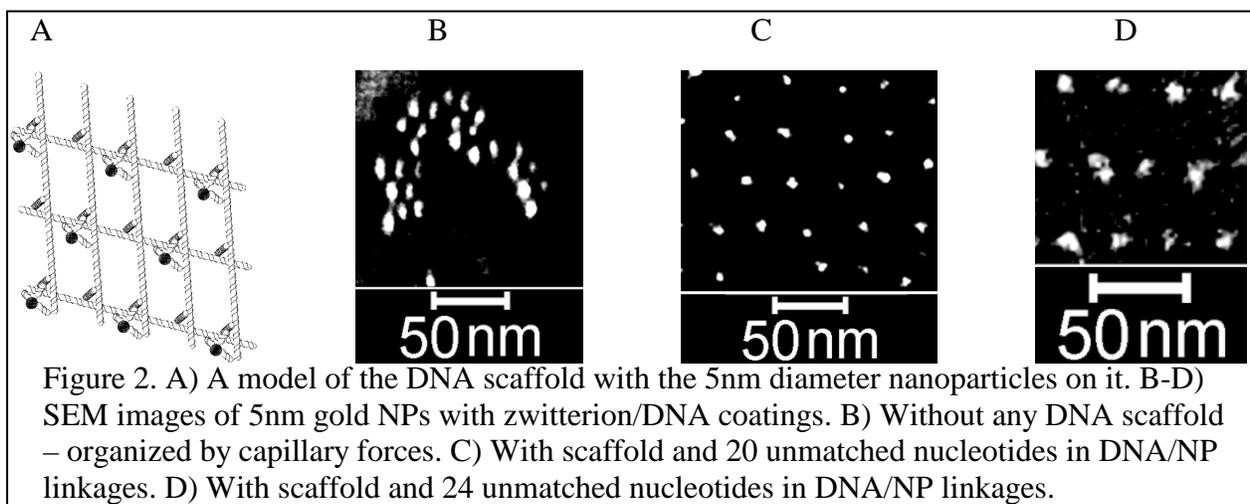


Figure 2. A) A model of the DNA scaffold with the 5nm diameter nanoparticles on it. B-D) SEM images of 5nm gold NPs with zwitterion/DNA coatings. B) Without any DNA scaffold – organized by capillary forces. C) With scaffold and 20 unmatched nucleotides in DNA/NP linkages. D) With scaffold and 24 unmatched nucleotides in DNA/NP linkages.

DNA provides no contrast for the SEM, but the unscaffolded particles are spaced about 9-12 nm apart, while the scaffolded NPs are in neat lines with neighbors approximately the expected 28 nm apart. In early attempts at attaching the NPs, we found that the system requires some extra flexibility in the DNA linkages between the scaffold and the NPs. If the connections are too flexible or not flexible enough, nanoparticles bind to multiple binding sites, or else multiple NPs bind to the same binding site. Numerous variations were tried to determine the optimal assembly parameters shown in Fig. 2. The patent application for the zwitterion/DNA coating is currently in the final stages of editing by BNL's Office of Intellectual Property. This project has already garnered interest in the field, after an invited presentation on the subject at the Foundations of Nanoscience 2009 conference, and is already being incorporated into other scientists' projects. This work will be helpful for countless branched DNA scaffolds of NPs.

The next step in this project will focus on scaffolding oriented pairs of NPs on each binding site. This will take better advantage of the unique orientation control provided by our multiple binding system. Oleg Gang has already made NP dimers that would be ideal for this project.

Photocatalytic Carbon Dioxide Reduction to Methanol using Metal Complexes with an NADH Model Ligand

LDRD Project 07-027

Etsuko Fujita and James T. Muckerman

PURPOSE:

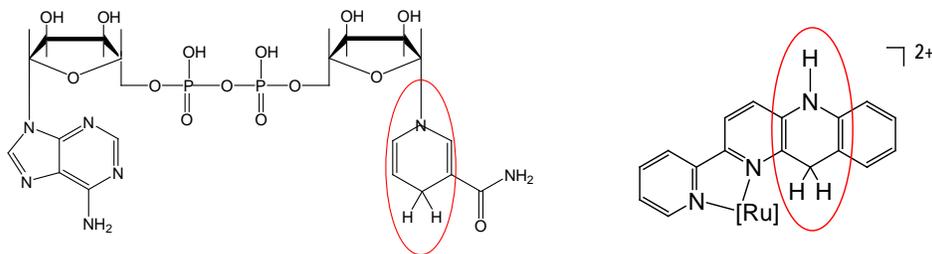
The aim of this project is to explore CO₂ reduction to methanol employing a new methodology to photochemically produce hydride donors using functionalized metal complexes with a reduced nicotinamide adenine dinucleotide (NADH) model ligand. This new bioinspired approach seeks artificial photosynthetic systems for catalytic hydrogenation/reduction of CO₂ beyond CO and HCOO⁻ (which have been produced as the only products of photoreduction of CO₂ in homogeneous systems). This is high-risk research, but it is a very important area to investigate to secure future energy needs.

APPROACH:

Stoichiometric chemical conversion of a coordinated CO to methanol or methane using NaBH₄ has been reported for [Ru-CO]²⁺ → [Ru-CHO]⁺ → [Ru-CH₂OH]⁺ (Ru = Ru(bpy)₂(CO)) and for [Re-CO]⁺ → Re-CHO → Re-CH₂OH → Re-CH₃ (Re = Re(Cp)(NO)(CO)). This raises the question: Can we replace NaBH₄ by a renewable (*i.e.*, visible-light-generated) hydride donor to produce solar fuels?

A combination of experimental and theoretical approaches is being pursued to investigate the mechanism and kinetics of several promising transition-metal complexes with NADPH-model ligands for the photocatalytic reduction of CO₂ to methanol. In particular, rhenium and ruthenium complexes containing the pbn (*i.e.*, 2-(2-pyridyl)-benzo[*b*]-1,5-naphthyridine) ligand may offer promise as photocatalysts for the hydride-transfer reactions required to reduce CO₂ beyond CO, all the way to methanol. This approach will create new directions for the solar energy conversion of CO₂ into energy-rich fuels through *low energy pathways* using functionalized transition-metal complexes as hydride ion donors. The basic knowledge obtained through this study – *e.g.*, the energetics of coupled proton and electron transfer for redox leveling and proton addition and removal, and catalysis *via* hydride transfer, and bond forming/cleavage – will be essential for designing more effective proton-coupled multi-electron-transfer reactions for fuel production.

Our collaborators are Dmitry E. Polyansky (BNL), Diane Cabelli (BNL), Jinzhu Chen (BNL), Patrick Achord (BNL), Takeshi Fukushima (IMS, Japan) and Koji Tanaka (IMS, Japan).



Structures of NADPH and a ruthenium complex with an NADPH-model ligand (pbnHH)

TECHNICAL PROGRESS AND RESULTS:

We have demonstrated that a hydride donor $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ is cleanly formed by the reductive quenching of the metal-to-ligand charge-transfer (MLCT) excited state of $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$ by triethylamine upon irradiation with visible light ($< 600 \text{ nm}$) with a quantum yield of 0.21 at $\lambda = 355 \pm 6 \text{ nm}$. These results open new opportunities for the photochemical generation of strong hydride donors for the *catalytic* hydrogenation of organic molecules (and hopefully CO_2 and related species) by visible-light irradiation as Nature does. This finding has also prompted us to carry out more detailed studies on the mechanism of the photochemical formation of the $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ species.

A comprehensive mechanistic study of $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$ conversion into $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ using steady-state and transient radiolytic and photochemical techniques was featured as a cover article of *Inorganic Chemistry* (May 19 issue, 2008).

Furthermore we found that $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$ undergoes stereo-specific hydrogenation to give two stereo isomers (*i.e.*, Δ -(S)- and Λ -(R)- $[\text{Ru}(\text{bpy})_2(\text{pbnDD})]^{2+}$ (pbnDD is 5,10-dideutero-2-(2-pyridyl)-benzo[b]-1,5-naphthyridine)) upon visible-light irradiation. This result clearly indicates the pathway *via* the π -stacked dimer of the deuterated one-electron-reduced species as shown in Figure 1. The chemical reduction of $[\text{Ru}(\text{bpy})_2(\text{pbn})]^{2+}$ with $\text{Na}_2\text{S}_2\text{O}_4$ in D_2O did not afford any stereospecific products. Furthermore, the more sterically crowded Ru complex, $[\text{Ru}(\text{dmb})_2(\text{pbn})]^{2+}$ (dmb = 6,6'-dimethyl-2,2'-bipyridine, did not produce the corresponding pbnDD species upon irradiation. These results are published as a communication (*Inorg. Chem.*, **2009**, 48, 11510-11512).

DFT calculations on the hydricities of $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ and other potential hydride donors and acceptors relevant to CO_2 reduction have been carried out. Significant among the findings from this work was the prediction of a stronger hydride donor, $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^+$, possibly produced upon further visible excitation of $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ followed by reductive quenching, and the prediction that this further-reduced species is capable of donating a hydride ion to a carbonyl ligand of a second (acceptor) transition-metal complex. Preliminary experiments have confirmed that $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^{2+}$ can donate a hydride ion to the trityl cation. Follow-on funding for the work was obtained from the DOE Solar Energy Utilization initiative, and experiments using $[\text{Ru}(\text{bpy})_2(\text{pbnHH})]^+$ are underway to explore the M-CHO formation from $[\text{M-CO}]^+$ by hydride ion transfer under the DOE Solar Energy Utilization initiative funding.

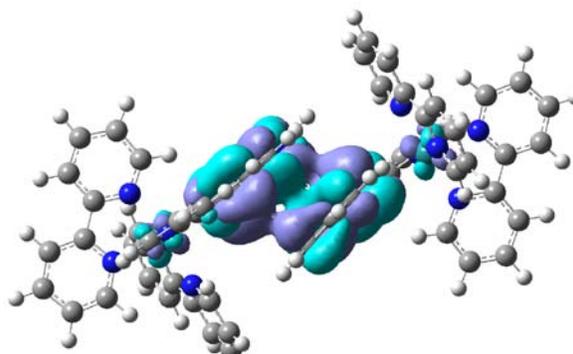


Figure 1. The HOMO of π -stacking Δ, Λ - $[\text{Ru}(\text{bpy})_2(\text{pbnH})]^{2+}_2$ showing the localization of the electrons in a bonding orbital between the π systems of the monomers.

Structure of Mass-Size Selected Nanoparticles by Scanning Transmission Electron Microscopy

LDRD Project 07-030

Michael G. White and Joseph Wall

PURPOSE:

The purpose of this project is to explore the atomic structure of small, supported nanoclusters utilizing high-resolution electron microscopy and scanning probe techniques (AFM, STM). This project addresses the critical need to understand how the atomic structure evolves from small clusters containing tens of atoms to larger particles whose structure mimics the bulk material. Our approach involves the coupling of novel methods for preparing nanoparticles over a very large size range (10 Å to 10 nm) with single particle imaging techniques (STEM, AFM, STM). The specific technical challenges involve (1) the development of a high-speed, 2D detector and software that enables high throughput, single particle diffraction at the Biology STEM; (2) the development of a vacuum load-lock system that allows transfer of air-sensitive samples between the deposition instrument in Chemistry and the scanning probe instrumentation at the CFN. If successful, this program would demonstrate the capability of probing the atomic structure of non-crystalline nanomaterials that could have significant impact on current nanoscience programs at BNL and future instrumentation developments at the CFN.

APPROACH:

We have recently developed new techniques for depositing metal and metal compound (oxide, sulfide) nanoclusters onto solid supports that act as model nanocatalysts that are key to our research in energy-related catalysis. Methods include the use of a novel, size-selected cluster deposition instrument that can pre-select mass (size) and chemical composition of nanoclusters prior to deposition and the use of block co-polymer templating which is a benchtop technique that provides independent control of nanoparticle size *and* interparticle spacing (density). The former is useful for small clusters up to a few hundred atoms (1-2 nm), while the latter technique can provide larger nanoparticle sizes in the range of 1-20 nm. Both techniques yield bare (unprotected) nanoparticles supported on metal oxide substrates (e.g., alumina, titania, silica), typical of heterogeneous catalysts. Our ability to understand and model the reactivity of such nanoparticles, however, is severely hampered by the lack of direct structural information, either in the gas-phase or deposited on surfaces. The two main obstacles are (1) the difficulty of imaging the atomic structure of small non-crystalline or 3D nanoparticles, and (2) practical limitations that require the sample to be exposed to air in order to load it into high resolution imaging instrumentation (STM, AFM, TEM). Air exposure can result in oxidation of the catalyst nanocluster and/or contamination of the nanoparticle and substrate with background contaminants (airborne organics) that often can't be removed without also altering the nanocatalyst surface.

Our original intent in this LDRD project was to develop single particle electron diffraction using the Biology STEM instrument (under the direction of Joe Wall) which has a unique load-lock system for loading air sensitive samples. Unfortunately, the Biology STEM facility was shut down in FY 09 and we were unable to sustain any developmental effort involving the STEM facility. As a result, the project has shifted its emphasis on nanoparticle synthesis techniques, both bench top and by size-selected cluster deposition, with the intention of performing atomic imaging and structural studies using the state-of-the-art scanning probe instruments (STM, AFM)

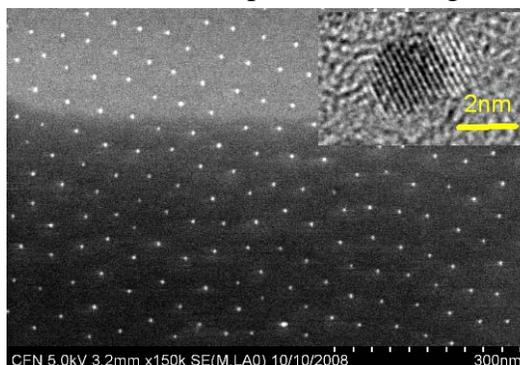
at the CFN (in collaboration with David Starr and Peter Sutter). Part of this effort involves the development of a vacuum suitcase sample transfer system so that samples prepared by size-selected cluster deposition in Chemistry can be moved to the CFN facility without exposure to air. The latter is based on a high speed getter pump (400 l/sec for N₂) and will use sample holders that are compatible with the RHK-STM at the CFN. The samples will be loaded directly into the STM for atomic imaging and investigations of thermally-induced diffusion and sintering.

TECHNICAL PROGRESS AND RESULTS:

FY2010

Over the last year we continued to fine tune the block-copolymer method for the preparation of metallic nanoparticles for imaging experiments (TEM, AFM, STM). This approach uses a hydrophobic polymer block (polystyrene) that is covalently linked to a hydrophilic polymer block (polyvinylpyridine) that forms micelles in a non-polar solvent. These “reverse” micelles act as nanopores for metal cluster growth. A number of different methods were tried to reduce the metal cations while simultaneously removing the polymer from the surface. Using a combination of SEM, AFM and XPS measurements, we found that an ozone treatment in the presence of UV radiation followed by a hydrogen plasma discharge is the best approach for reducing the metal cation and removing the polymer, while minimizing surface oxidation and particle sintering.

To date, we have successfully used the block copolymer technique to prepare nanoparticles of Au, Cu, Pd, Rh, Pt on SiO₂ surfaces with a sizes ranging from 2-50 nm. In 2009, we performed HR-TEM measurements on a few samples and have confirmed their size uniformity and crystallinity (see accompanying figure). Current efforts are focused on performing complementary synchrotron XRD and XAS experiments on the supported nanoparticle arrays at the NSLS using a newly designed in situ scattering cell.



SEM image of an array of Au nanoparticles on a SiO₂/Si surface prepared by block co-polymer templating; inset: HR-TEM image of individual Au nanoparticle.

In November 2009, we took delivery of the UHV capable “vacuum suitcase” (Tectra, Germany) for sample transfer from our size-selected cluster apparatus in chemistry and the STM instrumentation at the CFN. After installation and testing on our cluster apparatus in Chemistry, we will try our first sample transfers to the CFN where they will be loaded and imaged on the RHK STM instrument. Our initial goal is to study supported nanoclusters of molybdenum sulfide that act as models catalysts for hydrodesulfurization. The STM imaging experiments will be used to explore cluster dispersion, cluster structure and thermally-induced morphology changes. Such information will provide crucial information on the cluster substrate interactions as well the fate of the clusters under reaction conditions (high temperature).

Synthesis of Conjugated Polymers for Fundamental Questions in Solar Energy

LDRD Project 07-032

John Miller and Xiao-Qing Yang

PURPOSE:

This LDRD had three goals all connected to possible development of organic photovoltaics:

1. Create new conjugated polymers for investigations of intrachain charge transport over long distances.
2. Investigate whether an existing staff member with substantial expertise in polymer synthesis could be part of efforts to develop new funding in solar photovoltaics.
3. Make measurements of charge and exciton mobility on the new materials.

APPROACH:

Two principal barriers to high efficiencies in organic photovoltaic cells are 1) Insufficient charge mobilities and 2) Short, 10 nm or less, exciton diffusion lengths. This project seeks to synthesize new polymers that would enable experiments on fast charge transport. Electrons would then be injected into these molecules at the LEAF accelerator with spectroscopic measurements of charge motion utilizing the novel optical fiber single-shot detection (OFSS) system. One synthetic goal was to develop polymers having appended “trap” groups that would capture electrons, holes or excitons. Capture would be rapid, even with just one or a few trap groups on a chain, if transport along the chain were fast.

A second goal was to create such molecules with enhanced solubility in non-polar media to facilitate experiments. The time resolution of experiments that attach charges to polymer chains is limited by how fast the charges reach those chains. High mobilities of electrons in nonpolar fluids might therefore enable high time resolution in experiments that seek to observe long-distance motion along chains. A test of this hypothesis was an aim of this LDRD.

Mr. H. S. Lee worked on synthesis of polymers. Dr. Andrew Cook performed measurements with the OFSS with assistance from Dr. P. Sreearunothai.

TECHNICAL PROGRESS AND RESULTS:

The planned synthetic approach encountered difficulties in early parts of the project; new approaches were more successful. Polythiophenes are presently the most important class of polymers for organic photovoltaics. Synthesis in this project created several new thiophene monomers that were polymerized to create new polythiophenes having varied side chains. Structures of these, pictured in a previous LDRD report, included trimethyloctyl and 2-butyloctyl that conferred high solubilities in non-polar media as postulated. This was a success of this LDRD. A second success was that excellent solubility in the high mobility liquid, isoctane, gave very fast electron attachment to polythiophene with butyloctyl side-chains. Electron attachment became faster than the 15 ps time resolution of the OFSS instrument.

Less successful was the synthesis to attach trap groups to these polymers. Yields of incorporating the traps into polymers were not quantitatively measured, but were clearly much smaller than expected based on feed ratios in the synthesis. Polymers either showed no capture or complete

capture of electrons or excitons. A second deficiency is that we did not have a good measure of the lengths of the polymer chains.

An interesting possible side benefit emerged. One of the new polymers, a polythiophene with long, sixteen carbon hexadecyl side chains, was found to yield films having a strongly red-shifted optical spectrum. This finding emerged in experiments performed by Dr. Iona Raluca Gearba, working in Chuck Black's group at the CFN. The value of such a red shift has potential to create solar cells that absorb a larger fraction of the solar spectrum. Our additional investigations and those of Dr. Gearba led to the conclusion that the films of this polythiophene did not actually possess strongly red-shifted absorption, but instead gave strong, wavelength-dependent light scattering, probably due to formation of nano- to micrometer aggregates.

While this LDRD did not produce a publication, it did find and demonstrate an approach to create polymers that can capture electrons on a very short time scale following an accelerator pulse. The 2-butyloctyl side chains that accomplished this are being incorporated into other polymers by a Japanese collaborator. Further we still expect that the polymers created in this LDRD will result in published work.

Ultra-thin Graphite Analog Compounds

LDRD Project 07-035

Tonica Valla

PURPOSE:

The purpose of this LDRD is to develop methods of synthesis of ultra-thin graphene layers, to probe their transport and spectral properties and to explore possibilities of modifying those properties with the ultimate goal of “magnetizing” graphene and exploring possibilities of making spin-polarized transport devices.

APPROACH:

This project aims at inducing the spin-splitting in graphene bands by the magnetic proximity effect – a hybridization of the sp^2 orbitals of graphene with the d orbitals of a magnetic atom (or ion) of the substrate (or adsorbate). Graphene, a monolayer of carbon with honeycomb crystalline structure, has attracted huge interest because of its exotic electronic properties and its potential to serve as a base for carbon-based electronics. Graphene’s low energy electronic structure can be easily tuned - it can be electron/hole doped by applying an electric and/or magnetic field. Particularly attractive is the possibility of inducing magnetism into the graphene bands. Spin-splitting of graphene bands would turn graphene into an ideal candidate for spintronics devices.

In collaboration with Igor Zaliznyak and Liyuan Zhang from CMPMSD and colleagues from CFN and Zagreb Institute of Physics, we have developed several methods of synthesis of ultra-thin graphene layers. Spectral and transport properties of these systems have been measured. Effects of magnetic and electric fields as well as modifications of electronic properties due to different adsorbates/substrates have been studied and ways of modifying graphene’s properties and inducing the magnetism have been explored in order to find the optimal system for applications in devices.

TECHNICAL PROGRESS AND RESULTS:

After a successful synthesis of graphene layers on different substrates, we have focused on studying their physical properties and on fabrication of devices used in transport experiments. We have used angle-resolved photoemission spectroscopy (ARPES) as the most direct probe of the electronic structure on all synthesized systems to check the quality and the doping level of graphene layers and to study the interaction of the graphene layers with various adsorbates. In particular, we have succeeded in performing the first

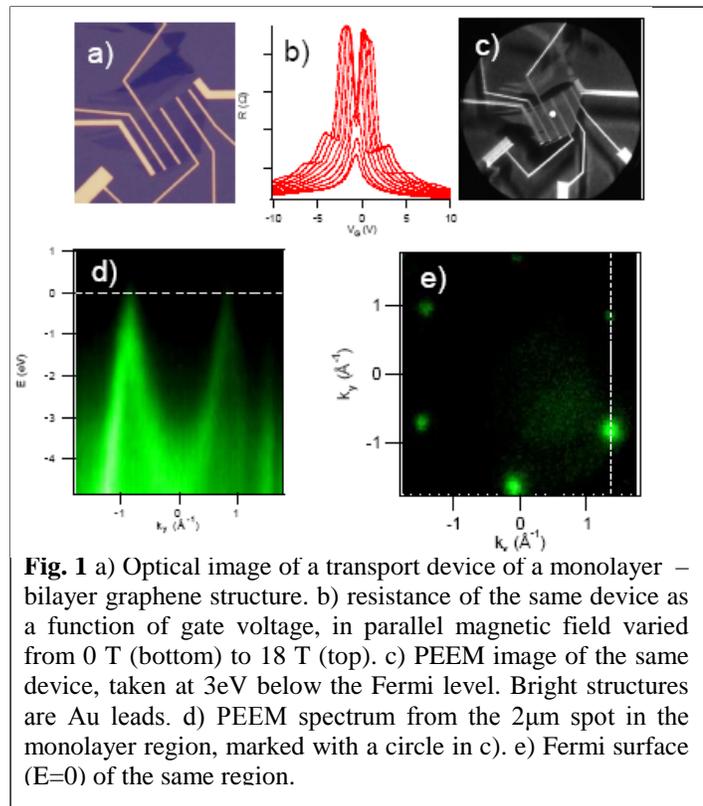
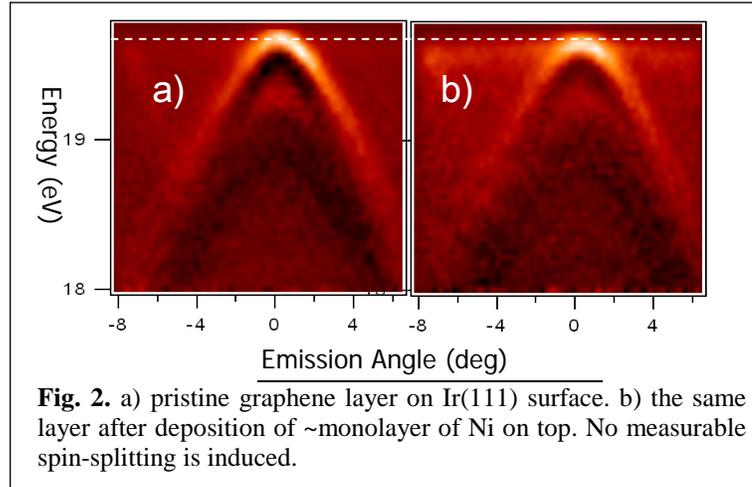


Fig. 1 a) Optical image of a transport device of a monolayer – bilayer graphene structure. b) resistance of the same device as a function of gate voltage, in parallel magnetic field varied from 0 T (bottom) to 18 T (top). c) PEEM image of the same device, taken at 3eV below the Fermi level. Bright structures are Au leads. d) PEEM spectrum from the $2\mu\text{m}$ spot in the monolayer region, marked with a circle in c). e) Fermi surface ($E=0$) of the same region.

microscopic ARPES from the very same sample that was used in transport measurements (Fig. 1).

We have demonstrated that our graphene layers are of extremely high quality and that adsorbates induce charge transfer into the graphene layers, cause weak or strong localization and open the gaps in the electronic structure. All of these effects allow modification of graphene properties in a targeted manner. We have also performed spectroscopic and transport studies of graphene layers upon adsorption of various ferromagnetic species in an attempt to induce magnetism into the graphene layers. In ARPES, we searched for the spin-splitting of graphene electronic states, and in transport, we looked for the change in resistivities after switching the magnetization of ferromagnetic overlayers and/or leads. Unfortunately, spectroscopic studies did not show any measurable spin-splitting of graphene states (Fig. 2).



We have also done transport measurements in a magnetic field at the National Magnet Lab. These experiments have been performed on our devices fabricated by L. Zhang and J. Camacho using lithographic facilities at the CFN. Mobilities of our graphene layers were amongst the highest ever measured on an SiO₂ substrate, demonstrating state of the art capabilities of our facilities and the world class quality of our devices. Studies at the National Magnet Lab showed a rich behavior of graphene conduction in high magnetic fields, still not understood by current theories. For example, we observed a peculiar metal to insulator transition in the N=0 quantum Hall state. These results will be submitted for publication in Science.

Although we could not demonstrate the magnetization and spin-splitting of graphene electronic states, this project has helped in developing the infrastructure and the expertise for synthesis and characterizations of graphene layers and transport devices of ultra-thin layered heterostructures. We are regular users of the CFN where our contact patterning and transport, structural and spectral studies (nano-lithography, STM, AFM, Raman) are done. Our ARPES and micro-ARPES or PEEM studies were performed at the NSLS and several other synchrotrons (ALS, Elettra). We have established strong collaborations with several CFN groups, the Condensed Matter Theory group and the Institute of Physics, Zagreb. The infrastructure, expertise and collaborations developed and established within this project will be used for future projects on similar systems. An immediate projects benefiting strongly from this LDRD is our new effort on so called topological insulators. Surfaces of these materials have exotic properties, very similar to those of graphene, with the additional advantage that they show intrinsic and very unusual magnetism, stemming from the strong spin-orbit coupling. These materials offer the same property that we were unsuccessfully trying to induce in graphene. We will use our infrastructure and expertise to explore the possibility of using those materials in spintronic devices.

Lipid-Coated Nanoparticles and Their Interactions with Lipid Membrane Surfaces

LDRD Project 07-036

M. Fukuto, L. Yang, and O. Gang

PURPOSE:

Exploring methods to render inorganic nanoparticles (NPs) both bio-compatible and bio-functional is important for facilitating biomedical and biomimetic-device applications of NPs. One method that is likely to be highly effective and versatile is to coat NPs with lipid bilayer or monolayer membranes. Lipid membranes provide a natural environment for membrane proteins and also have the potential to endow NPs with the ability to adhere to and penetrate into the cells by means of membrane fusion. This project aims to (I) explore methods for coating NPs of various sizes with simple lipid mono- or bilayer membranes, and (II) investigate the interactions of lipid-coated NPs with simple model lipid membrane surfaces.

APPROACH:

There already exist well-developed techniques for depositing lipid layers on *planar* solid substrate-aqueous solution interfaces (e.g., vesicle fusion method). We apply these to the highly curved surfaces of NPs and examine the effect of surface curvature on the ease and uniformity of lipid-layer coatings. NPs to be used are gold NPs (diameter > 5 nm dia.) and commercially available silica spheres (dia. > 20 nm). Matt Maye, a former Goldhaber fellow in CFN, synthesized the gold NPs. Sumit Kewalramani, the postdoctoral associate in CMPMSD supported by this LDRD, carries out the lipid-coating and dynamic light scattering experiments to extract size distributions and test the formation of lipid membrane around NPs.

Part II of our study will elucidate the interactions between the lipid-coated NPs (LCNPs) and other lipid membrane surfaces, which include a single lipid bilayer or monolayer at planar substrate-buffer or buffer-vapor interfaces. Lipid mixtures will be used to explore and tune the interactions that are based on, e.g., protein-mediated binding and electrostatic forces. Establishing expertise with these membrane surfaces is also an important aspect of this project. Flat membranes are well suited for initial studies because of their simple geometry and because we have the infrastructure for appropriate in-situ characterization tools (optical microscopy, AFM, synchrotron x-rays).

TECHNICAL PROGRESS AND RESULTS:

In FY07-08, we examined the role of surface ligand (biotin) density on a biotin-bearing lipid monolayer in controlling the 2D assembly of a model protein, streptavidin, at the aqueous buffer-vapor interface. The results of in situ synchrotron x-ray scattering and Brewster angle microscopy measurements as a function of the surface biotin density demonstrated that dense lateral packing of well-oriented proteins drove the 2D crystallization of streptavidin. Significantly, this study also demonstrated that the 2D assembly of nanoscale objects could be controlled by tuning the property of lipid membrane, which in this case was the surface density of protein-binding ligands.

In FY09, we focused on generalizing this lipid-membrane-mediated 2D assembly approach to nanoscale objects that assembled through electrostatic interactions (as opposed to the above, which was based on protein-ligand interactions). In particular, we studied the 2D assembly of

cowpea mosaic virus (CPMV) on cationic lipid monolayers at the aqueous solution-vapor interface (Fig. 1). Used here as a model monodisperse building block, CPMV is an icosahedral virus with an average diameter of 28 nm and is negatively charged when the solution pH is above its reported isoelectric point of $pI = 3.7 - 4.5$. The cationic lipid monolayer consisted of a binary mixture of lipids with neutral and positively charged head groups, and the monolayer surface charge density was controlled through the lipid composition. The interactions between the negatively charged CPMV and the cationic lipids resulted in the formation of a monolayer of lipid-bound CPMV at the interface. In order to understand the roles of electrostatic interactions and lateral packing density in the development of 2D order, we carried out extensive GISAXS measurements and mapped out the 2D phase behavior of lipid-bound CPMV as a function of the solution pH and the surface charge density in the cationic lipid monolayer. The results show that 2D crystallization of CPMV occurs when two conditions are met: (1) the solution pH is within a range of 4.4-5.0, which is just above the CPMV's isoelectric point such that CPMV carries a weakly negative charge; and (2) the charge density on the positively charged lipid monolayer exceeds a certain threshold. This demonstrates that the 2D crystallization can be induced by (i) reducing the charge (-) on the adsorbing particle and/or (ii) by increasing the surface charge (+) density on the substrate, both of which are expected to increase the lateral packing density of the adsorbed particles. We are currently extending this electrostatic 2D assembly approach to inorganic nanoparticles that are soluble and charged in water, such as citrate-stabilized gold nanoparticles.

In addition, in the fall of 2008, we designed, constructed, and commissioned the dual sample cell that was used in the above study. Use of this new dual-trough setup led to a 2-fold increase in the data-taking productivity at the synchrotron beamline and made it possible for us to map out, within the limited beamtime, the 2D assembly behavior of CPMV as a function of pH and lipid charge density.

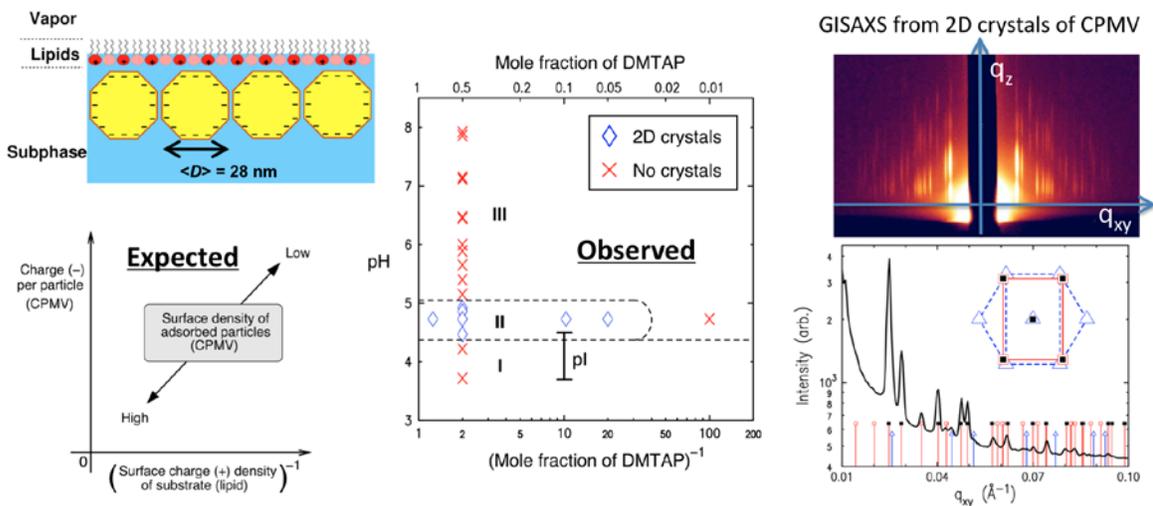


Fig. 1. (Left, top) Illustration of 2D assembly of negatively charged CPMV on a cationic lipid monolayer at the aqueous solution-vapor interface. (Left, bottom) Expected adsorption behavior of CPMV at the positively charged lipid membrane surface. (Middle) Observed 2D crystallization behavior of CPMV as a function of the solution pH and the inverse mole fraction of the cationic lipid (DMTAP) in the binary lipid monolayer. (Right) GISAXS pattern from a 2D crystal of CPMV at pH 4.9.

Angle-Resolved Time-of-Flight Ion Scattering Spectroscopy from MBE-Grown Oxide Thin Film Surfaces

LDRD Project 07-038

Adrian Gozar

PURPOSE:

We use the time of flight (TOF) low energy ion scattering and recoil spectroscopy (ISARS) technique in order to get information about surface properties of oxide films grown by molecular beam epitaxy (MBE). In particular, these properties are primarily related to the composition and the structure of the topmost atomic layers. Such information can provide real-time feedback for epitaxy and information about the atomic layer-by-layer (ALL) growth of single phase films or heterostructures. So far we have used the TOF-ISARS technique for the study of films of high temperature superconductors (HTS), a class of strongly correlated electronic materials.

APPROACH:

The ALL-MBE system was used to synthesize HTS films, multilayers, and superlattices. The TOF-ISARS setup consists of a pulsed source generating K^+ ions with energies in the 7-13 keV range. The intensities are measured in the scattering plane by micro-channel plate and mass spectroscopy of recoiled ions (MSRI) detectors mounted at several fixed angles. The system allows for a continuous change in the azimuthal angle. Surface composition and termination can be studied by monitoring the change in the cross section as a function of angular scattering geometry and as a function of the layer-by-layer deposition sequence. Experimental data is compared to the semi-quantitative information obtained from classical trajectory simulations based on the binary collision approximation.

TECHNICAL PROGRESS AND RESULTS:

- TOF-ISARS oscillations: we checked if TOF-ISARS can be used to study the layer-by-layer growth by recording of what we named ‘TOF-ISARS oscillations’. The most important real-time feedback during growth comes from reflection high energy electron diffraction (RHEED) and from monitoring the sequence and structure of RHEED oscillations which are observed during growth of atomically smooth films. However, electron diffraction is not chemically sensitive. TOF-ISARS data are shown in Fig. 1. They indicate that such oscillations can be used for studying deposition and real-time calibration of absolute rates for specific elements.
- Chemical profile at interfaces: we used TOF-ISARS to determine the chemical profile (cation interdiffusion) at interfaces in bilayer films where transport data indicates the existence of high temperature interfacial superconductivity. We studied the evolution of the Sr peak intensity during the growth of $La_{2-x}Sr_xCuO_4 - La_2CuO_4$ bilayer systems and we found that our data can put a limit of one unit cell for cation mixing, see Fig. 2. This is an upper bound because of subsurface scattering (that can be clearly seen also in Fig. 1 where the oscillations minima are not zero). A simple phenomenological model including such effects and assuming an interdiffusion proportional to the nominal difference in Sr concentration between adjacently deposited layers reveals indeed a more abrupt profile, consistent with transmission electron spectroscopy and soft X-ray diffraction data in superlattices. This is a great advantage because it can be done in-situ and does not involve either sample preparation or expensive instrumentation (e.g. synchrotron light) in order to obtain such important information. Substrate surface termination studies using TOF-ISARS are planned for precise determination of the initial layer sequence and achieving defect-free interfacial layers in ultra-thin bilayer films (2-3 unit cells).

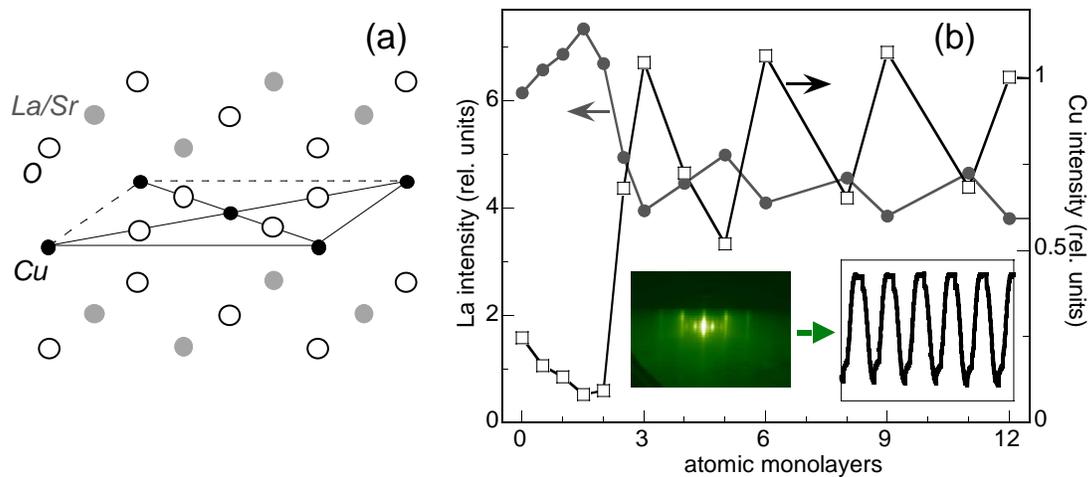


Fig.1: (a) The '214' structure of La_2CuO_4 (LCO) crystal. (b) TOF-ISARS oscillations: MSRI intensities of La and Cu peaks during the layer-by-layer deposition. Three atomic monolayers correspond to the structure in (a); the deposition sequence was $[\text{2LaO-CuO}_2]_{12}$ which corresponds to 6 unit cells of LCO. The inset shows typical RHEED oscillation pattern during growth of LCO films.

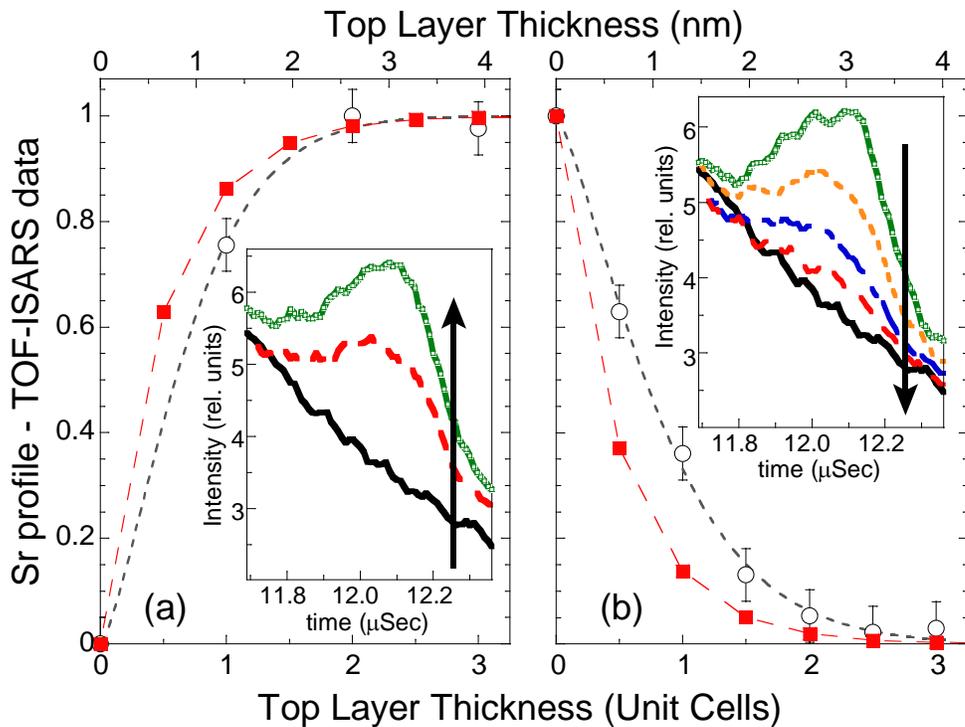


Fig.2: (a) TOF-ISARS data as a function of top layer thickness in a La_2CuO_4 (I) - $\text{La}_{1.55}\text{Sr}_{0.45}\text{CuO}_4$ (M) (I-M bilayer film (the last letter denotes the top layer)). The main panel displays the normalized integrated intensity of the Sr recoil peak in M (open circles). The Sr concentration profile, estimated from a phenomenological model assuming sub-surface scattering, is displayed by filled squares. Dashed lines are guides for the eye. The inset shows the evolution of the Sr recoil peak with each unit cell of M deposited on the I bottom layer as recorded in the TOF data. (b) Same as (a), but on the I side of M-I structure.

Characterization of Enzymatic *O*-acylation to Facilitate Biomass and Bioenergy Production

LDRD Project 07-047

Chang-Jun Liu

PURPOSE:

Enzymatic *O*-acylation and de-acylation are the common biochemical modifications for plant cell-wall lignocellulosic components and a variety of plant secondary metabolites. Acylation of lignocelluloses changes cell wall structure and biodegradability. The acylated non-structural metabolites play vital physiological and ecological roles for plant survival. Despite the wide occurrence of *O*-acylation in plant metabolisms and cell wall modifications, the enzymes involved in these processes remain largely elusive. The goals of this project are to systematically characterize plant acyl-CoA dependent acyltransferases and acylesterases using biochemical genomics and reverse genetics approaches. We expect to identify the specific enzymes involved in cell wall modification and biomass production, and then to explore the potential application in modulating acylation enzymes to promote plant biomass sustainability and cellulosic biomass digestibility.

APPROACH:

Biochemical genomics approach: we propose to identify all the putative acyltransferase and acylesterase genes from Arabidopsis and poplar genomes; followed by bioinformatics and transcriptional profiling analysis, we conduct comprehensive *in vitro* biochemical assay to systemically characterize the gene functions involved in cell wall biogenesis and modification.

Reverse genetics approach: as a complementary approach, the corresponding Arabidopsis T-DNA insertion mutant lines will be screened and analyzed to detect the compositional changes of plant cell wall resulting from the deficiency of particular acyltransferase and/or acylesterase genes.

In collaboration with NSLS Scientist, Dr. Lisa Miller, the NSLS FT-IR facility will be used for cell wall compositional analysis to monitor the changes of the cell wall acyl esters.

TECHNICAL PROGRESS AND RESULTS:

In the previous fiscal year, in order to understand the molecular mechanism of cell wall acylesterification, we analyzed the wall-bound acylesters of poplar by using Liquid Chromatography-Mass Spectrometry (LC-MS), Fourier Transform-InfraRed (FT-IR) microspectroscopy, and the synchrotron InfraRed (IR) imaging facility. The results revealed that the cell wall of dicotyledonous poplar, as the walls of many monocot grasses, contains a considerable amount of acylesters, primarily acetyl and *p*-hydroxycinnamoyl molecules. The “wall-bound” acetate and phenolics display a distinct tissue specific-, bending stress responsible- and developmental-accumulation pattern, indicating distinct roles of different “wall-bound” acylesters in poplar cell wall structural construction and/or metabolism of cell wall matrix components. This study affords valuable information in understanding the physiological roles of cell wall modification and in guiding genetic manipulation of cell wall biomass to facilitating its conversion. The work was published in the *Planta* (2008). We also produced a number of recombinant proteins for the poplar putative acyltransferases and continually performed comprehensive *in vitro* functional screening in FY 2008.

During FY 2009, we continually refined/clean up the bioinformatics and expression analyses on Arabidopsis and poplar acyltransferase genes. We revealed several unique features of acyltransferase family members for their gene structure, organization and distribution on genomes in both species; and we discovered a batch of tissue-specific and stress-inducible expressing genes. Those analyses afford a strong knowledge basis for understanding acyltransferase genes' evolutionary relationships, and the gene functions implicated in plant growth, development and metabolism. Those studies lead to a publication in the *Plant Molecular Biology* (2009).

We characterized a group of cell wall acylesterases from bioenergy crop Poplar. We conducted a detailed biochemical and gene expression analysis on one of the acylesterases and demonstrated that it is preferentially responsible for modifying the primary cell wall component pectin. Expressing this gene in plants caused severe growth and development effects, particularly for the development of plant reproductive organs. Using transgenic plants, we studied the biological functions of this identified pectin acylesterase on pollen grain development, germination and on the biogenesis of primary cell wall.

Based on the bioinformatics studies on Arabidopsis acyltransferases genes, we screened about 30 homozygous lines from more than 60 of the Arabidopsis BAHD family of acyltransferase T-DNA insertion mutant lines. We prepared cell wall materials from the selected mutant lines and isolated different fractions of cell wall components. After that, we performed a comprehensive chemical analysis on the cell wall compositions of mutant plants. Those studies led to the identification of a set of the wall-bound phenolics reduced mutant lines. By analyzing one of those mutant plants, we characterized a novel acyltransferase responsible for synthesizing the aromatic domains of cell wall lipid polyester (suberin) in roots and seeds and subsequently we demonstrated the physiological functions of suberin phenolics in plant growth and resistance to environment stresses. We expected that this gene can be used to engineer bioenergy crops to enhance the capacity of stress resistance, therefore, enabling crops to grow on marginal land for biomass feedstock production, meanwhile, to re-route polyphenolic biosynthesis to modulate cell wall digestibility. Currently we are conducting the proof of concept experiments using model plants.

In addition, we are continually characterizing several other identified acyltransferase mutant lines to elucidate the gene functions in cell wall acylation.

Functional Neurochemistry

LDRD Project 07-048

Elisabeth C. Caparelli

PURPOSE:

Functional magnetic resonance imaging (fMRI), the method of choice for mapping brain function, is sensitive to unwanted contributions from large blood vessels, is not quantitative, and does not provide neuronal markers to study the dynamics of metabolic events during neuronal activation. Quantitative proton magnetic resonance spectroscopy (1H-MRS), on the other hand, can accurately determine metabolite concentrations and provides important information for the study of brain metabolism, which could validate fMRI measures and help understand brain function at the chemistry level. Thus, we aim to develop functional 1H-MRS (1H-fMRS) to measure changes in metabolites during brain activation, a technique that could be a powerful tool to study synaptogenesis, neurogenesis, or processes involving structural changes in the brain.

APPROACH:

Brief, as well as, prolonged blocked visual stimulation will be used to induce measurable changes of metabolite concentrations in primary visual cortices, while fMRI and fMRS will be acquired in an interleaved fashion. Novel RF surface coils will be developed for improved MRS acquisition. Accurate spectral analysis, with increased sensitivity, will be developed for the detection of metabolic activation changes that cannot be determined in conventional fMRS approaches.

TECHNICAL PROGRESS AND RESULTS:

During this project we have developed new RF coil prototypes, new methods for data acquisition and analyses, and stimulation paradigms, more suitable for the proposed experiment.

RF coil development: We developed a novel slot-and-hole surface coil operating at 170.2 MHz, the resonance frequency of protons at 4-Tesla magnetic field. Since images acquired with this probe have higher SNR ratio and better uniformity than standard surface coils, this RF coil design is a good candidate for different MRI and MRS applications.

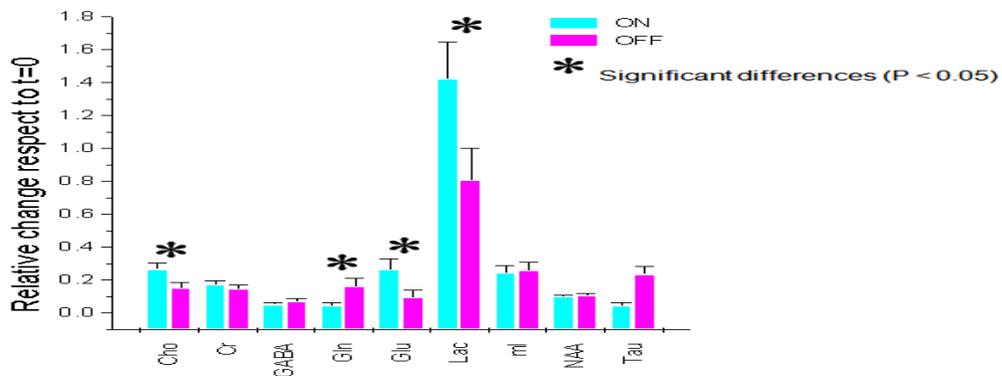
Data acquisition: We adapted a single, voxel double, spin-echo sequence (PRESS) with short echo time (TE/TR = 30/2000 ms) to collect a time series of water-suppressed spectra. Figure 2 demonstrates that this technique provides quantifiable concentrations, with good temporal stability, for the major brain metabolites (total acquisition time = 40 minutes).

Automatic LC data analysis method: We implemented an automatic metabolite quantification approach using a spectra database of brain metabolites at 4-Tesla magnetic field, the commercial LC software package, and the Matlab software that allows us to determine time-varying metabolite concentrations from the MRS time series (Fig 2).

Stimulation paradigms: We developed flickering checkerboard paradigms for brief and prolonged visual stimulation using the Matlab, Visual Basic, and Visual C languages. Stimuli are presented to the subjects on MRI-compatible LCD goggles connected to a personal computer. A trigger signal from the MRI console precisely synchronizes the stimuli with the fMRI/fMRS acquisition,

allowing the use of time-locked 1H-MRS techniques. Specifically, the brief (3 minutes) stimulation paradigm has a 30-seconds flickering (5-Hz) checkerboard vs. 30-seconds baseline (black screen) blocked design. This paradigm robustly stimulates the occipital cortices during fMRI. The prolonged visual stimulation uses a similar flickering checkerboard (12-minutes long) that starts after 5 minutes of resting baseline. An additional 15 minutes long resting baseline follows the stimulation block.

Studies in humans: A group of healthy volunteers were evaluated with our fMRI and fMRS techniques. The fMRI scan was done first and the corresponding activation pattern was used to identify brain regions in the occipital cortex that were stimulated by the 5-Hz flickering checkerboard paradigm. This information was used for planning individual locations and sizes of the MRS voxels. MRS spectra were acquired every 2 seconds using a short TE (30 ms) and averaged in groups of 16 to increase SNR. Thus, time series with 57 spectra resulted from each of the 29 minutes long fMRS acquisitions. The time-varying MRS data was fitted to our spectra database using our automatic LC model approach. The results indicate that visual stimulation increases choline [Cho], GABA, glutamine [Gln], and lactate [Lac], and decreases N-acetyl-aspartate [NAA] and glutamate [Glu] in activated areas of the occipital cortex; however these changes seem to be significant just for a few metabolites Cho, Gln, Glu and Lac (see figure).



These observations suggest that brain activation may also be associated with metabolic changes other than only the change in blood oxygenation. However, the local induced magnetic susceptibility change during activation produced by blood oxygenation level dependent (BOLD) effects, which represents just 2-3% of signal change in the MR imaging, can mask the MRS results by modifying the baseline, phase, line width and the resonance frequency of the spectra. For these reasons, we have also evaluated the magnetic field distribution of the human head under the high magnetic field (Paper in press – see data collection). We finally verified that our results are affected by the susceptibility artifacts that are responsible for changes in the local magnetic field distribution and are generated by the physiological noise, magnetic field changes arising from the draining veins and subject head motion.

In conclusion, this project has shown that functional MRS can be helpful to better understand the association between metabolic changes and hemodynamic response. However, a method to reduce the susceptibility artifacts in the MRS measurements needs to be implemented to validate the results.

Miniaturized RF Coil Arrays for MicroMRI

LDRD Project 07-054

S. David Smith

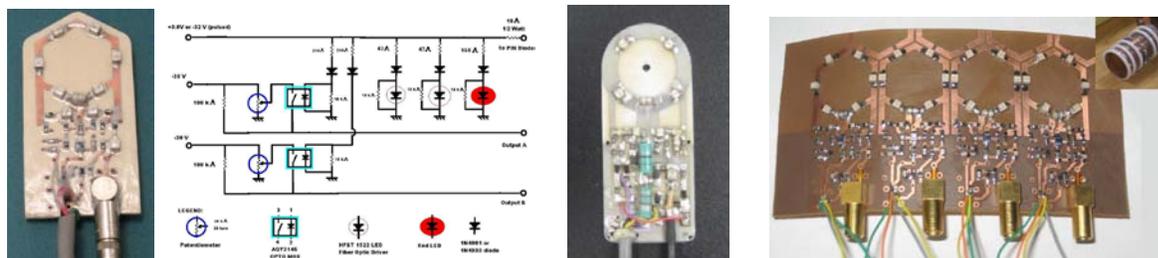
PURPOSE:

Our project's goal is the development of novel, high performance radio frequency (RF) coil arrays for improved imaging on the Medical Department's 9.4 Tesla (400 mhz) micro MRI system. We will design and build several coil arrays, specifically for use in the 'parallel imaging' mode. The greatest challenge in designing array coils for high field small animal MRI systems, is in the fabrication of the *highly miniaturized* RF coil arrays that are fully integrated with their associated electronics. Independent receiver chains and tuning circuitry are required for each coil element and maximum performance can be achieved only if the early stages of the receiver chains, such as the tuning circuitry and signal pre-amplifiers are incorporated into the construction of the coil array itself. Coil arrays, when used in the parallel imaging mode, can dramatically improve imaging performance in terms of increased signal to noise ratio (SNR), reduced image acquisition time and image coverage. The benefits provided by array coils are based on the fact that smaller coils will provide a better sensitivity (i.e. increased SNR) over a smaller imaging volume or "field of view" (FOV). The reduced field overlapping views of the multiple coils are then combined into a single image, providing further benefits of increased FOV, SNR and acquisition speed. Realization of the goal of providing increased SNR will benefit every aspect of the Medical Department's Micro MR Imaging research program, yielding the same increased performance as might be obtained in a much more costly fashion by upgrading to a higher magnetic field strength.

APPROACH:

Parallel imaging is a recently developed technique, widely applied in the most advanced commercial clinical MRI systems. Comparable devices are not yet commercially available for small animal Micro MR imaging systems. MicroMRI applications need reduced imaging volumes for small animal subjects, vis a vis, clinical MRI applications. The small size of the imaging volume leads to more difficult requirements for miniaturizing and more exacting tolerances in coil construction and assembly. Expertise in these areas is being provided through collaboration with the Central Shops' Tom Lambertson, William Lenz of the Physics Department, and the Instrumentation Division's Sergio Rescia.

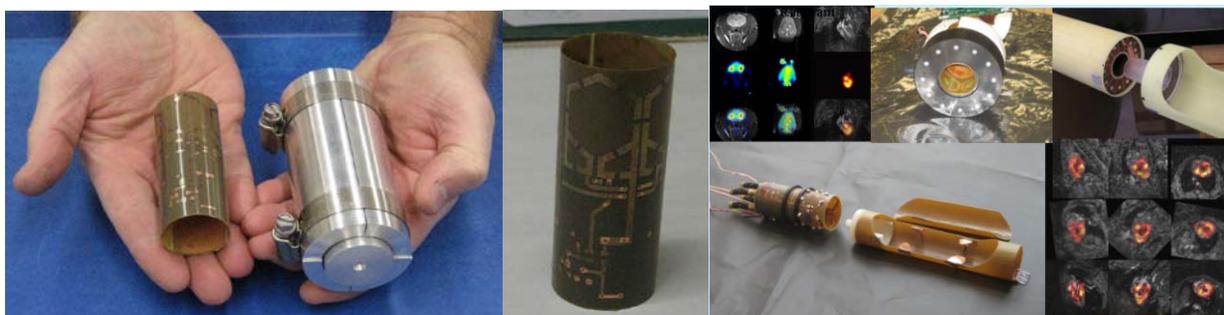
TECHNICAL PROGRESS AND RESULTS:



The research focus in the first half of fiscal 2008 was the completed single coil design and component evaluations begun in FY 2007. The basic single coil design shown in the upper left hand corner of the figure above, together with the modified detuning circuitry described in the schematic has been shown to give superior performance to that of the original coil provided with our 9.4 Tesla MR Spectrometer system by the manufacturer. It is now being used for all MR

Imaging and MR spectroscopy studies at our MicroMRI laboratory. Further reductions in size can be accomplished upon the receipt of components currently on order. We have planned fabrication coils at $\frac{1}{2}$ and $\frac{1}{4}$ scale to the present design.

During the second half of FY2008, efforts centered upon the development of fabrication techniques for making coil arrays with *precisely* controlled geometrical relationships amongst coil elements. Printed circuit techniques allow for exacting geometrical specification on a two dimensional surface. In order to extend this precision to a three dimensional space, we developed a lamination technique which forms the *planar* printed circuit layout into a cylindrical array. Components can then be mounted on the outside of the cylinder. This technique maintains the full precision of the printed circuit layout, while providing sufficient structural rigidity to ensure that intra coil couplings (mutual inductances) are stable and measurable.



During FY2009, variations of the four coil array pictured above were fabricated using our coil form molding technique and, after testing, put to use in a specialized MicroMRI application in which BNL's RatCAP PET ring was operated inside the 9.4 T Bruker MR system, simultaneously with the MR. Significant technical issues had to be overcome to fit all components together and still provide access to imaging volume sufficient to accommodate in vivo studies of both rat brains and whole body mice. Excellent quality results were obtained with this configuration, where the four individual coils were combined electronically to operate as a single quadrature transceiver coil. We have submitted additional PC layouts for fabrication, which can be formed using the same mold and which would operate as a four independent receiver coil array. Other PC layouts in the pipeline for fabrication, would allow evaluation of the performance of newly available MEMS (Micro Electro-Mechanical Switch) devices as replacements for the PIN diodes used for coil detuning. When MEMS technology variable capacitor devices are finally available, we plan to incorporate them into an improved transceiver design also. Such devices, once available, would provide significant benefits to the PET/MRI device and also allow development of more practical transmitter arrays.

A Non-Fermentation Route to Convert Biomass to Bioalcohols

LDRD Project 07-059

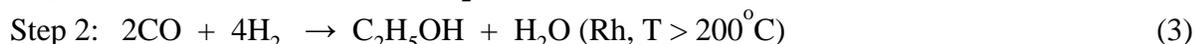
Devinder Mahajan

PURPOSE:

In the commercial biomass fermentation route, ethanol-producing microorganisms utilize only C-5 and C-6 sugars leaving other complex molecules unconverted and produce 2 moles of undesirable CO₂, wasting 2 carbon atoms in the feedstock (equation 1). The alternate “Thermochemical route”, is a two-step process through which biomass from a variety of sources can be converted into useful fuels and chemicals. In the latter route, the first step is biomass depolymerization via gasification to yield synthesis gas (or syngas), primarily a mixture of CO and H₂ (equation 2). The second step follows with conversion of syngas into ethanol with Rh-based catalysts (equation 3), although total carbon utility remains a challenge due to production of unwanted side products such as methane.



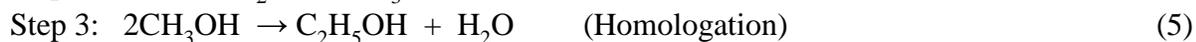
Two-step “Thermochemical” Route:



Our focus is on designing highly active catalysts that: 1) operate in aqueous media, 2) can efficiently convert syngas into ethanol under low temperature/pressure conditions. The objective of this research aligns with the BNL strategic goal to synthesize biofuels. A successful proof-of-concept will lead to new technologies for synthesis of higher alcohols and/or other oxygenates that are of interest as commercial transportation fuels.

APPROACH:

The literature studies show that Rh-based systems are the catalyst of choice for ethanol production vis equation 3. However, ethanol yields are low due to poor selectivity at temperatures >200°C and a copious amount of undesirable methane is also produced. Our proposed approach envisions efficient methanol synthesis (equation 4). Methanol can then undergo homologation (carbon-carbon coupling) to produce ethanol (equation 5) or dehydration (C-O-C formation) to yield dimethyl ether (equation 6).

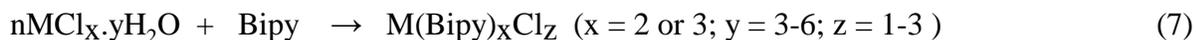


A typical experiment was conducted as follows. A Parr batch unit consisting of a 300 mL pressure vessel was utilized for catalyst screening studies. The unit was fitted with ports for gas/liquid inlets, liquid/gas sampling valves and a rupture disc as a safety device. Each run involved mixing 1 mmol catalyst, 100 mL methanol and 0.1 mol base (if added) in the vessel and pressuring with 300 psig N₂ (inert) gas. The vessel was heated after sealing and any pressure change was recorded. The reactant/product were analyzed before/after heating to identify products produced. In addition to gas chromatographs, infrared spectroscopy was used to confirm products.

The work was coordinated with Drs. K. Ro and P. Hunt from the Agriculture Research Service-United States Department of Agriculture (ARS-USDA), Florence, South Carolina facility for application to syngas produced from animal waste.

TECHNICAL PROGRESS AND RESULTS:

In FY 07, two tasks were initiated. First, synthesis of water-soluble metal complexes was developed. This involved refluxing metal chloride with a basic ligand (2,2'-Bipyridyl or Bipy) in methanol/water solvent for 15 minutes, followed by cooling to yield yellow or green crystalline compounds, depending on the metal used (M = Rh, Ru, Ni; Ligand/M = 1/1 or 2/1). The synthesized complexes were characterized via infrared and elemental analysis. However, it was found that the same complexes could be prepared *in situ*.



The second task was to evaluate the synthesized catalysts for methanol conversion to higher oxygenates via equations 5 or 6. Two catalysts, Rhodium on alumina (Rh/Al₂O₃) and triruthenium dodecacarbonyl (Ru₃(CO)₁₂) were screened. No reaction occurred at 150°C but at 200°C, reaction 6 dominated to produce dimethyl ether (DME) and only trace ethanol was quantified. The activity followed the order: Ru (5.9%) > Rh (2.9%) where the values in parentheses are DME volume % in the collected liquid after the reaction.

In FY 08, the focus was to maximize DME production since this molecule is considered a replacement for diesel. A total of 15 runs were conducted to compare activities of Ni and Co, metals that are less expensive than Ru. The total reaction time was typically 6.5 hours at 200°C. NiCl₂ produced 6.6 vol.% DME and 52.3% H₂ but no CH₄ was produced. With CoCl₂, the product distribution was: DME: 8.8%; H₂: 38.8% and CH₄: <0.5%. The data with CoCl₂ showed that: 1) added base (KOH) increased DME production: 3.1% vs 8.7%, 2) increasing reaction temperature decreased reaction time: 250°C (1.5 h) vs 200°C (6.5 h) and 3) CoCl₂ was more effective for DME production: CoCl₂ (8.7%) vs NiCl₂ (5.6%). Neither Ru₃(CO)₁₂ nor CoCl₂ catalysts produced ethanol, showing methanol homologation was not preferred under the moderate reaction conditions. The co-production of DME and H₂ is of interest. H₂ is likely first produced by methanol decomposition and then it is augmented by the water-gas-shift reaction. The absence of CO₂ in the product is due to its reaction with the base. Results also show that with NiCl₂, the product shifted from DME to ethanol (8.47 vol%) by increasing the temperature from 200°C to 250°C, suggesting a change of reaction pathway from dehydration to homologation.

In FY 09, the work focused on extending the concept to form oxygenated fuels from glycerol, a by-product of biodiesel production. A series of runs in which methanol was replaced with 90% glycerol in water were conducted at 200°-280°C in the presence of H₂. With Mo(CO)₆ as catalyst precursor, the yield of mixed (C1 – C4) alcohols was 3-5 wt%. In the presence of a base, the yield increased to 15wt% that included about 2% ethanol. The post-run analysis of the catalyst showed that Mo(CO)₆ decomposed to produce Mo that catalyzed the alcohol production reaction.

Fate and Reactivity of Carbon Nanoparticles (CNPs) Exposed to Aqueous Environmental Conditions

LDRD Project 07-062

Barbara Panessa-Warren and Kenya Crosson

PURPOSE:

The current use of carbon nanoparticles (CNPs) in numerous types of commercial products (building materials, paints, lubricants, filters, electronics, sensors, various personal care products, tires, nanotextiles, sports equipment, cosmetics and bio-medical diagnostic and therapeutic preparations), has dramatically increased globally in the past few years¹. Following nanoproduct use and disposal, these nanomaterials are now in sewer water and landfills, where the possibility of biodegradation and leaching of nanoparticles (NPs) into environmental waters is high. Yet, little is known about CNP, and especially carbon nanotube (CNT), reactivity and toxicity in these aqueous environments (PBS-saline and fresh water), and even less is known about risks to human health from environmental NP contamination. This investigation examines how CNPs may change their physico-chemical characteristics and subsequent toxicity following extended aqueous exposure (0.4 to 3 years) in 3 aqueous environments; pure fresh water; saline and fresh water with Suwannee River² natural organic matter (NOM); and how CNP changes affect human epithelial cells functioning as the protective lining in the respiratory and digestive tracts.

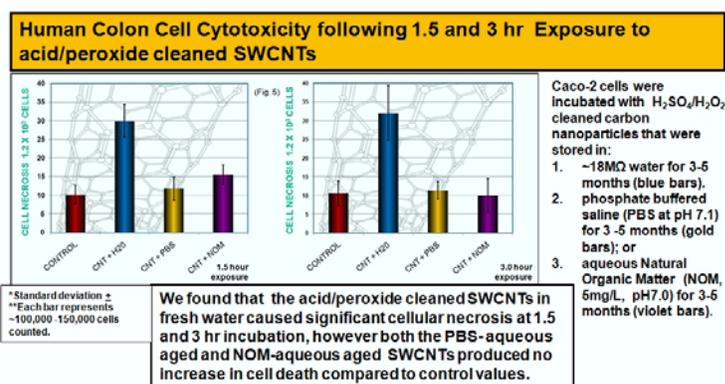
The objective of this study was to evaluate if CNPs (currently in commercial products), exhibited altered inherent physico-chemical characteristics or cytotoxicity, when exposed (3mos. to 3.5 yrs) to aqueous environments (ultrapure fresh water; saline; and freshwater with NOM); and how this information could be used to **1.** predict and reduce CNP reactivity during handling and storage, to work more safely with these new NPs; **2.** develop safe disposal strategies that could ameliorate risk to environmental waters; **3.** identify if CNPs in surface waters (due to disposal via drains, waste water or leaching from landfills), were capable of damaging human protective epithelia from the lung and colon; and **4.** determine by analyzing ultrastructural NP-cellular interactions following exposure to aqueous-aged CNPs, what risks, if any, these CNPs in environmental waters posed to exposed human cells. BNL has a commitment to environmental stewardship and is continually assessing how to improve laboratory safety. With the new Center for Functional Nanomaterials on site, it is now possible with state-of-the-art equipment to do this type of research developing safer strategies for handling, storing and disposing of engineered NPs.

APPROACH:

By using defined (simulated environmental) aqueous-aging of the NPs, it was possible to identify **(a)** what NP physico-chemical characteristics (analysis of size, shape, surface defects, surface reactive groups, formation of agglomerates etc. done by FTIR, UV-VIS, DLS and TEM at the Center. For Functional Nanomaterials, Dr.O.Gang) were altered following aqueous-aging/over time; **(b)** how these changes effected NP-human cell interactions (CNP binding, entry, cellular processing, and nanoparticle fate) studied by TEM, SEM, electron diffraction and elemental analysis); **(c)** cell viability of exposed monolayers analyzed by SEM, and light microscopy vital staining; **(d)** CNP agglomeration or aggregation formation (ultrahigh TEM and STEM imaging, UV-VIS and elemental analysis at the Center for for Functional Nanomaterials, Drs. E.Sutter & L.Zhang); and **(e)** how this affected living cell-NP reactivity and cytotoxicity (thin section TEM analysis of nanoparticle intracellular degradation, bioaccumulation/ excretion done at the Instrumentation Division, Dr.J.Warren).

Follow-on Implications: Our results revealed that even highly damaging CNPs were made minimally damaging to both human lung and colon cells, following aqueous-aging (at least 3 mos) in fresh water with NOM, or PBS-saline, which caused the CNPs to become embedded in agglomerates. The resultant agglomerates had protruding open-ended nanobundles and CNTs, which were associated with plasma membrane and organellar cell damage, and increased necrosis. At the time of this report, an NIEHS proposal has been submitted (May, 2009), and we are continuing to pursue funding (USDA and NIH/NIEHS proposals) for early spring 2010. We are exploring collaborations (NATO, EU) with Italian National Physics Laboratory scientists also.

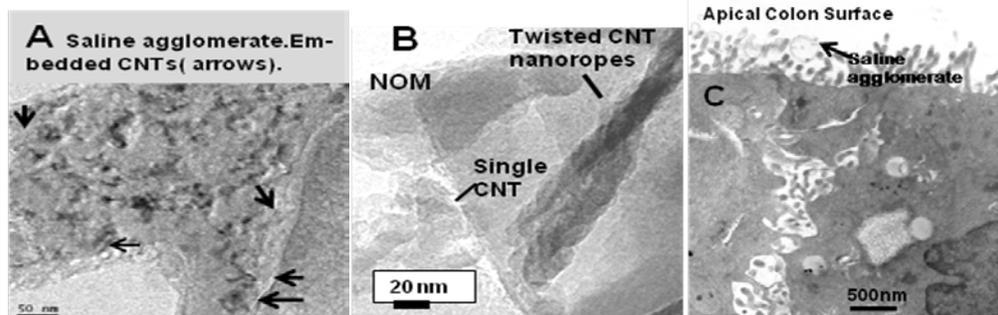
TECHNICAL PROGRESS AND RESULTS: Previously we found that cleaned single walled carbon nanotubes (CNTs and nanoropes), stored in ultra-pure 18 MΩ fresh water for 0.7- 7 years showed increased CNT oxidation (by FTIR) with exposure time. In all cases these CNPs when exposed to human lung monolayers produced a 4-5 fold increase in cell death compared to controls, with severe damage to lung cell membranes³. However when lung cells were exposed to CNTs aged for 90-120 days in NOM, or PBS-saline, the CNTs produced no surface cellular membrane damage, nor increased cell death (compared to controls), suggesting reduced toxicity³.



LDRD Second year: Human colon monolayers, were incubated with acid/peroxide cleaned CNTs, and as-produced(uncleaned) CNPs, that had been aqueously-aged for 3 mos to 3 years in 18MΩ ultrapure water; fresh water with NOM; or PBS-saline. Pure water-aged CNTs produced more than 2 times the colon cell death seen in controls at 1.5 and 3 hr exposures (**Fig.1**).

However the NOM and saline aged CNTs produced no cell death above control levels following the same exposures (**Fig.1**). We found by TEM that this reduced toxicity was due to the formation of agglomerates with embedded CNPs. See **Fig. A** where the CNTs (arrows) were surrounded and embedded in salt; and **Fig. B** which shows twisted bundles of CNTs embedded within a NOM-agglomerate. TEM thin sections of cells exposed to saline- (**Fig. C**), and NOM-aggregates, showed no internal organellar colon cell damage or NP-bioaccumulation. However the uncleaned CNPs aged in saline, that originally contained Ni and Y metal catalyst, appeared biocompatible in viability studies, but intracellular TEM imaging revealed organellar damage associated with lysosomal agglomerate degradation and metal release within the cells.

1. The Project on Emerging Nanotechnologies (Aug.2009).Inventory database. PEW Trusts.
2. International Humic Substance Society (IHSS), St. Paul, MN.
3. Panessa-Warren et al., 2009.J. Environ. Pollution, 157:1140-1151.



Development of Room-Temperature CdMnTe Gamma-Ray Detectors

LDRD Project 07-073

Yonggang Cui

PURPOSE:

The goal of this project is to develop new room-temperature gamma-ray detectors based on CdMnTe (CMT) crystals. Its wide band-gap, high resistivity, and good electron-transport properties make it a viable candidate for detecting gamma rays. In addition, its relatively low-temperature growing process ensures good compositional uniformity and fewer impurities, potentially resulting in a high yield of the crystals for making detectors and large-area detector arrays.

In this project, we investigated the required characteristics for CMT as a material for gamma-ray detectors. The success of this work led to increased knowledge of the crystals for radiation-detection applications and new results for CMT's properties and their relationships to device response.

APPROACH:

CMT crystals have been proposed as potential gamma-ray detectors. Mycielski *et al.* (2005) discussed the current state-of-the-art of CMT crystals specifically grown for nuclear-detector applications. Indium (at $\sim 10^{17} \text{ cm}^{-3}$)-doped $\text{Cd}_{0.87}\text{Mn}_{0.13}\text{Te}$ crystals grown at the Institute of Physics, PAS (Warsaw, Poland) exhibited resistivity and mu-tau products exceeding $10^{10} \Omega\text{-cm}$ and $10^{-5} \text{ cm}^2/\text{V}$, respectively. These crystals were used to fabricate devices that could detect 5.5-MeV alpha particles from an ^{241}Am source, and gamma radiation from ^{241}Am and ^{57}Co sources. The present electron mu-tau value of $\text{Cd}_{0.87}\text{Mn}_{0.13}\text{Te}$ detectors ($\sim 10^{-5} \text{ cm}^2/\text{V}$) is too small to assure good spectral performance for long drift-length detectors. This project seeks to improve the transport properties of CMT materials to produce a new class of solid-state gamma detectors for spectroscopy and imaging.

In this project, we collaborated with PAS on crystal growing. Dr. Mycielski grew CMT ingots. All the CMT samples were tested at BNL, and the results were fed back to PAS for improving the crystal growing process. We repeated this loop to accomplish higher resistivity, higher mobility-lifetime product, and lower defect density crystal growth methods.

For each CMT sample, we proceeded with the crystal polishing first, followed by IR measurement to investigate the Te inclusions in the bulk of crystals, and I-V curve measurement to select high resistivity samples. For the high resistivity samples, we developed contacts on the surfaces using an electroless gold method. In addition to characterizing and testing these detectors with sealed sources, we also used x-ray beams at the NSLS to characterize the electrical-, structural-, and transport- properties of CMT on a micron scale. These properties were correlated with other material properties to understand nonuniformities and improve surface preparation processes.

We also did EPD (etch pit density) measurements on CMT samples. This measurement helps us identify the defects that are invisible under infrared light.

Another investigator involving in this project is A. Hossain.

TECHNICAL PROGRESS AND RESULTS:

Several low-resistivity CMT:V samples were examined. Twins, grain boundary and dislocations were identified in these samples. These findings would help the crystal grower to improve the technique of crystal growth.

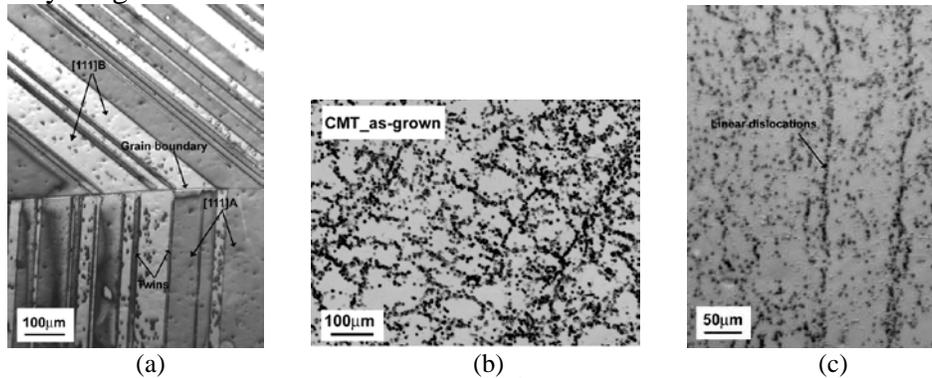


Fig. 1. (a) Twins and grain boundary in a CMT:V ($6 \times 10^{16} \text{ cm}^{-3}$) sample revealed by etching with EAg-1 solution. (b) and (c) dislocations in a CMT:V ($3 \times 10^{16} \text{ cm}^{-3}$) sample revealed by etching with Nakagawa solution.

We tested a few In-doped CMT samples. We were able to get an ^{241}Am spectrum from a bar-shaped detector. The result was better than CMT:V detectors that were tested before. The $\mu\tau$ -product was higher than that of CMT:V samples. It looks as if In-doped CMT crystals are more promising for applications of radiation detections.

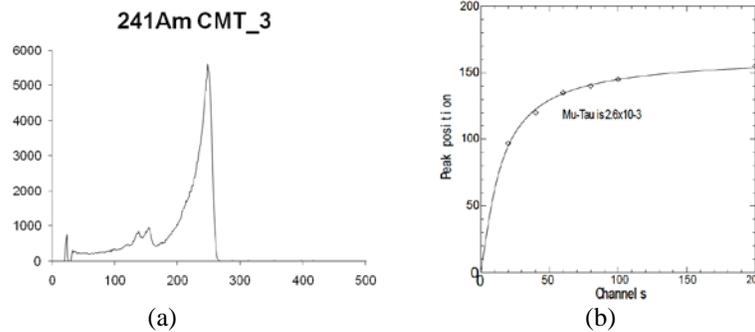


Fig. 2. (a) ^{241}Am spectrum obtained with a CMT:In detector; (b) Measurement of $\mu\tau$ value for the same sample.

Test results showed that CMT:In samples have more Te-inclusions than CMT:V samples. In addition, dislocations (similar to those in CZT crystals) were identified during EPD measurements.

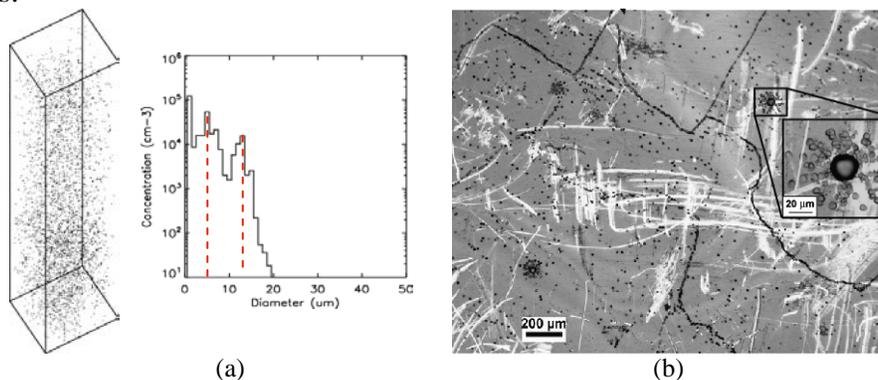


Fig. 3. (a) Left: 3-D visualization of Te-inclusions in a bar-shaped CMT:In detector; Right: Distribution of the size of Te-inclusions in this detector. (b) Dislocations in a CMT:In crystal revealed by Nakagawa solution.

Developing a New Framework for Investigating Earth's Climate and Climate Change

LDRD Project 07-075

Yangang Liu

PURPOSE:

The overarching goal is to develop a new framework for studying Earth's climate and climate change, with two major objectives. The first objective is to examine the role of entropy (budget) in shaping Earth's climate and its change. The second objective is to seek simple guiding principles that govern Earth's climate as a whole without knowing the "microscopic" details. The two objectives are complementary to each other as the state of a large system is likely constrained by entropy-related principles such as the maximum entropy principle for equilibrium systems, minimum entropy production principle for near-equilibrium systems, and maximum entropy production principle for systems far-from equilibrium. This work will shed new light on many crucial issues regarding Earth's climate and climate change, and enhance our ability to predict them. Specifically, the work will lead to improved quantification of the role of entropy in shaping Earth's climate and new understanding of climate forcings from aerosols and greenhouse gases. The success of this work will give BNL an edge in competing for funding in ongoing and future programs (e.g., ARM, ASP, CCPP and SciDac) because understanding and modeling Earth's climate and human induced climate change is a central part of the DOE science mission. The results from this research will also find additional applications in studies of complex systems (e.g., ecological and biological systems) in general. The proposed task is directly tied to the BNL strategic areas of climate sciences, computational sciences, and basic and applied sciences, and indirectly related to that of energy sciences.

APPROACH:

Climate involves (infinitely) many interacting subsystems that themselves consist of ever smaller units, and a proper theoretical framework is central for virtually all climate-related scientific issues targeted by the DOE mission. Despite of its successes over the last few decades, the current mainstream framework suffers from two major deficiencies. First, current climate studies center on the concept of energy but overlook entropy, especially in studies of climate change. This neglect of entropy is problematic because any change of a system is related to entropy no less than to energy. Second, current climate models such as general circulation models are built upon the idea of breaking down Earth's system into ever-smaller interacting subsystems, which, in a sense, is like trying to describe the behavior of a gas by tracking every molecule. Despite the advantages of being able to have detailed investigation into individual processes, accurate representation of increasingly detailed subsystems, their interactions/feedbacks, along with the increasingly high demand for computer resources, poses both theoretical and practical challenges to such reductionism approach.

A major thrust of this research is its focus on entropy and entropy-related principles (e.g. second law of thermodynamics for nonequilibrium systems) in addition to energy (budget). Theoretical studies, model simulations, and analysis of both observational data and model simulations will be carried out in parallel to achieve the objectives. Theoretical studies will start with a simple system, and gradually increase the level of model complexities. We intend to use the analogy with thermodynamics and statistical mechanics and take advantages of the development in these fields to explore the new theoretical framework. Theoretical analysis can be used to assist

examination of data from observations or model simulations. A major motivation to analyze model simulations is to discern the model problems and to determine if the problems are related to the neglect of entropy-related issues.

TECHNICAL PROGRESS AND RESULTS:

In this fiscal year, progress has been made on three fronts. First, we have completed a review on the concept and theory of radiation entropy and approaches for calculating the radiation entropy flux and entropy production rate of the Earth’s system. Best formulations for calculating Earth’s shortwave and longwave radiation entropy fluxes were proposed with the review. This work clarifies long-standing confusion in calculating radiation entropy fluxes and Earth’s entropy production rate, and shows potential applications of entropy constraint to studying Earth’s climate. We have finished a final revision of the review paper for *Review of Geophysics* and it is now in press. Second, we established a new global mean one-dimensional radiative equilibrium climate model to investigate entropy and energy constraints of Earth’s climate system using the best formulations derived in the review paper. Figure 1 shows that an atmosphere with a larger overall longwave optical depth exhibits a smaller net radiation entropy flux at all altitudes. This work shows an evidence of the intrinsic connection between the overall strength of the atmospheric irreversible processes and the amount of atmospheric greenhouse gases, and thus suggests potential applications of entropy constraint to Earth’s climate study. A paper has been submitted to *Philosophical Transactions of the Royal Society B* and is now accepted. Finally, a new radiative-convective model is under construction to investigate the long-standing puzzle of if and how atmospheric convection such as clouds regulates Earth’s climate. Preliminary results indicate that convection causes significant decrease of low-tropospheric net longwave radiation entropy flux but does not affect much on net atmospheric entropy flux. Further investigations are under way.

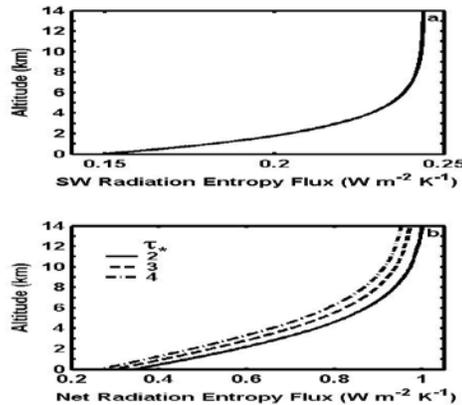


Figure 1. Vertical profiles of the atmospheric shortwave (“SW”) (a) and net (b) radiation entropy fluxes when the overall atmospheric longwave optical depth τ_* is 2.0, 3.0 or 4.0.

A Novel Approach for Efficient Biofuel Generation

LDRD Project 07-080

Dev Chidambaram

PURPOSE:

The objective of this work is to create a functionally-bioactive microorganism encapsulated polymer fiber material for the first time. Traditional methods of immobilizing microbes have not had much success in terms of survival rates of the immobilized bacteria. One of the drawbacks has been the solid nature of materials used; solid materials provide bacteria with no channels for respiration or for obtaining nutrients. We have hereby achieved this goal and completed our proposed LDRD work.

APPROACH, TECHNICAL PROGRESS AND RESULTS:

Although microbes have been used in industrial and niche applications for several decades, successful immobilization of microbes while maintaining their usefulness for any desired application has been elusive. Such a functionally bioactive system has distinct advantages over conventional batch and continuous flow microbial reactor systems that are used in various biotechnological processes. Our approach is shown in figure 1 on right. In this work, we used PEO99-PPO67-PEO99 triblock polymer (PEO: Polyethylene oxide and PPO: Polypropylene oxide) fibers, created via electrospinning, to encapsulate microbes of three industrially

relevant genera, namely, *Pseudomonas*, *Zymomonas*, and *Escherichia*. The presence of bacteria inside the fibers was confirmed by fluorescence microscopy and scanning electron microscopy. While the electrospinning process typically uses harsh organic solvents and extreme conditions that are generally harmful to bacteria, we describe techniques that overcome these limitations. Not only were the encapsulated microbes viable for several months, but also their metabolic activity was not affected by immobilization and thus they could be used in various applications. Furthermore, we have engineered, for the first time, a microbe encapsulated cross-linked fibrous polymeric material that is insoluble. Also, the microbe encapsulated active matrix permits efficient exchange of nutrients and metabolic products between the microorganism and the environment. The present results demonstrate the potential of the electrospinning technique for encapsulation and immobilization of bacteria in the form of a synthetic biofilm, while retaining

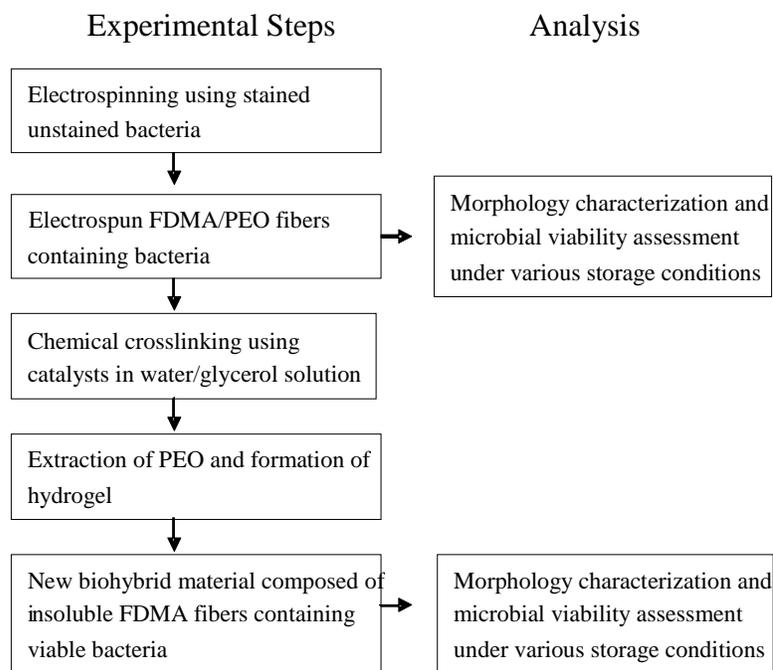


Figure 1: Experimental Approach

their metabolic activity. This study has wide ranging implications in the engineering and use of novel bio-hybrid materials or biological thin-film catalysts.

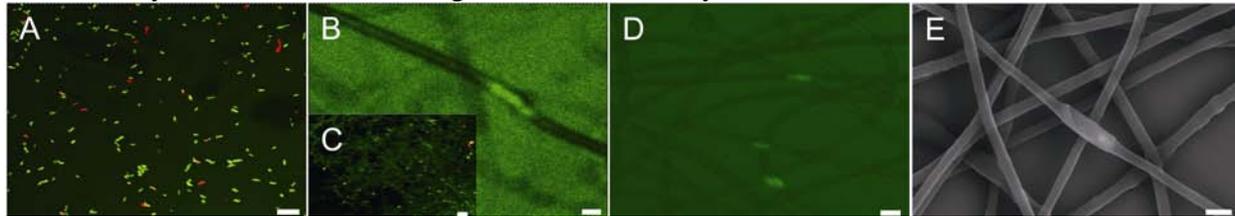


Fig. 2. Confocal images of stained and fluorescent *P. fluorescens* cells (the red and green spots) (A) before electrospinning. (B) and (C) show the morphology of the bacteria inside the dry electrospun FDMA/PEO blend fibers. (D) Image of stained and fluorescent *Z. mobilis* cells in dry electrospun FDMA/PEO blend fibers. SEM micrographs of uranyl acetate stained *P. fluorescens* cells after electrospinning (E).

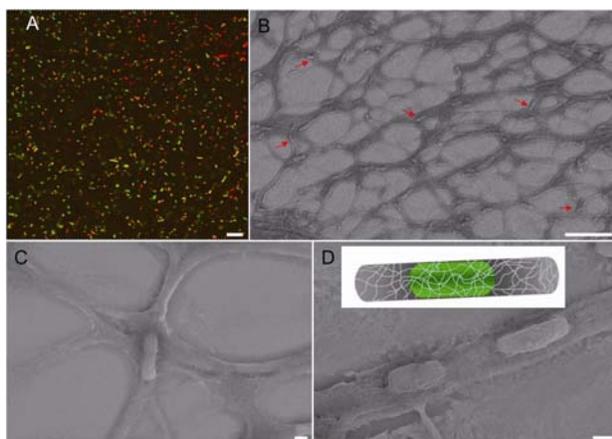


Fig. 3. SEM images of *Z. mobilis* in the cross-linked FDMA fibers. Normally, the cross-linked FDMA fibers are multi-layered. A mono-layer of *Z. mobilis* cells encapsulated FDMA fibers is shown here, because it provides better contrast between the microorganism and fiber. Arrows in image (A) indicate the position of the bacteria. Magnification is indicated individually on data bar at the bottom of micrograph. Bars, 1 μ m (A), 1 μ m (B, C). Sketch (D) illustrates a bacterium encapsulated in the cross-linked FDMA fibers.

Novel FDMA fibrous hydrogel material containing encapsulated microbes was created via electrospinning. To our knowledge, this is the first insoluble fibrous material containing viable microorganisms that has been reported. The microbes in the material were found to be viable for over a week in the dry FDMA/PEO blend scaffold at 4°C and for over two months at -70°C. The mesh-like network of the polymer effectively immobilized the microbe, while allowing the exchange of nutrients and metabolic products between the microorganism and the environment.

Investigations of Hygroscopic Growth and Phase Transitions of Atmospheric Particles by Non-contact Atomic Force Microscopy

LDRD Project 07-084

S. E. Schwartz and B. Ocko

PURPOSE:

Interactions between aerosol particles (nanometer to micrometer sized particles suspended in air) and water affect cloud microphysics, aerosol dynamics, and atmospheric chemistry and radiative forcing of climate change. Understanding these interactions, which are not well understood at a fundamental level, is essential to accurate representation of these processes in atmospheric chemistry and climate models. The objective of this LDRD was to demonstrate the ability of non-contact atomic force microscopy (ncAFM) to provide a better understanding of these processes on the nanoscale. Proving the ability to conduct such studies by working with prototype laboratory-generated aerosol particles would strengthen any proposal for support of research on this topic from OBER and/or BES. Climate studies and fundamental understanding of processes on a nanoscale are both key strategic elements at BNL. This project brought together capabilities in the pertinent two directorates of BNL, EENS and BES.

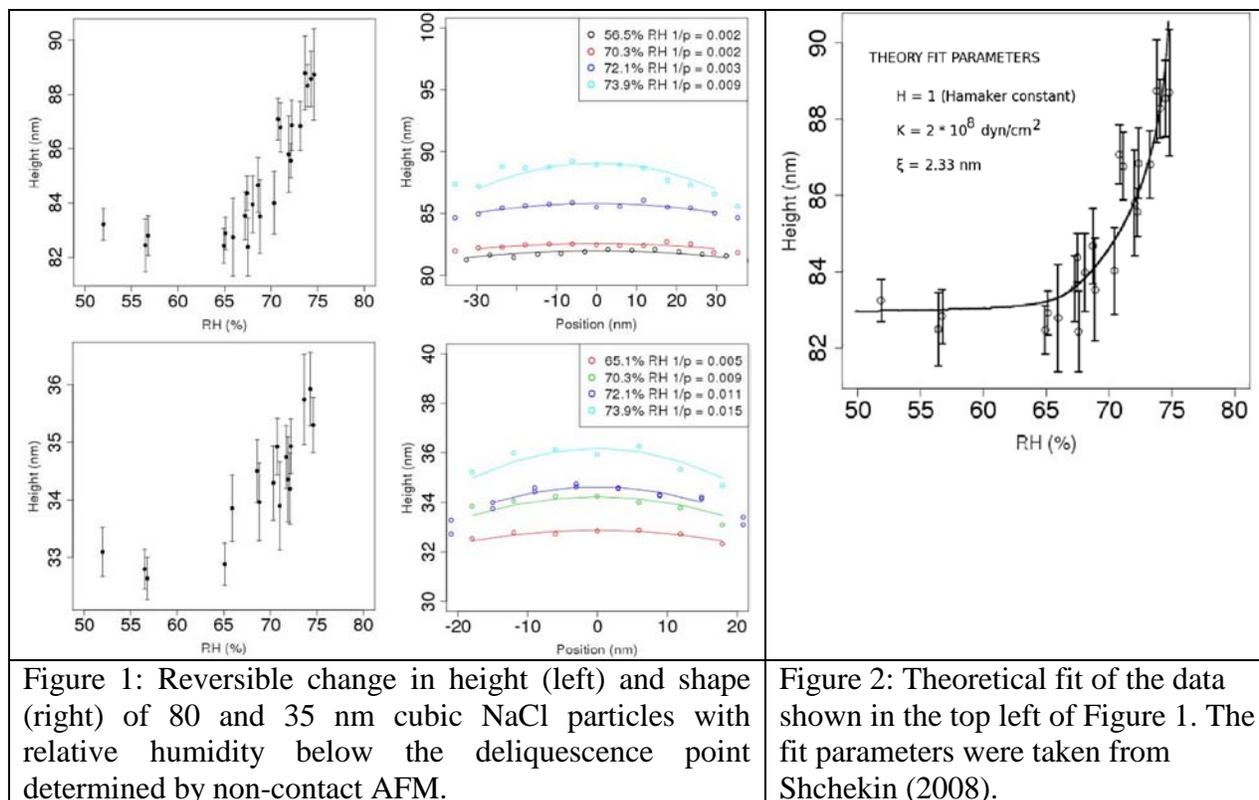
APPROACH:

AFM studies examined water uptake and changes in morphology with varying relative humidity (RH) for sodium chloride aerosols, a well characterized compound and major component of sea salt aerosols. Aerosol particles were produced by atomization from a chilled solution (-1 – 2 °C); the aerosol size distribution is manipulated by varying the concentration. Particles were collected on polished silicon substrates that had been treated with an organic surfactant and oxidizing UV light; this treatment provides control over the surface energy of the flat substrate that facilitates the imaging process by helping to hold the aerosol particles in place while minimally interacting with the deposited material. The salt nanoparticles were characterized with AFM in non-contact mode using a silicon cantilever; changes in height as small as ~ 1 nm can be determined. RH in the chamber is controlled to ± 1.5 °C. Laboratory studies were carried out by Derek Bruzewicz, a post-doc supported by this LDRD together with A. Checco, CMPMSD. Interpretation was carried out with contributions from R. McGraw and E. Lewis, ESD.

TECHNICAL PROGRESS AND RESULTS:

Methods of generating, depositing, and characterizing particles were refined. The described technique yields 30–150 nm cubic particles. The hygroscopic behavior of NaCl aerosol particles deposited on a substrate was studied by ncAFM as a function of RH. Deliquescence---the phase change from solid particle to liquid droplet, was observed near 75% at 20° C, in agreement with literature values for the bulk deliquescence point and for micrometer sized aerosol particles. This deliquescence was observed to be irreversible, requiring nucleation of crystallization, as is found also in aerosols and suspended single particles.

At RH between ~ 65 % and 75% RH, nanometer-sized particles were found to undergo *reversible* uptake of water at the surface as evidenced by increase of height and curvature (Figure 1). For an 80-nm particle, the thickness of the quasi liquid layer reaches approximately 5 nm, equivalent to



approximately 15 layers of water (Figure 1, top left). In contrast, a 35-nm particle grows by only ~3 nm (Figure 1, bottom left). The smaller liquid layer on the 35-nm particle is consistent with a nanosize effect that shifts the deliquescence point to a value of RH above that of the bulk deliquescence point. The theory accounts for the thick liquid layer by assuming long-range electrostatic effects, as proposed by Shchekin (*J. Chem. Phys.*, **129**, 214111, 2008) and others (Figure 2).

Several software routines have been written and employed in the course of this work to deconvolve the AFM signal to retrieve particle shape. These algorithms have been made freely available as a software package that is downloadable at <http://www.solids.bnl.gov/~derek/index.html>.

This investigation has met its objective by demonstrating that the hygroscopic behavior of particles similar to atmospheric aerosols can be characterized by ncAFM. The study also has contributed to understanding the interactions between hygroscopic salts and water in addition to atmospheric implications.

FUTURE WORK:

A manuscript that includes a theoretical model of the liquid layer is in preparation for *J. Chem. Phys.* A second manuscript that explains the instrumentation and techniques required for this type of study is in preparation for *Ultramicroscopy*.

Chemical Imaging of Living Cells in Real Time

LDRD Project 07-089

Lisa M. Miller and Roger Phipps

PURPOSE:

The objective of this work is to develop methods for high-resolution, chemical (infrared) imaging of living cells in real time. To date, infrared imaging of biological materials has primarily been performed on dried samples due to the infrared absorbance of water. In addition, most infrared microscopes are equipped with single-element detectors that hamper real-time imaging because the sample needs to be raster-scanned through the infrared beam. Here, we propose to develop a specialized incubator for living cells that is adapted for infrared microscopic imaging in real time. This incubator will be coupled to an infrared microscope with a new focal plane array detector system, where a 128x128 pixel array is used to image large areas quickly. This new technique will become a key element in the development of biomedical imaging programs at the NSLS that will take advantage of the high brilliance and stability of NSLS-II.

APPROACH:

Synchrotron-based Fourier transform infrared microspectroscopy (FTIRM) is a powerful method for sub-cellular spatial resolution imaging (2-10 μm in the mid-infrared region) of chemical components such as lipids, proteins, nucleic acids and carbohydrates, which are often altered in disease states or in response to external stimuli (e.g. drugs, radiation). One of the major drawbacks of FTIRM is the absorbance of water in the mid-infrared region. The O-H stretching mode of water spans from 3600 – 3100 cm^{-1} and the O-H bending mode overlaps the protein Amide I band ($\sim 1650 \text{ cm}^{-1}$). Due to this potential interference, most FTIRM data on biological cells and tissues published to date have been collected on dried samples.

In this work, we proposed a series of developments so the technique can be extended to studying living cells in culture. The motivation behind this new technology is 4-fold: (1) The synchrotron infrared beam is non-ionizing and does not induce any heating effects so samples can be probed for weeks to months. (2) Since FTIR vibrational frequencies are sensitive to isotopic labeling, individual chemical components can be tracked spatially and in real time. (3) This technique can be used simultaneously with other optical-based imaging techniques such as epifluorescence or confocal microscopy and can complement lower resolution, in vivo techniques such as Positron Emission Tomography (PET) and Magnetic Resonance Imaging (MRI). (4) As part of NSLS-II, infrared beamlines are proposed that will be optimized for infrared imaging. Development of this technology is expected to increase the user base dramatically.

The specific aims of this proposal are to (1) design an incubator for living cells that is compatible with infrared micro-spectroscopic imaging, (2) adapt the infrared imaging microscope with focal plane array detector to a synchrotron infrared beamline at NSLS and (3) apply the newly developed technology to study bone mineral production and the effects of a current, isotopically-labeled osteoporosis drug on this process.

TECHNICAL PROGRESS AND RESULTS:

Due to the catastrophic loss of 3000 data files in FY08, the postdoctoral fellow working on this project, Dr. Imke Bodendiek, left BNL in December 2009 with very little data for publication. Essentially, these lost files represented almost 1 year of research, which was resumed in FY09

with graduate students Meghan Ruppel and Alvin Acerbo. Thus, the following progress report represents a repeat of many experiments that were performed in FY07, plus additional progress made in FY09.

During FY07, Dr. Bodendiek found that ZnSe, diamond, and ITO-coated (low-e) glass slides were acceptable substrates for the growth and adherence of cells in culture. Thus, in FY08, we proceeded to grow MC3T3 mouse osteoblasts on low-e slides. In FY09, we found that spin-coating a few nanometers of sulfonated polystyrene (SPS) also helped cell growth, adherence, and mineralization.

Cells were grown in culture over the course of a 28-day mineralization cycle. Over this time course, cells were examined with the infrared imaging microscope and representative images can be seen in **Figure 1**. Both the collagen matrix and mineralization can be visualized in the same dataset and overlaid. Results showed that risedronate-treatment delayed the onset of collagen matrix production, which also caused a delay in mineralization. However this lag was temporary and the cells recovered by 28 days. While these experiments were very successful, and led to a chapter in the PhD thesis of Meghan Ruppel and a manuscript under review at *Calcified Tissue International*, we have not yet achieved our goal of studying incubated cells at the beamline. These cells were removed from the incubator for imaging because we have not yet completed the implementation of an *in situ* incubator on the FTIR microscope. Ongoing efforts involve examination of wet cells and the development of algorithms for water correction in the spectra.

Also in FY09, we were able to complete the coupling of the focal plane array FTIR detector to the synchrotron. We have been successful with a single mirror for illumination of the FPA detector. In addition, a 74X objective is now being used to illuminate a 32 μm area of the sample with 0.5 μm pixel resolution. Point spread function deconvolution algorithms have been designed by Mr. Alvin Acerbo for the Schwarzschild FTIR objective in order to further improve the spatial resolution of the images. By combining synchrotron light with 10X oversampling and a sample substrate with a high index of refraction, the next steps will be to image living osteoblasts at a resolution of $< 1 \mu\text{m}$.

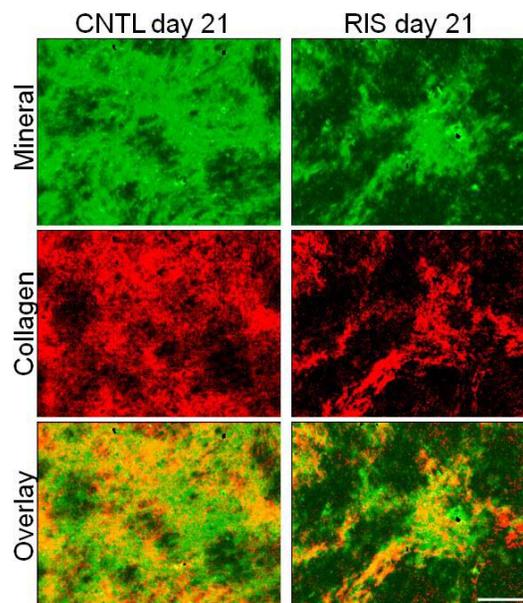


Figure 1. Infrared images of mineralizing osteoblasts after 21 days in control (left column) and risedronate-treated (right column) culture. The mineral and collagen images are shown, along with the red-green overlay. As can be seen, risedronate-treated cells had a slower collagen production that led to reduced mineralization after 21 days. Scale bar is 20 μm .

Coherent Bragg Rod Analysis of High-T_c Superconducting Epitaxial Films

LDRD Project 07-090

Ron Pindak

PURPOSE:

Recent years witnessed an exciting discovery of interface superconductivity in complex oxides. In particular, bilayer films consisting of a non-superconducting metal La_{1.55}Sr_{0.45}CuO₄ (LSCO) and an insulator La₂CuO₄ (LCO) on La₂AlO₄ substrates showed superconductivity with the critical temperature T_c ≈ 30 K, occurring in an interfacial layer about one unit cell (1UC) thick [1]. The origin of the interfacial superconductivity and T_c enhancement is a matter of intense current debate; the *scientific objective* of this LDRD is, through a better understanding of structural changes, to gain insights on how we might unlock a way to enhance T_c even further.

Four *technical objectives* of this LDRD project that were required to achieve its *scientific objective* included. (1) Improvement of the experimental procedures for measurement of Bragg rods from epitaxial thin films. (2) Improvement of the analytical procedures to recover x-ray phases and directly reduce Bragg rod reciprocal-space data to real-space three-dimensional electron density (ED) maps. (3) Development of a method to quantitatively estimate the accuracy of parameters extracted from the real-space ED maps. (4) Development of a procedure to use multiple energies to measure the concentration profile of a substitutional atom by doing Bragg rod measurements at different energies across the absorption-edge of the atom. The first three technical objectives were crucial because it was discovered that the location of weakly scattering oxygen atoms, which are a challenge to measure, could play a key role in interfacial superconductivity. The last technical objective was important because in LSCO the Sr concentration determines whether the material is metallic, insulating, or superconducting.

APPROACH:

We used the high brightness insertion device beamline ID-33 at the Advanced Photon Source (APS) and refined our LABVIEW-based data acquisition system to collect high-accuracy complete data sets of symmetry inequivalent Bragg rods from different LSCO bilayer and single phase epitaxial thin films. We refined our Bragg rod data analysis procedures based on the COBRA phase retrieval method, which was co-developed by two PIs on this LDRD project (R. Pindak and Y. Yacoby). A post-doctoral research associate, Hua Zhou, joined the project in November 2007 and worked through mid-January 2010.

Other principal investigators on the LDRD, I. Bozovic, V. Butko, and G. Logvenov (CMPMSD) prepared the bilayer and single phase LSCO samples using their ALL-MBE growth facility and characterized the thermal and transport properties exhibited by the films.

TECHNICAL PROGRESS AND RESULTS:

Technical Objective 1 -- We incorporated a pixel array area detector into our data acquisition system, which enabled us to more accurately fit and subtract the background signal. We also minimized filter changes and unnecessary alignment checks (the area detector allows minor alignment inaccuracies to be corrected in software), which reduced the data acquisition time for a complete data set from 50 hours to 30 hours - both significant advances.

Technical Objective 2 -- To improve accuracy of the electron density (ED) maps, the data was analyzed first by the COBRA phase retrieval method, and then the results were further refined by

the Difference-Mapping method resulting in convergence to ED maps with a reliability factor of 0.02 (comparable or better than other published Bragg rod analyses); but, with convergence in 27 iterations compared to over 2000 iterations required by other approaches. The ED maps enabled us to accurately determine the positions of all the atoms including oxygen in the LSCO/LCO Unit Cells (UCs) with sub-Ångstrom resolution.

Technical Objective 3 -- We developed a variation of the bootstrap resampling method of error analysis, introducing random artificial noise to the data, reanalyzing the new data set, and recalculating the parameters of interest. This process was repeated a number of times and the scatter in the values of the parameters of interest provided a reliable estimate of the error bars.

Technical Objective 4 -- Although the beamline hardware was not optimized for differential energy measurements, we 'worked-around' hardware inaccuracies to collect high-quality (00L) Bragg rod data at 3 different energies above, at, and below the Sr absorption edge. Careful analysis indicated that a factor of 5 improvement was needed to unambiguously determine the Sr concentration profile. Potential improvements have been identified for a future run.

Scientific Objective -- Our measurements are reported in Ref. [1]. We studied a number of La-cuprate ultrathin films including overdoped metal (M) and optimally-doped superconductor (S) single layers, and $(n \times M + m \times I)$ bilayers, where (n,m) indicates the thickness of the respective metal (M) and insulating (I) layers expressed as the number of UCs. Combining transport and X-ray measurements, we arrived at the following conclusions: (1) Sharp superconducting transitions were observed at $T_c = 34$ K in a (2,3) bilayer and $T_c = 36$ K in a (2.5,2.5) bilayer, significantly higher than the values reported for thicker (n,m) bilayers, which is remarkable given that these films are only 5 UCs thick. (2) The measured lattice constants of the bilayer films were the same for all UCs and had a value of $c_0 = 13.304 \text{ \AA}$, which was larger by 0.131 \AA than that of the bulk LCO. This was expected from the strain and elastic properties. (3) However, quite unexpectedly, we observed large variations in the Cu-apical O distances. In the metal layer closest to the substrate the Cu-apical O distance was 0.11 \AA smaller than the bulk LSCO Cu-apical O distance and steadily increased to being 0.34 \AA larger at the surface - a remarkable change of 0.45 \AA . (4) In contrast, in the single layer (M) or single layer (S) samples, the Cu-apical O distances were approximately constant throughout the film. (5) Comparing all the data shows a compelling picture: the copper-apical oxygen distance in the bottom metallic UCs of M+I bilayers is equal within the experimental error to those in M and S single-phase samples, while the apical-oxygen displacement occurs only in the I layers of bilayer samples. This indicates that the anomalous behavior is associated with the M-I interface. It has been argued that the Coulomb interaction along the c-axis direction is strong, poorly screened and long ranged; we speculate that the origin of anomalous expansion of the copper-apical oxygen bond in M+I bilayers must likewise be in the long-range Madelung energy contributions.

Variations in the apical oxygen position are known to strongly affect T_c . We conclude that in cuprates the crystal structure can be modified in near-surface layers, and in such a way that superconductive properties are dramatically altered. This result amplifies the importance of high quality surface structure determination in conjunction with surface sensitive probes of electronic states such as scanning tunneling microscopy or angle-resolved photoemission spectroscopy.

Finally, we note that with improvements in the size of pixel array detectors, parallel detection should be achievable at NSLS-II, further reducing the data collection time to several hours. Moreover, a UHV PLD growth chamber is currently being designed by Randy Headrick, an NSLS contributing user that will be suitable for in-situ Bragg rod studies during processing.

[1] "Anomalous Expansion of the Copper-Apical Oxygen Distance in Superconducting Cuprate Bilayers", H. Zhou, Y. Yacoby, V. Butko, G. Logvenov, I. Bozovic and R. Pindak, submitted to the Proceedings of the National Academy of Sciences.

Development of a Planar Device Technology for Hyperpure Germanium X-Ray Detectors

LDRD Project 07-091

D. Peter Siddons and Abdul Rumaiz

PURPOSE:

The project aims to bring a new manufacturing method for the fabrication of multi-element monolithic planar radiation detectors using germanium as the semiconductor. Manufacturing methods for this material have not followed the same development as that of silicon-based devices. As a result, multi-element detectors are not easily made, and more sophisticated devices such as drift-detectors are impossible to make. This program will open up a new range of applications for germanium detectors for use with synchrotron radiation sources.

APPROACH:

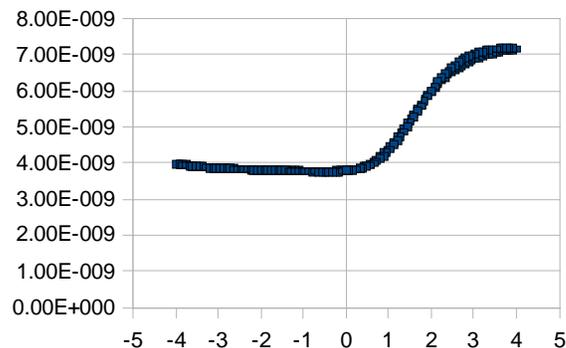
Germanium technology ceased to be of commercial interest in the 1970's when silicon became the dominant semiconductor. It is still used to fabricate large volume gamma ray detectors for scientific and nuclear engineering applications, but electronics applications were not pursued. More recently, the industry has begun to look at germanium again, due to its superior carrier mobility. As a consequence, there is modern literature trying to address some of the issues which caused it to be abandoned previously. We have taken some of those ideas and arrived at a viable process based on high-k dielectrics as passivating layers and ion implantation as a doping method.

TECHNICAL PROGRESS AND RESULTS:

We have developed a room-temperature process for forming thin layers of zirconium and hafnium oxide layers on germanium wafers. This process consists of first depositing by sputtering a thin metallic layer, e.g. 20nm of zirconium, onto the clean germanium surface. This layer is then oxidized in-situ by exposing the metal to an ozone-rich atmosphere. The process can be repeated without breaking vacuum using a chamber we have built for the purpose.

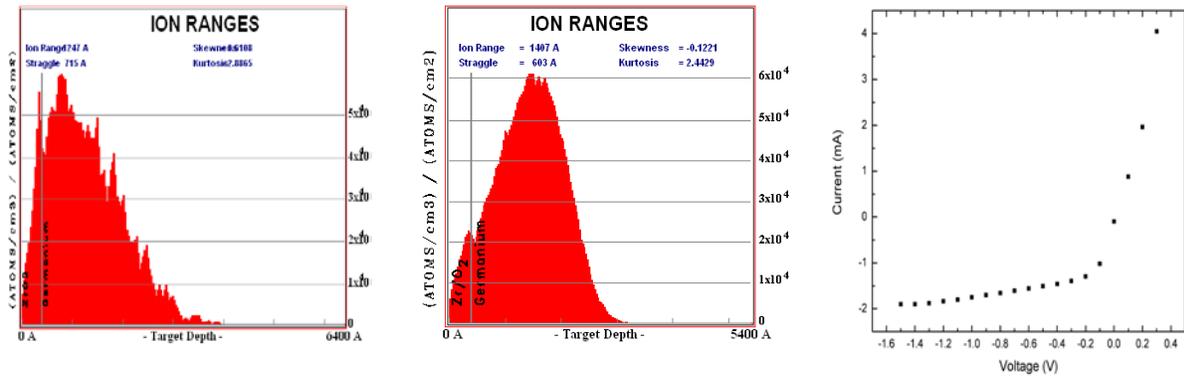
One of the key issues with such a layer is the nature of defects at the interface between the semiconductor and the insulator. Defects can cause charge trapping and hence poor energy resolution and/or high leakage current in a device. C-V curves performed on metal-oxide-semiconductor (MOS) capacitors reveal that our films are good in that respect, showing little hysteresis.

CV curve of MOS capacitor, demonstrating very low hysteresis, and showing the expected flat-band shift due to the



The germanium wafers we procured were slightly P-type. This introduces some slight complication when making monolithic segmented detectors. The adjacent detectors must be isolated from each other. The standard method of achieving this for silicon detectors has been to make use of the fact that thermally grown silicon dioxide is positively charged. This grown-in charge acts to induce charges in the semiconductor which then perform the isolation function. This trick only works for detectors formed by implanting P dopants in an N substrate. In our case, the charge has the wrong sign, and so we need to work harder. In fact we must make a uniform P implant over the whole of the segmented side of the sensor, and then over-dope our N detector pattern through this. We have tried this scheme using boron and phosphorus species to form P and N doped areas respectively. These implants could be successfully activated by a rapid thermal anneal, and diode structures successfully formed.

The figures below show the calculated dopant profiles for boron and phosphorus under our chosen conditions, and a diode transfer function measured for a device made using the processes developed. Our next steps are to repeat these process steps using detector-grade germanium and try to operate such a diode as an x-ray detector at cryogenic temperatures.



P on ZrO/Ge, 80, 140, 200 keV

B on ZrO/Ge, 60keV

Study of Epigenetic Mechanisms in a Model of Depression

LDRD Project 07-096

Fritz A. Henn

PURPOSE:

The project was initially conceived as an investigation into the circuits mediating depression and the gene changes caused by early life stress which might modify these circuits. The hope was to define the alterations caused by stress which would lead to the disease of depression. Defining the genes responsible and the circuits involved would provide information for the development of new treatment approaches. However, in view of the intervening decision by DOE (BER) to eliminate funding for studies on human disease and animals, the project was bifurcated. We continued the depression project with a narrow focus on drug development and chose to initiate a new project aimed at looking at the effect of changes in temperature and CO₂ content on changes in gene expression in plants, i.e., the epigenetics of climate change. In view of the success we have had in defining the circuits involved in depression, we have focused on the control of these circuits using electrophysiology and microdialysis with the goal of defining novel potential sites for antidepressant drug development. The plant project became the primary effort of Dr. Liu and has resulted in the establishment of a new lab for this purpose and the hiring of a post doctoral fellow in this area through the LDRD. The goal here is to build a bridge between atmospheric science and biology related to biofuels production. This has been presented to BER last week as a potential growth area which they are considering.

APPROACH:

Project 1: The use of inbred strains of rats developed over many years, one of which was susceptible to learned helplessness, an analog of human depression and one which was resistant to stress and learned helplessness allowed us to define a circuit which was overactive in the helpless condition. This circuit involved a structure, the lateral habenula, which appeared to act as a control point defining the change in affect and behavior. This structure appears to be overactive in helplessness and by analogy in depression. We have used PET imaging, structural MR and microdialysis and behavioral analysis at Brookhaven and electrophysiology done in collaboration with the Malinow Lab at Cold Spring Harbor to define the defect at the habenular synapse. A collaborative effort involved the NIMH imaging group to verify the overactivity in human depressed patients.

The use of these strains allows us to ask if the vulnerability has to do with the genes defining the different strains. Both strains have been exposed to stress early in life and gene arrays for differential expression have been constructed in co-operation with nimblegene and we will begin looking at the differences as a result of the strain background.

Project 2: Dr. Liu set up a lab and growth chambers to expose arabidopsis to varying CO₂ concentrations and temperatures. She hired a post doctoral fellow and has developed gene arrays working with nimblegene to begin a study of gene expression changes as a function of these 2 variables. The approach is straight forward to initially look at the methylation patterns as a function of temperature and CO₂ concentration.

TECHNICAL PROGRESS AND RESULTS:

Project 1: The circuit has been defined using animal imaging and human imaging, overactivity has been demonstrated in the animals with considerable precision, and the synapses are being defined using selected inhibitors. In humans, overactivity was demonstrated and neurosurgical intervention using deep brain stimulation to inhibit the habenula was carried out by collaborators in Heidelberg Germany with good results. We determined, using binding studies and microdialysis, a likely cause of pathology within this circuit was excessive glutamatergic activity due to decreased astrocytic transport of glutamate from the synaptic cleft. We were able to reverse helplessness, using compounds known to increase glutamate transport, suggesting a new target for antidepressant drug development. A patent application is being filed this month for the use of K_{ATPase} channel openers as antidepressants since they increase glutamate uptake by astrocytes. The coming year should see NIH funding to continue this project and the development of new antidepressant drugs, ideally with corporate funding, both for follow-on funding after this project has ended. Two publications are in press and a major grant has been submitted.

Milestones:

1. Patent filing - this calendar year
2. Papers on Mechanism - 2 high profile within 6 months
3. Deal with a major pharmaceutical firm within this fiscal year

Project 2: The foundation has been laid for obtaining information on gene changes caused by climate change. The data will be gathered next year and presented to BER as the foundation for a larger epigenetic study of the effects of climate change. An initial step is the determination of the methylation levels of the arabidopsis gene which is being done in collaboration with a group at Johns Hopkins and is currently underway. A method using HPLC to look at methylation is being developed and should be applied within 3 months.

Milestones:

1. First data on role of T and CO₂ in altering gene expression within 6 months.
2. Presentation to BER in the Spring – Summer
3. SFA for the next fiscal year written within this year.

Polarized Electron SRF Gun

LDRD Project 07-097

Ilan Ben-Zvi and Jörg Kewisch

PURPOSE:

The purpose of the project is to carry out research on the feasibility of using a superconducting, laser-photocathode RF electron gun (SRF photoinjector) for the production of polarized electrons. We expect to show that a cesiated gallium arsenide photocathode (which is necessary for the production of polarized beams) maintains its quantum efficiency in an RF gun and that the migration of cesium from the cathode to the SRF cavity is so small that the properties of the gun will not be affected. This is a most desirable result since SRF guns outperform DC guns for high brightness beams. The motivation of this research is twofold: First, demonstrate that a SRF photoinjector can be used at the International Linear Collider (ILC) to eliminate the need for an electron damping ring. Second, such a gun would be at the heart of the linac for eRHIC, thus having a large impact on the future of the QCD laboratory strategic initiative at BNL.

APPROACH:

State-of-the-art polarized electron guns rely on the use of direct band gap III/V semiconductor NEA cathodes. When illuminated with circularly polarized laser light, the cathode emits polarized electrons. Cathodes made of strained GaAs have been especially successful. The laser excites electrons from the valence band into the conduction band. To achieve reasonable emission efficiency, the work function of the material has to be lowered. This can be accomplished by adding a monolayer of cesium and oxide to the surface[i]. This surface layer is subject to rapid aging, which leads to a decrease of quantum efficiency of the cathode.

In DC polarized guns, we recognize two main contributions to the cathode aging process: Oxidation through reaction with the background residual gas in the vacuum system and ion impact on the cathode surface will both lead to degradation of the quantum efficiency. Both effects are proportional to the vacuum pressure in the gun. While DC guns typically have a vacuum pressure of 10^{-11} torr, a normal conducting RF gun reaches only 10^{-9} torr due to out-gassing caused by the RF field. Under such conditions, the cathode life time can be as short as 10 seconds [iii]. In a superconducting RF gun, the cryo-pumping of the cavity walls improves the vacuum and the pressure can match that of a DC gun. While in a DC gun all ions are accelerated towards the cathode, only ions generated at the correct RF phase will reach the cathode and the maximum kinetic energy is limited due their high masses. With identical vacuum conditions, the ion back-bombardment in a SRF gun can be an order of magnitude lower [ii]. In an RF gun, electron back bombardment is an additional cause of concern. The source of these electrons is field emission in the gun. However, the same extensive cleaning procedures that are used to improve the quality factor (Q) of the SRF gun cavity have been proven to reduce field emissions significantly.

The experiment consists of three major parts: a cryostat containing a 1.3 GHz SRF electron gun with a beam transport system, vacuum system and diagnostics; a cathode preparation chamber for the development of a strained gallium arsenide, cesiated photo-cathode under ultra-high vacuum (10^{-11} torr or better) and a transporter system allowing the cathode to move between the two systems while maintaining an ultra high vacuum. We use parts that became available from other projects to the largest extent possible.

The goal of the experiment is the measurement of the quantum efficiency lifetime of the cathode and the SRF performance of the gun over a sufficiently long time to demonstrate the compatibility of the cathode with SRF performance and the compatibility of operation of the photocathode in high RF field in the gun.

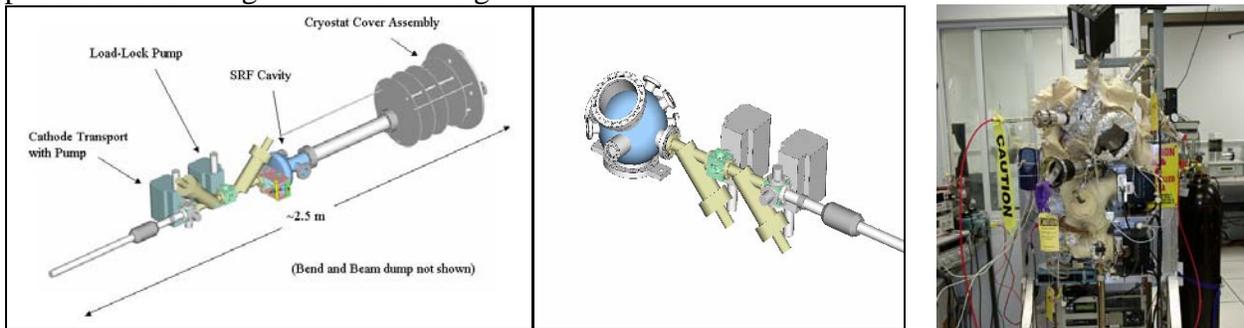


Figure 1: Gun assembly (removed from the cryostat) with attached transporter system and the preparation chamber with the attached transporter. Shown are also the valves and vacuum pumps that allow attaching and separating the transporter to both systems. The assembled preparation system with transporter is shown on the right.

TECHNICAL PROGRESS AND RESULTS:

The preparation chamber is completed and has been used to prepare cathodes with a quantum efficiency of better than 10%, fulfilling the requirements. This goal was reached after repeated baking of the vacuum components, improvements of the cathode heating system and testing of different cesium sources. The cathode lifetime inside the transporter has reached 12 hours after adding a NEG pump. Cold cathode vacuum gauges are used, which are equipped with a radioactive source allowing vacuum measurements at the 10^{-11} torr level. We expect that additional vacuum baking will increase the lifetime further.

The gun assembly parts have been baked in a vacuum oven and are ready to be assembled in a clean room. An additional vent pipe was added to the gun assembly with a burst disk to prevent an explosion if liquid helium is trapped behind the cathode. A high temperature superconducting magnet is used for focusing of the beam. The magnet and its quench protection system were built at BNL. The gun has been tested with an installed cathode at Jefferson Lab. Problems with heat generated by the RF field in the Gallium-Arsenide have been remedied by using thinner GaAs wafers and recessing the cathode into the niobium.

We obtained a DOE permit to operate our experiment as an “experimental accelerator”. A concrete enclosure was built in Building 912, which satisfies radiation safety and oxygen deficiency hazard requirements. The installation of the access control system is expected to be completed in March 2010. Measurements of the cathode lifetime inside the RF gun will then begin.

[i] R.L.Bell, *Negative electron affinity devices*, Clarendon Press, Oxford, 1973.

[ii] R.P.Fliller, H. Edwards, H.Blum, J.Rathke, C.K.Sinclair, M.Huening, *Progress on Using NEA Cathodes in an RF Gun*, Proc. of the 2005 Particle Accel. Conf., (2005).

[iii] A.V.Aleksandrov, E.S.Konstantinov, P.V.Logatchov, A.V.Novokhatski, A.A.Starostenko: *High Power Test of GaAs Photocathode in RF Gun*, Proc. of EPAC 98, (1998).

High End Scientific Computing

LDRD Project 07-101

James Davenport and Sam Aronson

PURPOSE:

The purpose of this LDRD is to establish at BNL, a Laboratory competence in the efficient and effective utilization of large-scale, high-end computers in support of our multi-program research environment. The goal is to increase the number of applications which can take advantage of the new machines which are being deployed throughout the DOE complex.

We will accomplish this task by bringing together scientific expertise in Laboratory mission areas with experts in computational science, applied mathematics, and computer operations.

APPROACH:

The current direction in high end computing is to build massively parallel machines with tens to hundreds of thousands of processors connected through complex communication networks. IBM's Blue Gene architecture is one example of such a machine, which currently is among the world's fastest. With a \$26 million grant from the State of New York and in collaboration with Stony Brook University, BNL acquired a 100 teraflops Blue Gene/L in 2007 and a 28 teraflops Blue Gene/P in 2008. Called New York Blue, these machines contain 36,864 and 8,192 processors respectively and are orders of magnitude faster than typical departmental cluster computers. This unique resource enables investigations that are of a scale and complexity previously unavailable to BNL scientists.

Unfortunately, most codes and algorithms are not designed to take advantage of the immense power these machines offer. Typically, dividing a large problem among many processors does not lead to a comparable speed up in the calculation because of an imbalance between computation and communication. Therefore most codes need to be rewritten to be effective in this environment. This process requires a team approach with expertise in the scientific, mathematical and computational aspects brought to bear.

This project therefore involves a large number of collaborators in nuclear and elementary particle physics, nanoscience, computational biology, applied mathematics, fluid dynamics, and climate modeling. Numerous such teams have formed and are now producing results.

TECHNICAL PROGRESS AND RESULTS:

Blue Gene/L has been in full operation since November 2007 and Blue Gene/P since January 2008. There are currently 334 authorized users with 250 accounts. An additional 160 terabytes of disk storage and 460 terabytes of tape archival and back up storage were added in 2008. Utilization has consistently been above 90% of the cycles each month. Scaling studies (showing how various codes speed up with increasing number of processors) have been conducted in several fields. A climate model has run on the full Blue Gene/L machine. Codes have been ported and run in a wide range of disciplines including computational biology, quantum chromodynamics, nanoscience, climate modeling, astrophysics, fusion, accelerator design, and fluid dynamics. More than 60 publications are in press or submitted based on work done on the

machines. Ten posters and a movie were presented at the Annual SuperComputer conference in Portland, Oregon in November 2009.

There were two Intel Competition finalists and one Siemens Competition grand prize winner whose work was based on protein molecular dynamics computations carried out on New York Blue.

In summary, operations are going well with results in a wide range of scientific disciplines by a large number of users and with numerous publications.

How Does Color Flow in a Large Nucleus: Exploring the Chromo-Dynamics of QCD Through Diffractive and Jet Measurements at eRHIC

LDRD Project 08-001

Raju Venugopalan

PURPOSE:

An important aspect of Quantum Chromodynamics (QCD) studies with eRHIC is to understand how the fundamental quark and gluon fields manifest themselves in nuclei. A key property of quarks and gluons is their “color” charge and their *chromo*-dynamics is what distinguishes the strong interactions from other fundamental forces in nature. The flow of color in nuclei differs greatly from process to process. This LDRD project focused on understanding the *chromo*-dynamics of two processes in deeply inelastic scattering (DIS) off nuclei at high energies: a) diffraction and b) jet production. The purpose of studies with the former was to explore whether diffraction off light and heavy nuclei at an electron ion collider can provide an unambiguous signature of strong color field dynamics in QCD—in particular a putative novel saturated form of matter called the “Color Glass Condensate” (CGC). Jet studies, while also providing a novel channel to measure the nuclear gluon distribution, may provide a powerful diagnostic tool of the interaction of colored particles with an extended colored medium.

APPROACH:

Very few studies have been performed on diffraction in nuclei; in particular “incoherent” diffraction where the nucleus breaks up while preserving a “rapidity” gap has not been studied previously. We decided that dipole models that easily incorporate the saturated CGC physics offered much promise. Such dipole models had previously been applied to study the DIS data from electron proton scattering experiments at the HERA collider in Germany. However a consistent application to *all* the relevant HERA data (especially diffractive data) was lacking. The PI and colleagues decided to first obtain a consistent treatment of this data in the dipole framework and then subsequently develop techniques to apply this approach to nuclei. An important constraint was to make sure that the results were consistent with the available nuclear data from earlier experiments. With regard to jet studies, the goal was to employ novel state-of-the-art jet finding techniques developed by co-investigators Gregory Soyez and Gavin Salam to reliably determine the gluon distribution in different kinematic ranges. It turned out that the novel jet finder techniques were of great value to the search for jets in heavy ion collisions and some part of the effort was diverted in that direction. The techniques were also then applied to nuclear DIS where the jets are more easily isolated relative to heavy ion collisions.

TECHNICAL PROGRESS AND RESULTS:

The dipole approach alluded to gives a consistent description of HERA data. Important to a consistent description are the treatment of the heavy quark contribution [1] and the impact parameter dependence of the dipole cross-section [2]—both of these issues were addressed by Gregory Soyez, who was hired as a research associate on the LDRD. As a first test of its extension to nuclei, it was shown that “inclusive” nuclear data from previous nuclear DIS (fixed target) experiments could be reproduced with no additional parameters [3]. This approach could then be extended to diffractive nuclear scattering. A first detailed study was performed and published in [4]. (See also [5] for a briefer presentation.). In performing these studies, we had valuable technical advice from Henry Kowalski from DESY, Alberto Accardi and Vadim Guzey from JLAB, who visited us under the aegis of the LDRD.

A novel feature of this study was to separate coherent nuclear diffraction (the nucleus remains intact) from incoherent nuclear diffraction (the nucleus breaks up into nucleons). This is potentially very important for eRHIC because incoherent diffraction can be measured while coherent diffraction on heavy nuclei can only be inferred (except perhaps for light nuclei). About 25% of all events in nuclear DIS are diffractive and 30% of these are incoherent—these processes are therefore a significant part of the total cross-section and therefore a significant potential diagnostic tool of color (less) diffractive dynamics at eRHIC.

This project had two important outcomes. Firstly, it has led to a follow-up LDRD with Thomas Ullrich as PI (with Venugopalan as co-PI) on developing an e+A event generator. The diffractive studies performed in the present LDRD will be an important input into the Monte Carlo event generator studies. Secondly, it suggested to one of our collaborators (Kowalski) that our results could be used in exclusive J/ψ photo-production to extract information about the QCD nature of short-range nuclear forces. The PI is currently involved in follow-up studies on this very promising prospect.

In jet studies, there has been considerable progress under the LDRD (see Refs. [6,7,8,9,10]) in development of jet finder algorithms by Salam and Soyez (in collaboration with Matteo Cacciari of Univ. of Paris). The SIS cone and anti- k_t algorithms developed by them are free of known pathologies of earlier jet finding algorithms. These jet studies were also applied to eRHIC- the results were presented at the electron ion collider collaboration meeting in Berkeley in December 2008 and have been written up as a report detailing prospects for extracting nuclear gluon distributions at eRHIC as well as the use of jets as a tool to extract other properties of the colored medium.

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- 4) “Nuclear enhancement and suppression of diffraction structure functions”, H. Kowalski, T. Lappi, C. Marquet and *R. Venugopalan*, *Phys. Rev. C* **78**, 045201 (2008).
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- 9) “Quantifying the performance of jet definitions for kinematic reconstruction at the LHC”, M. Cacciari, J. Rojo, *G. Salam* and *G. Soyez*, *JHEP* **12** (2008) 32.
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Strongly Correlated Systems: From Graphene to Quark-Gluon Plasma

LDRD Project 08-002

D. Kharzeev and A. M. Tsvetik

PURPOSE:

Graphene is essentially carbon film. Electrons in graphene have an unusual spectrum resembling the spectrum of two-dimensional relativistic particles with the effective “speed of light” being 1/300 of the speed of light in vacuum. Being essentially relativistic particles, electrons in graphene have a very unconventional response to disorder (no localization) and may give rise to various novel types of collective behavior. The purpose of the project is to explore these aspects of graphene taking advantage of the expertise of condensed matter physicists (Tsvetik, Khodas) and nuclear physicists (Kharzeev) working in close contact with the experimental group (Zaliznyak, Valla, Zhang). At the same time, the methods developed for the studies of strongly correlated systems can be used in the description of novel phenomena observed in heavy ion collisions, for example, the local parity violation.

APPROACH:

The methods used in our theoretical studies include the renormalization group approach and various forms of bosonization. We work in close contact with the experimental groups of Valla and Zaliznyak (BNL). Our postdoctoral fellow (Maxim Khodas) is the most active participant on all projects related to this LDRD. We also interact closely with the theorists and experimentalists involved in the RHIC program at BNL.

TECHNICAL PROGRESS AND RESULTS:

We completed the work on a spintronics application of graphene. The experimental work on graphene’s behavior in strong magnetic field led to the discovery of a transition to a highly insulating state which we interpret as a form of a Wigner crystal. This work was performed in collaboration with experimental groups at BNL. The corresponding paper was published in PRB and later selected for the Virtual Journal for Nanoscale Science and Technology. Since graphene is two-dimensional system and perfect ordering is impossible in 2D, this led us logically to study the influence of order parameter fluctuations on observables in 2D systems. Two papers on that subject were written and are now under consideration in PRL and PRB. The work performed paved the way towards possible practical implementation of graphene-based spintronic devices, such as the ones described in our patent application BSA07-12 “Nanodevices for Spintronics and Methods for Using Same”, US Patent 60/892,595. This work has also rather general implications well outside the field of graphene studies.

The theoretical ideas generated during this work have led to further collaborations between Nuclear Physics and Condensed Matter Theory groups in BNL. These include the collaborative project on the study of the Quarkyonic phase – a hypothetical state of superdense quark matter is under way (McLerran, Pisarski, Tsvetik) and work on the role of the chiral anomaly in the properties of strongly correlated quark-gluon matter in strong magnetic field that is produced at RHIC (Kharzeev, Khodas).

In the remaining year, we plan to continue close collaboration with the experimental group in the CMPMS Department on the physics of graphene and to extend collaboration with the Center for Functional Nanomaterials. We expect to offer new results on the structure of quarkyonic phase and on the physics of local strong parity violation in hot quark-gluon matter at RHIC.

Getting to Know Your Constituents: Studies of Partonic Matter at the EIC

LDRD Project 08-004

Werner Vogelsang

PURPOSE:

The goal of this LDRD is to develop and commission an operational framework for the extraction of the distributions of quarks and gluons, the elementary particles of the strong interactions in nature, inside nucleons and atomic nuclei from future data taken at an Electron-Ion Collider (EIC). The expected main technical result of the work pursued in this LDRD will be an extensive computer (Fortran) code that will be used to carry out sensitivity studies for quark and gluon distributions in future EIC measurements. The code is expected to help determine the optimal choices for the collision energies and detection capabilities at an EIC and would therefore be an essential part of the preparations for this machine.

APPROACH:

The EIC, with its unique assets of high energy and availability of polarized and nuclear beams, will be the ideal place for investigations of the quark and gluon (or “parton”) sub-structure of nucleons and nuclei. Other lepton scattering experiments, as well as RHIC, are presently already providing information and will continue to do so in the pre-EIC era. In making the science case for an EIC, it is therefore important to assess the impact that EIC measurements would have. This is also closely tied to the developments of the optimal design of an EIC. This need for detailed early studies is the background for the present project. The specific implementation of analyses of quark and gluon distributions in polarized nucleons and in nuclei and their application to the needs at an EIC had not been achieved so far.

Our investigations are being done in a staged approach. Stage 1 is the development of the global analysis technique and its benchmark application to RHIC data. This stage has been completed in 2009. The results obtained here serve as proof of the concept and feasibility of the LDRD project. We are presently in Stage 2 of the project, in which we are adding simulated EIC data to the analysis. Here the goal is to investigate the impact that future EIC data would have on our knowledge about polarized parton distributions. Our approach is as follows: in collaboration with Michael Savastio at Stony Brook University, we have used PYTHIA to simulate deep-inelastic scattering events at the EIC. The generated sample has been used to obtain estimated statistical uncertainties for spin asymmetry measurements at the EIC. We have next used the results of the benchmark analysis discussed above and computed the actual spin asymmetries at the EIC. These asymmetries were then randomly shifted with a Gaussian distribution, making use of the uncertainties previously determined with PYTHIA. The resulting EIC “data” and their “uncertainties” were added to the full global analysis. The analysis was then run with all data sets, including the “EIC data sample”, and new sets of parton distributions and their uncertainties were obtained. The main technical analysis method we are using to carry out the work is a mathematical approach known as the “Mellin technique”. This technique allows to incorporate all presently available data at “next-to-leading order” of QCD. The actual analysis can then be done in terms of a χ^2 analysis. This also includes a proper treatment of the experimental and theoretical uncertainties and their impact on the extracted quark and gluon distributions.

The co-investigators on this LDRD project are A. Deshpande (Stony Brook) and R. Milner (MIT) (for the parton distributions of the nucleon) and D. Kharzeev and R. Venugopalan (BNL) (for

studies of the structure of nuclei). We decided to choose a somewhat unusual “strategic” approach for realizing the goals of this LDRD: rather than hiring a postdoctoral researcher for the duration of the project, we only did a part-time contract hire and are using the remaining funds for attracting more senior visitors for short and/or long-term visits to the laboratory. We hired Dr. Swadhin Taneja on a contract basis from Stony Brook University for the past year. This strategy has worked out exceptionally well, and we plan to continue Dr. Swadhin’s contract in 2010.

TECHNICAL PROGRESS AND RESULTS:

Fiscal year 2009 was the second year of funding for this project. As mentioned above, we have completed Stage 1 and are now in Stage 2. A sample result of a global analysis that includes projected EIC data is presented in the figure, which shows the spin-dependent gluon distribution of the proton, as a function of momentum fraction. As can be seen, EIC measurements would be

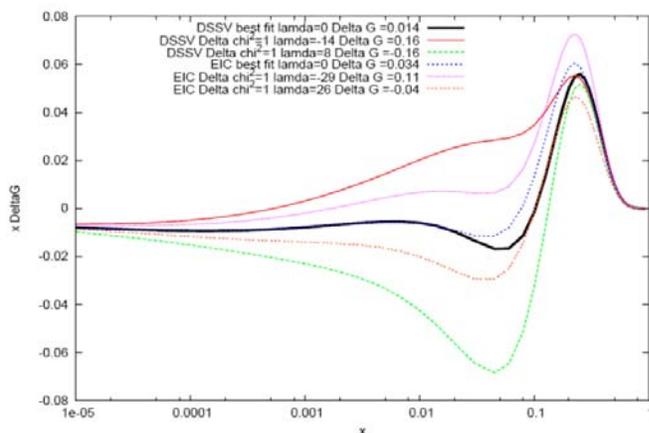


Fig.1: Spin-dependent gluon distribution Δg as function of gluon momentum fraction x , extracted from RHIC and DIS data. The solid line is the “benchmark” result of Stage 1, published in **Phys. Rev. D80 (2009) 034030**, along with its uncertainties. The inner band shows the uncertainties resulting after inclusion of EIC “data”. These are markedly decreased compared to the situation without EIC data.

expected to give a much decreased uncertainty of the gluon distribution, compared to the present situation. While additional studies are needed, this is a significant step forward, as it demonstrates the feasibility of using projected EIC data in a global analysis. Our current efforts aim at completing Stage 2 by improving the analysis of the uncertainties and adding more realistic assumptions about detection capabilities at the EIC. This work is done in large part by Dr. Taneja, with help by M. Stratmann and D. de Florian. Our first milestone for year 3 of funding will be to complete Stage 2. In Stage 3 we plan to identify the requirements for energies and detectors at the EIC, and to further apply the results of the earlier stages. We also plan to extend our technique to the case of nuclear parton distributions. This part of our analysis has not yet progressed as much as for the case of spin-dependent parton distributions, since the latter has been more consuming than anticipated.

Development of the Deuteron EDM Proposal

LDRD Project 08-005

Yannis Semertzidis

PURPOSE:

One of the requirements of a high precision storage ring electric dipole moment (EDM) experiment is to develop a lattice that keeps the polarization of the stored proton or deuteron beam polarized for $\sim 10^3$ s. This time is known with the name spin coherence time (SCT). Professor Yuri Orlov, a world's renown accelerator physicist has analytically estimated that 10^3 s is possible by applying non-linearities at strategic locations around the ring. However, we needed a confirmation of this analysis using particle and spin tracking through software. In addition, particle and spin tracking has the added advantage that it can be more complete when all the effects possible are taken into account.

APPROACH:

A “natural” SCT for a beam with the parameters readily available at BNL is of the order of 1ms due to, mainly, the finite momentum spread of the beam of $(\Delta P/P)_{\text{rms}}=2.5 \times 10^{-4}$. The linear part of the momentum spread is taken out using a regular RF-cavity, which causes the particle momenta to oscillate over the (almost) same value. The second order effects are taken care of by applying magnetic or electric sextupoles at specific places around the ring.

Right at the beginning we had to find a program that can be 1) efficient (fast), 2) accurate, and 3) capable of tracking in the presence of E-fields. We have used the LDRD funds to hire a post doc, Dr. Fanglei Lin, whose Ph.D. subject was in particle and spin tracking with her advisor being S.Y. Lee of IUCF, a world caliber expert on the subject. Dr. Lin was an expert in using a program used at RHIC to do spin tracking. All of them proved to be very challenging tasks. We took the approach of benchmarking the program for accuracy and efficiency in the presence of only magnetic fields. We used cases where the effects could be estimated exactly using analytical methods also used in the muon g-2 experiment, like the so-called pitch correction. To our dismay we found that the program did not take into account the second order effects which are very important for the EDM project. We therefore had to modify the program to do that. Dr. Lin, working together with Nikolai Malitsky and Alfredo Luccio managed to modify the program so that it accurately tracks the momentum and spin of the particle to second order. Those results have been presented at conferences and have been published in several journals. However, this development took two years and Dr. Lin took another position with BNL's Light Source II before she could finish her work on implementing the E-fields in the lattice.

Currently Alfredo Luccio and Waldo MacKay, both of C-AD, are working hard to implement the E-field capability. For the ALD review of Dec 2009 we chose to add a presentation using an alternative tracking program for comparison reasons.

TECHNICAL PROGRESS AND RESULTS:

Horizontal and vertical oscillations have a similar effect on the SCT. Dr. Lin has studied simple cases where she has shown that using sextupoles can indeed prolong the SCT, as shown in Fig. 1.

Horizontal & Vertical oscillation

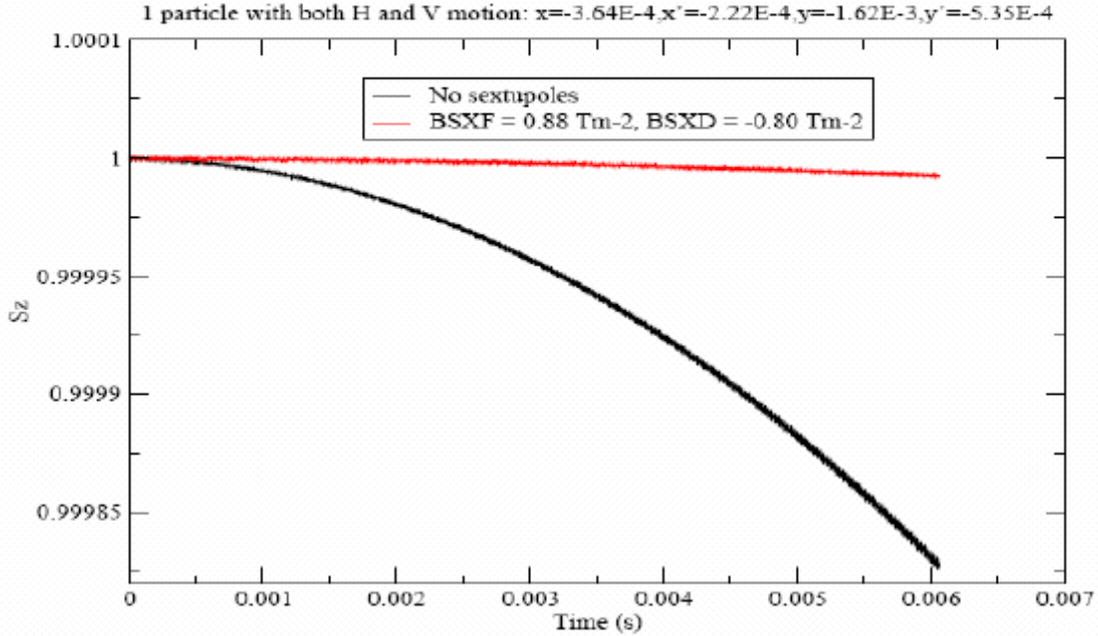


Figure 1. Simulated particle motion in a storage ring shows that horizontal and vertical oscillations depolarize the beam as a function of time or otherwise, it shortens the SCT (black curve). However, adding sextupole magnets at strategic locations around the ring can significantly prolong the SCT (red).

We have accomplished two of the three goals of the project, with the E-field implementation the remaining one. We've estimated the pitch correction, which is also estimated analytically, and found an excellent agreement with the analytical estimation. The agreement is best when using the largest segmentation for the lattice elements, see Figure 2.

Approach	$\frac{\omega_a - \omega_0}{\omega_0} (\times 10^{-8})$	CPU time (ms)
Analytical formula	7.42	
UAL, IR=1	6.48 ± 0.01	0.86
UAL, IR=4	7.34 ± 0.02	2.97
UAL, IR=8	7.38 ± 0.02	5.81
UAL, IR=16	7.39 ± 0.02	10.66
UAL, IR=32	7.40 ± 0.02	21.72

Figure 2. The analytical result of so-called pitch correction gives 7.42×10^{-8} , and the program approaches this value with high precision when the largest segmentation (IR=32) of the lattice elements is used.

Development of Small Gap Magnets and Vacuum Chamber for eRHIC

LDRD Project 08-008

Vladimir N. Litvinenko

PURPOSE:

The development of small gap magnets, both dipoles and quadrupoles, and vacuum chamber compatible with a multi-pass energy-recovery linac (ERL) has high potential for making the ERL a cost effective solution for eRHIC using the RHIC tunnel for four of its five return loops. Using the RHIC tunnel is the only viable option of operating eRHIC with electron energies at and above 10 GeV. Otherwise - like in the ring-ring option - the power of synchrotron radiation will be too high and energy consumption will be prohibitive. Designing and testing the quality of mini-gap (gaps ~5 mm) dipole and quadrupole magnets with a common vacuum chamber are a critical step for developing this concept. Using results of the magnetic field quality for tracking particles through 4 passes around the RHIC is a critical validation of this approach.

APPROACH:

Using an ERL for eRHIC provides an electron beam with very small emittance and as a result as with very small sizes. In return, it allows one to design loop magnets for eRHIC with very small gaps (few millimeters) and install them at a single vacuum chamber. Small gaps and low magnetic fields of the magnets provide for an energy efficient lattice extending for about 16 kilometers. The main research was focused on checking the viability of this concept, including studies of the quality of magnetic fields in prototype dipole and quadrupole magnets, stresses and deformation of thin-wall convolutions of the vacuum chamber. The small gap of the magnets allows the use of low-current coils, which are low weight and can be inexpensive. The approach was to design such magnets and test various manufacturing techniques (grinding, EDM, etc.) and check the quality of the resulting field. The resulting field errors should be compared with requirements coming from numerical tracking.

Year 1 milestones: a) model, design and manufacture dipole magnet; b) develop tracking code; c) design and simulate vacuum chamber stresses and sagging with ANSYS

Year 2 milestone: a) design and manufacture quadrupole magnet; b) complete magnetic measurements; c) manufacture prototype of vacuum chamber

Year 3 milestone: a) analyze the data and make decision on next step

TECHNICAL PROGRESS AND RESULTS:

We have simulated and designed dipole and quadrupole magnets with 5 mm gap. We also developed a tracking program suitable for multi-pass ERL using Tracy-3 as initial step-stone.

3D magnetic simulations predicted the quality of the field sufficient for lossless transport of the electron beam in the ERL and for preserving its quality. We established high quality 3D magnetic measurements as well as a mechanical QA system.

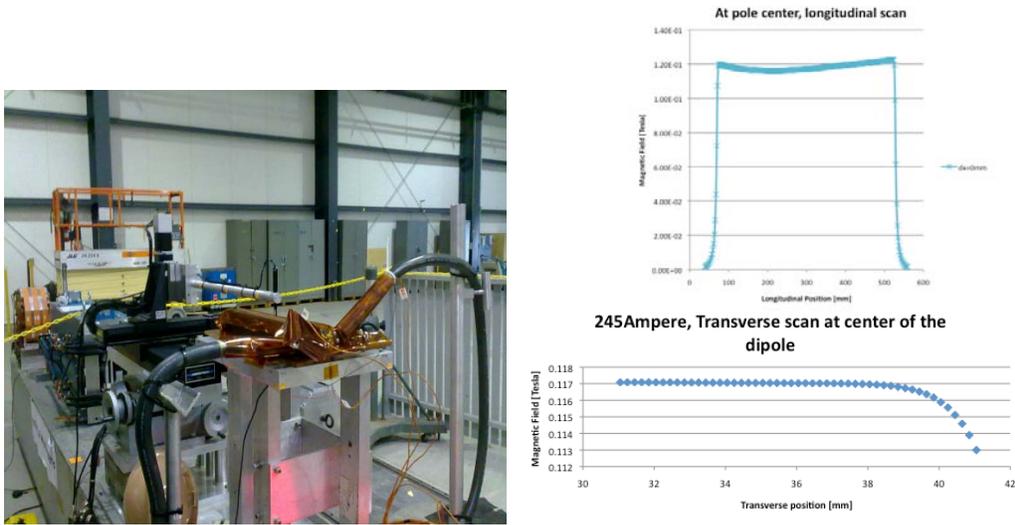


Fig. 1 (a) left - Set-up for small gap magnet measurement with installed dipole magnet under test, (b) top-right measured magnetic field profile as function of longitudinal coordinate; (c) bottom-right: measured transverse field profile.

Three sample magnets were manufactured at BNL’s Central Fabrication Services using EDM and grinding techniques. The quality of the manufacturing did not meet required tolerances. This was confirmed by both magnetic measurements and mechanical survey. Magnetic measurements of the quadrupole are underway, but based on the mechanical survey we expect very poor results.

Due to the Central Fabrication Services’ difficulties in meeting the required tolerances for the dipole and quadrupole magnets, we are proceeding with ordering the magnetic cores outside of BNL.

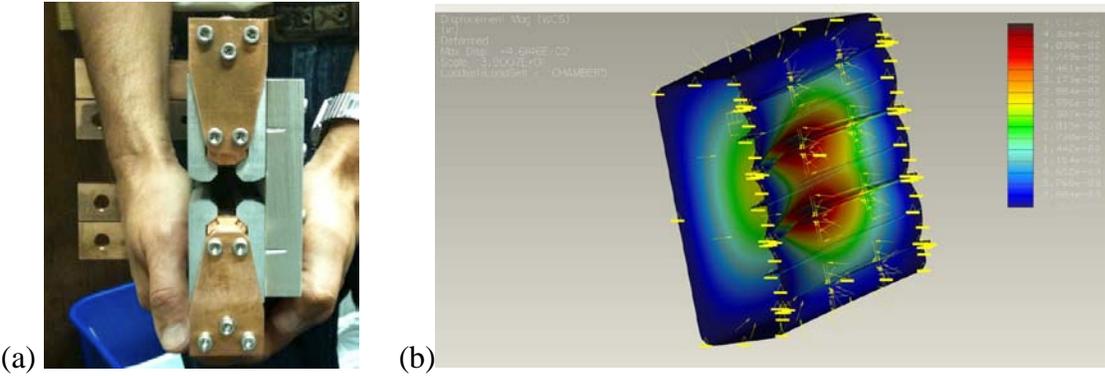


Fig. 2 (a) left – Assembled small gap quadrupole with coils; (b) 3D ANSYS analysis of stressed in small gap vacuum chamber

The prototype of the vacuum chamber is designed (see Fig. 2.b) and is being manufactured; it will be available for test in about one month.

Novel Methods for Microcrystal Structure Determination at NSLS & NSLS-II

LDRD Project 08-022

Allen M. Orville, Alexei S. Soares, Howard R. Robinson and Annie Héroux

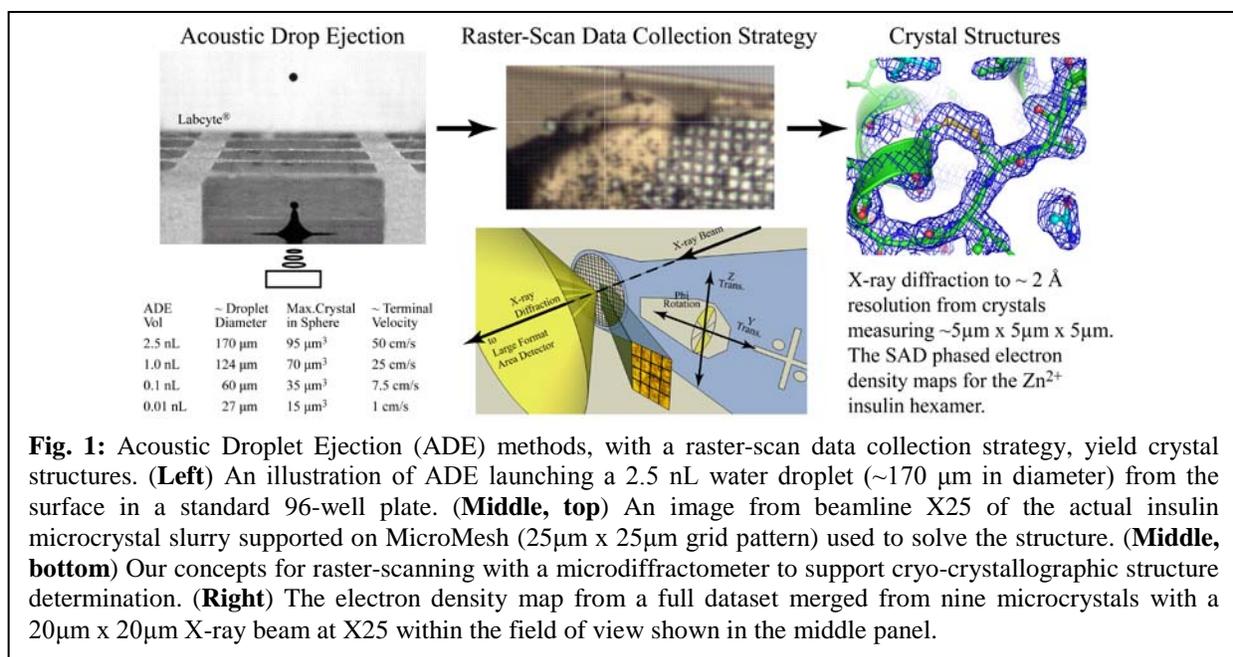
PURPOSE:

The frontier of structural biology is defined in part, by the structural analysis of membrane proteins, large macromolecular complexes of proteins and/or protein-nucleic acids, and whole virus particles. Unfortunately, the complexity of these systems frequently limits the availability of large, single crystals. In contrast, microcrystals measuring only a few microns along an edge are often easy to obtain even from these systems; but they are difficult to use because they are too small to yield a suitable diffraction pattern with conventional macromolecular crystallography (MX). Therefore, a major barrier that remains to be overcome in MX is how to manipulate microcrystals for structure determination. This is especially true at existing third-generation synchrotron X-ray sources and for the NSLS-II under construction at Brookhaven National Laboratory. This new source, and indeed all third generation sources, requires either significant attenuation of the X-ray beam, or radically new methods of data collection to prevent radiation damage within several milliseconds of exposure. This proposal addresses these critical gaps.

APPROACH:

Our plan is to use a statistically large number of randomly oriented microcrystals for high throughput crystal structure determinations. We believe that our results will push back the frontiers of structural biology research highlighted above, as well as establish time-resolved crystallography as a generally applicable technique for the first time.

Research Plan: The essence of our plan, termed “Serial Micro-Crystallography”, is to use a statistically large number of randomly oriented microcrystals. Each will be taken potentially to the X-ray radiation dose limit with highly-focused, unattenuated X-ray beams. However, only a small fraction of the whole dataset will be collected from each microcrystal. Consequently, the complete dataset will be built-up serially from many narrow slices of reciprocal space. Although each dataset will derive from a large number of microcrystals, each microcrystal will experience relatively little manipulation during the data collection. As a result, we envision that our methods will also be very high throughput. As illustrated on the next page, we are following two parallel strategies to collect X-ray diffraction data from microcrystals: **A) Raster-Scan**, and **B) Micro-Droplet Stream**. In the first strategy the X-ray beam is scanned in a logical raster pattern across a support grid containing a microcrystal slurry. In the second strategy, a stream of microdroplets is created from a microcrystal slurry such that each drop contains one microcrystal on average. The droplets will traverse the X-ray beam one by one, and those containing a crystal will yield a diffraction pattern. We are currently designing microfluidic devices to deliver the microcrystal slurry to either the raster-scan grids or to create the microdroplet streams. Because structure and function are linked fundamentally, another frontier aspiration of many biochemists and structural biologists is to determine molecular movies of enzymes engaged in catalysis. In our most ambitious plans, we will fabricate a novel microfluidic, vortex micromixer immediately upstream of the droplet nozzle. This will provide a means to introduce known delta-time intervals appropriate for most catalytic reactions, and thus enable time-resolve serial micro-crystallography. Most importantly, for the first time this technology will be truly general.



TECHNICAL PROGRESS AND RESULTS:

This LDRD project currently supports partial salaries for Dr. Marc Allaire with his graduate student, Mr. Matthew A. Engel (full salary, enrolled in the Biomedical Engineering Program at Stony Brook University), as well as Drs. Soares and Orville (PI). We routinely produce microcrystal showers of several well-know standard proteins including lysozyme, Zn²⁺ insulin, taumatin, and nitroalkane oxidase. We are currently focusing on the **Acoustic Droplet Ejection** (ADE) technology and the Raster-Scan strategy at beamline X25. The concepts of the LDRD proposal but at their enhanced stage of current development are illustrated above. This graphic was included in the grant proposal that Drs. Orville, Allaire, and Soares submitted to the NIH on January 22, 2010 for follow-on funding. Some of the metrics of the proposal are listed in the *LDRD Data Collection Form*.

Dr. Soares and Mr. Engle visited our new collaborators, Labcyte (Sunnyvale, CA) from November 8-10, 2009 to develop ADE methods and test them for suitability with micro-crystallography. Drs. Soares, Allaire and Mr. Engle also traveled to beamline ID23-D at the Advance Photon Source (APS) from December 18-21, 2009 to use their minibeam facility for data collection from microcrystals mounted with ADE methods (see below). We believe that our most important innovation to date is our plans and development of ADE technology for use in microcrystal structure determination. Consequently, these concepts are the basis of the record of invention and our initiation of the patent process.

ADE is a “touchless” method that focuses ultrasonic acoustic energy into a liquid, which mixes and ejects small droplets from the surface and deposits them to a specified location with micron accuracy (see Fig. 1). This strategy also has the advantages of precision, speed (up to 200 Hz), ultra-low-volume transfer, and the technology eliminates cross-contamination of samples. The droplet size is controlled over a range of ~10 picoliters to 2.5 nanoliters by selecting different frequencies and harmonic overtones. ADE technology is a gentle process and Labcyte has

demonstrated that it can be used to transfer proteins, high molecular weight DNA, and live cells without damage or loss of viability. ADE can also be used to “print” droplets in a programmable 2D grid pattern on, for example, a MiTeGen LLC, (Ithaca, NY) MicroMesh crystal mount, which is compatible with standard goniometers and cryostreams. ADE therefore, introduces a means to control the location of the flash-cooled microcrystal droplets and naturally complements our Raster-Scan strategy.

As illustrated in Fig.1 above, we have very recently shown that ADE methods can eject 2.5 nanoliter droplets of a suspension of microcrystals in Mother Liquor. We prepared two types of microcrystal slurries, Zn²⁺ insulin and lysozyme that each contained high concentrations of microcrystals in the 2-20 μm size range. We then brought our samples to the Labcyte facility to use ADE methods to transfer 2.5 nanoliter droplets (~170 μm in diameter) through the air to a conventional MiTeGen MicroMesh, which spread to cover about a 200 μm region of the grid. We observed numerous microcrystals in the 2-20 μm range in their largest dimension disperse on the grid that transferred with the droplet. These crystals were subsequently rapidly cryo-cooled with liquid nitrogen, a standard procedure in crystallography, and then analyzed for diffraction quality and structure determination. The X-ray diffraction data were collected at two different minibeam-capable synchrotron beamlines: X25 at the NSLS and ID23-D at the Advance Photon Source (APS). Our preliminary results indicate that ADE does not alter the crystal quality as deduced from the X-ray diffraction data and refined crystal structures. Both molecular replacement and SAD phasing techniques were used to solve the three-dimensional structures of ADE-transferred microcrystals. Of particular importance we note that ADE methods provide very fine control over the amount of Mother Liquor surrounding the microcrystals, yielding improved signal in the diffraction data by reduced background noise.

Our *blue-sky* vision for follow-on funding to this LDRD project includes the last objective of our proposal submitted to the NIH Roadmap Initiative (RFA-RM-09-022) Transformative Research Projects Program (R01). We plan to develop a very high throughput, **Optical Goniometer** as illustrated in Fig. 2. We will start with an ADE system that launches ~150 picoliters (~65 micron diameter) droplets into the air from a well or sitting drop containing a microcrystal slurry. In the final development, the transducer frequency and microcrystal slurry concentration will be optimized such that each droplet is ~10 picoliters (~25 microns in diameter), contains approximately one microcrystal each, and maximizes the ratio of crystal volume to droplet volume. We will hold each droplet in the X-ray beam with an optical trap comprised of a single laser beam. Furthermore, linearly polarized laser light will also apply a torque to birefringent crystals, and thus orient and rotate each microcrystal. With laser powers in the 10 – 100s mW range, optical traps can manipulate a range of sizes of aerosol droplets, and generate several hundred pN•nm of torque to rotate micron size particles with angular velocities up to 200 rad/s. Therefore, our

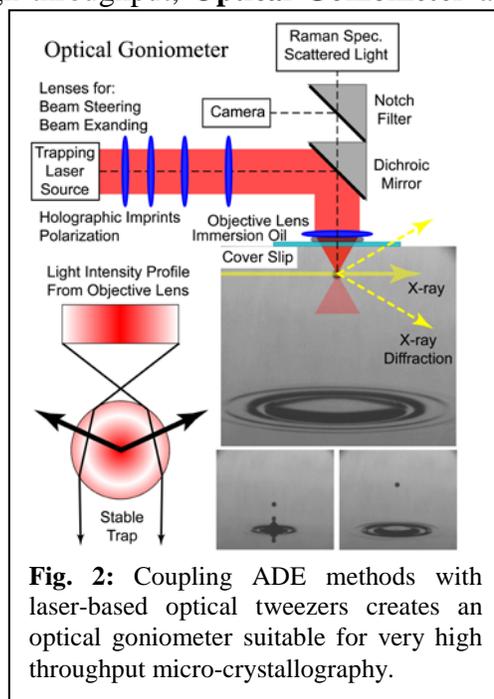


Fig. 2: Coupling ADE methods with laser-based optical tweezers creates an optical goniometer suitable for very high throughput micro-crystallography.

optical goniometer will also provide a means to mix and initiate enzyme reactions within ADE droplets, as well as to collect diffraction datasets with duty cycle that matches the lifetime of each sample used at the NSLS-II, other third generation X-ray sources, or the intense X-ray pulses at the FELs.

Combined PET/MRI Multimodality Imaging Probe

LDRD Project 08-025

David J Schlyer

PURPOSE:

The goal is to design a multimodal imaging probe for use with our combined MRI-PET animal imaging system which will allow simultaneous PET and MRI measurements. The probe will contain both a positron emitting radionuclide and a superparamagnetic MRI contrast agent in a single iron oxide nanoparticle. There is mounting evidence that most disease processes can be identified by altered molecular profiles and/or cell behavior prior to visual anatomic alterations. Insight into these processes could potentially allow for (1) the early detection of disease, (2) more accurate prognoses and personalized treatments, (3) the ability to monitor the effectiveness of therapeutic treatments, and (4) improvements in our understanding of how cells behave and interact in their intact environment in living subjects. This dual probe concept combines the strengths of both PET and MRI into a powerful new tool for quantitative molecular imaging.

APPROACH:

Molecular imaging with PET has already had a profound effect on our understanding in both preclinical and clinical areas including cancer research and many aspects of neuroscience from cognition to psychiatric diseases. MRI is beginning to move from structural and functional imaging to molecular imaging, but this is in the early stages and requires considerable development. The combined use of PET and MRI with our proposed imaging agents could be a quantum leap forward in synergistically addressing problems of cellular pathophysiology. One key advantage of this approach is that the radionuclide probe is included in the nanoparticles which means that the radionuclide will stay with the nanoparticles as opposed to some other radiolabel nanoparticles in which the radionuclide is attached to the nanoparticles using a chelating agent which may release the radionuclide under biological conditions.

We will address each of our specific aims in the following ways.

Specific Aim 1 - Incorporate Iron-52 in Nanoparticles: Superparamagnetic iron oxide (SPIO) MR imaging contrast agents consist of an iron oxide nanoparticle core covered with a coating material (such as dextran). A diagram of the probe is shown in Figure 1.

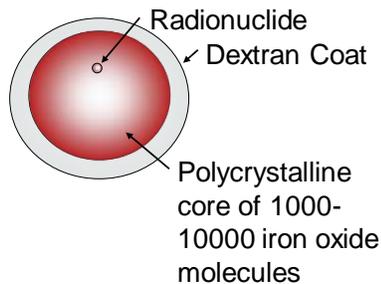


Figure 1. Schematic diagram of the radiolabeled nanoparticle molecular probe

We have prepared magnetic particles doped with the radionuclide Fe-52. They were synthesized by microemulsion technique in the lab with controllable sizes of 4-150 nm using a method developed by Molday [1]. The nanoparticle is coated with dextran to reduce agglomeration. The labeling with biologically active molecules will be done in collaboration with the Center for Functional Nanomaterials (CFN) at Brookhaven National Lab (BNL) and the BNL Medical Department radiochemists.

Specific Aim 2 - Use Simultaneous PET/MRI: We have developed a scanner that will allow the simultaneous acquisition of quantitative physiological data using PET, and high resolution anatomical or even complementary functional data using MRI.

TECHNICAL PROGRESS AND RESULTS:

The iron oxide nanoparticles synthesized by the Molday method gave a good magnetic signal as shown in Figure 2. The darker the circle, the better the contrast agent.

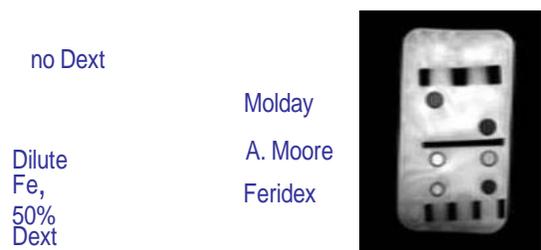


Figure 2 Comparison of magnetic characteristics with different methods of synthesis (Molday [1] and Moore [2]) with commercial iron oxide nanoparticles (Feridex).

As can be seen, the preparation using the Molday approach gave a signal that was very similar to the signal from the commercial Feridex particles. These particles were used in PET experiments and the whole body distribution in the rat is shown in Figure 3.

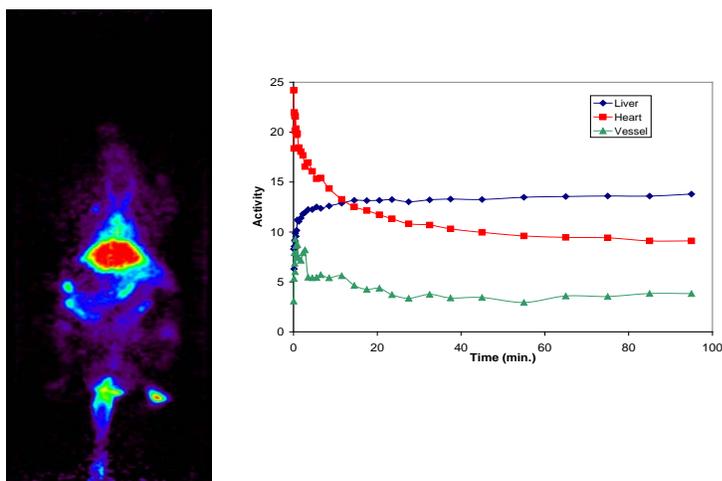


Figure 3 Iron-52 labeled iron oxide nanoparticle biodistribution in a rat over 95 minutes.

The iron oxide nanoparticles were also imaged in a mouse using MRI. The same pattern of accumulation is shown with a high accumulation in the liver as shown in Figure 4.

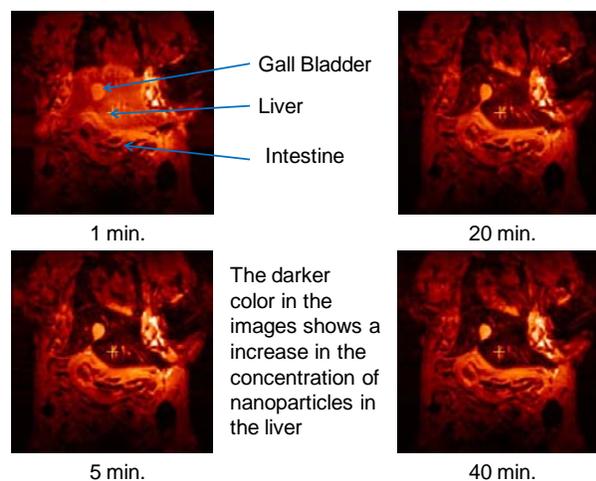


Figure 4. Iron oxide nanoparticle biodistribution in a mouse liver over 40 minutes.

The final step in these experiments will be to carry out the simultaneous imaging. This can happen as soon as we have access to iron-52 again at the BLIP.

References:

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Genomic DNA Methylation: The Epigenetic Response of *Arabidopsis Thaliana* Genome to Long-Term Elevated Atmospheric Temperature and CO₂ in Global Warming

LDRD Project 08-028

Qiong (Alison) Liu

PURPOSE:

The goal of this project is to determine the changes of DNA cytosine methylation in the genome of *Arabidopsis* plants in response to elevated ambient temperature and CO₂ concentrations such as would occur during global warming. This epigenetic information will help us identify genomic and genetic loci that are regulated by elevated temperature and CO₂ that can impact on plant development, flowering time, grain and biomass production, and to understand how regulation of DNA methylation in the plant genome can help plant's adaptation to environment.

APPROACH:

Exponential emission of CO₂ into the atmosphere resulting from human activities has led to an enhanced greenhouse effect or global warming. Prolonged increase of temperature has been shown to increase the growth rate and induce early flowering of plants in laboratory experiments (Balasubramanian S. et al. PLoS genetics. 2006 2(7): 980-9), and is correlated to biomass and grain reduction in crops (Peng S. et al. Proc Natl Acad Sci U S A. 2004 101(27): 9971-5). Paleobotanical evidence has linked a fourfold increase in atmospheric carbon dioxide and an associated 3° to 4°C greenhouse warming to a well-documented major faunal mass extinction during the period of the Triassic-Jurassic boundary (McElwain JC et al. Science 1999 285: 1386-90). Some prior evidence suggests that plants may respond to altered temperature and CO₂ level via an epigenetic response. For example, microarray studies have identified many gene expression changes in *Arabidopsis* when the plant is grown at a few degrees higher temperature (Balasubramanian S. et al. PLoS Genetics, 2006, 2(7); 980-9). A few small RNAs are also generated or altered in *Arabidopsis* growing at a lowered temperature (Oh M. et al. Journal of Plant Biology, 2007, 50(5); 562-67).

We have taken several approaches to understand how elevated ambient temperature can function to affect the epigenome. We used both HPLC and LUMA assays to analyze the overall genomic DNA methylation. We have also analyzed the deep sequencing results of small RNA libraries, and the altered siRNAs expression indicates regulation of genomic DNA methylation. We are also working to profile the genomic DNA methylation in these plants using methylated cytosine immunoprecipitation in combination with an Affymethix *Arabidopsis* tiling array, and are working towards the single nucleotide resolution of cytosine methylation profiling of the genome using new generation sequencing methods.

For this project, Alison Liu has collaborated with (1) Alistair Rogers of the Environmental Science Dept. at BNL to obtain the *Arabidopsis* plants grown under FACE conditions at Oak Ridge, Tennessee. (2) With Cold Spring Harbor Laboratory Genome Research Center for sequencing small RNAs, and (3) with Dr. Michael Zhang at Cold Spring Harbor Lab for bioinformatics work.

TECHNICAL PROGRESS AND RESULTS:

This LDRD project started in March, 2008. The summarized results to date are as follow:

(1) Phenotypic characterization: *Arabidopsis* plants were grown in our newly purchased growth chambers at 23°C and 26°C. We found that elevated temperature can reduce significantly biomass and seed production in *Arabidopsis*. We have characterized these phenotypes in details.

(2) Gross evaluation of genomic DNA methylation in *Arabidopsis* grown at different temperatures: using HPLC assay, we have detected a significantly lower level of genomic DNA methylation in plants grown at elevated temperature, compared to those grown at 23°C.

(3) *Arabidopsis* small RNA deep sequencing. Small RNA libraries were generated using *Arabidopsis* plants grown at 22°C and 28°C, and 400ppm and 800ppm CO₂ concentrations, indifferently by following the Illumina small RNA preparation instruction manual. We have obtained 6 to 8 million sequencing reads using the Illumina Solexa sequencer at Cold Spring Harbor Lab. We have identified a few dozen known miRNAs that have altered expression in elevated temperature and CO₂ concentrations. We have also found novel miRNAs and siRNAs with differentiated expression rates at different temperature and CO₂. These results also revealed the interaction between CO₂ and temperature. These results suggest that small RNAs might play an important role in plant adaptation to elevated temperature and CO₂ concentration in global warming conditions.

In summary, in the previous six months, we have completed the characterization of *Arabidopsis* phenotypes induced by elevated ambient temperature. We have also nearly completed the analysis of small RNA expression induced by elevated temperature and CO₂. In addition, we have confirmed the reduction of genomic DNA methylation resulted from elevated temperature using both HPLC and LUMA assays. We are currently working with Joe Ecker's lab to complete the full study of genomic DNA methylation changes of plants in response to different temperatures and CO₂ levels.

Fabry-Perot Interferometer & Hard X-Ray Photoemission

LDRD Project 08-034

Elio Vescovo

PURPOSE:

The purpose of this LDRD is to manufacture a Fabry-Perot (FP) etalon by micro-etching techniques on a single crystal Si wafer. The etalon has the advantage of easy construction and robust alignment, and could have energy resolution below 0.1 meV. The etalon could be characterized combining two resonators in series and measuring the optical output of the system as a function of a temperature gradient between the two.

APPROACH:

Recently the feasibility of high-resolution FP resonators working in the hard x-ray region (~14 keV) has been demonstrated [1]. The resonator consisted of two single crystal of $\alpha\text{-Al}_2\text{O}_3$ separated by 50 mm. However, the two crystals must be aligned to nanometer precision. Therefore, we propose to manufacture the etalon by micro-etching techniques on a single crystal Si wafer, and the critical alignment between the two diffracting Si planes is automatically guaranteed with atomic level precision. The single piece interferometers will be produced using the facilities of the CFN and will be tested at beam line X13B at NSLS.

TECHNICAL PROGRESS AND RESULTS:

This is the second year of this LDRD, and last year we used the deep reactive ion etching (RIE) technique available at the CFN to fabricate the diffracting plates on Si wafers, and then characterized the structures at beam line X13B. We improved the resolution of beamline X13B to 3 arcsec, and within the 3 arcsec resolution, there was no additional stress from the etching process.

We started applying for beam time at synchrotron sources with high energy resolution capabilities. However, we were not successful. So we decided to use the existing resources at NSLS. In order to do experiments at NSLS, two things needed to be done. First, we need to modify the geometry of the FP interferometer to lower the energy resolution. This way, we don't have the extreme high energy resolution, but we can still demonstrate the interference. New photolithography masks were made through an outside vendor, and new structures were fabricated at the cleanroom. Due to the lower energy resolution, the gaps between the Si walls are narrower than before (10 micron compared with 60 micron before). This creates new challenges for the etching process due to the larger depth to gap ratio. A new etching recipe was recreated and tested. Figure 1 shows the cross section of the etched structure. We are still working to improve the quality of the interferometer in this new geometry.

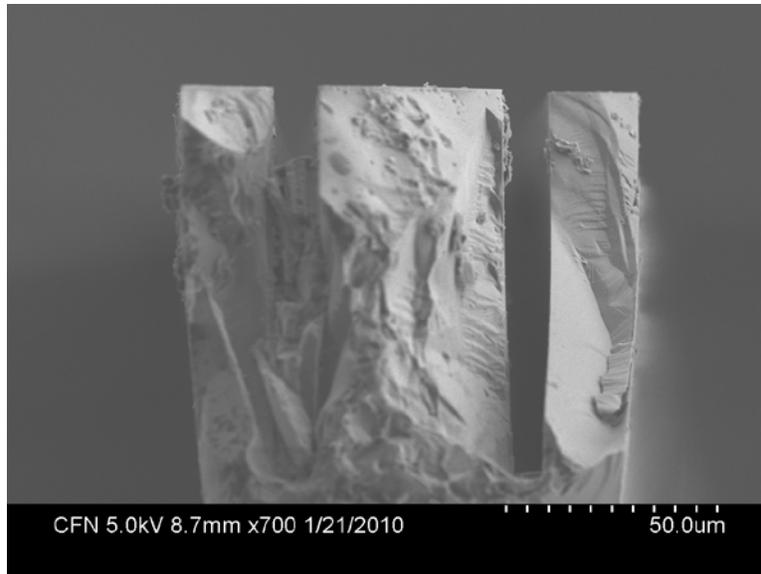


Figure 1: SEM image of the cross section of FP interferometer. The gap shown is decreasing with deeper etching, which would cause the interference pattern to change.

Second, we need to improve the energy resolution of beam line X13B. For the FP experiment, we need to measure at 14.44 keV, where Si (12 4 0) diffraction is at exact backscattering. We installed another monochromator to improve the energy resolution of X13B at 14.44 keV to 5 meV. Angular mesh scan of the theta and phi angles was measured to align the interferometer (see Figure 2a). Once the exact backscattering condition was achieved, we tilted the sample a little to avoid multiple scattering and started measuring the energy scan. Figure 2b shows an energy scan of a single wall Si structure with 100 micron wall thickness. The transmission shows a dip with about 17 meV FWHM. However, the design of the monochromator makes the energy scans very noisy, and we are designing a new monochromator to solve the problem: the scan of energy will be accomplished by rotation of a single motor in the new design, where in the existing one, this has to be done by rotating two motors collectively.

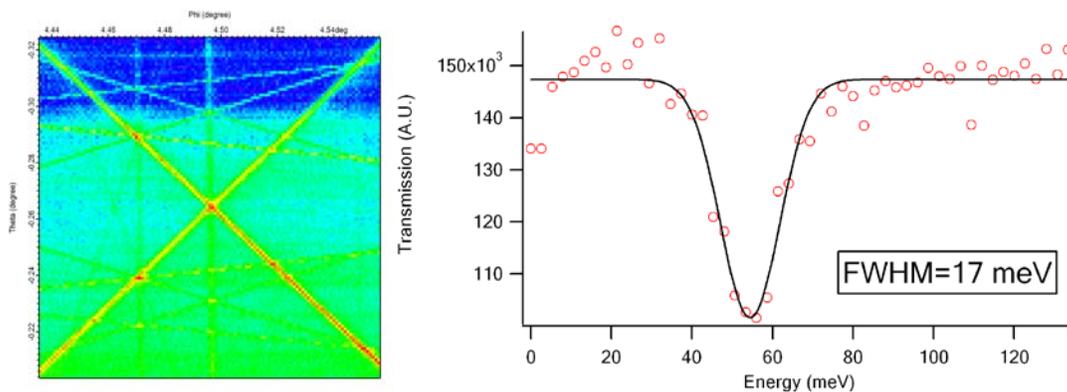


Figure 2: a) Left: Angular mesh scan of the phi (horizontal) and theta (vertical) angles of the interferometer. The detector measures the direct transmitted x-ray beam, and the warmer colors indicate less transmission due to the multiple Bragg diffractions. The lines converged in the center is where the exact backscattering condition is. b) Right: Energy scan of a single wall Si structure with 100 micron thickness.

Ultrafast Electron Diffraction for Transient Structure and Phase Transition Studies at the NSLS SDL

LDRD Project 08-037

X.J. Wang, I. Bozovic, Y. Hidaka, C.C. Kao, J.B. Murphy, S. Pjetrov and Y. Shen

PURPOSE:

Ultrafast electron diffraction (UED) is a promising technique that allows us to observe a molecular structure transition on the time scale less than 100 femtoseconds (fs). UED has been continuously developed as a complementary technology to the X-ray Free Electron Laser (X-FEL) for probing ultrafast events of ultra-small objects. UED has advantages over X-FEL in terms of its compactness, 10^6 times larger cross section, and less damaging ability to the samples. Our goal is to design, optimize, and experimentally demonstrate a single-shot MeV UED system with an atomic scale spatial resolution and a time resolution on the order of 100 fs. The SDL UED system will be a unique tool for ultrafast science and beam physics at BNL.

APPROACH:

The time resolution of conventional UED has been limited to over 1 picosecond (ps) when the system is operating at an energy of 10 to 100 keV. It can be reduced to the order of 100 fs by decreasing the number of electrons in the bunch at the cost of reduced signal-to-noise ratio (SNR), which requires multiple shots to obtain resolvable diffraction patterns. One of the main causes for this limitation of UED is the space charge effect that prohibits a further compression of the electron beam bunch length. To overcome the space charge effects, we pioneered the idea of using a photocathode RF gun for the UED application. The photocathode RF gun is capable of producing MeV electron beam, which will significantly reduce the space charge effect, and lead to short electron bunches. Beside ultrashort electron generation, we also developed unique electron beam instrumentation and a single-photon UED detector. Our electron beam instrumentation is capable of characterizing electron beam charge, energy and bunch length. The RF deflecting cavity we developed with Haimson Industry will have a time resolution of 20 fs. The UED detector features a 16-bit EMCCD camera and donut-shaped phosphor screen.

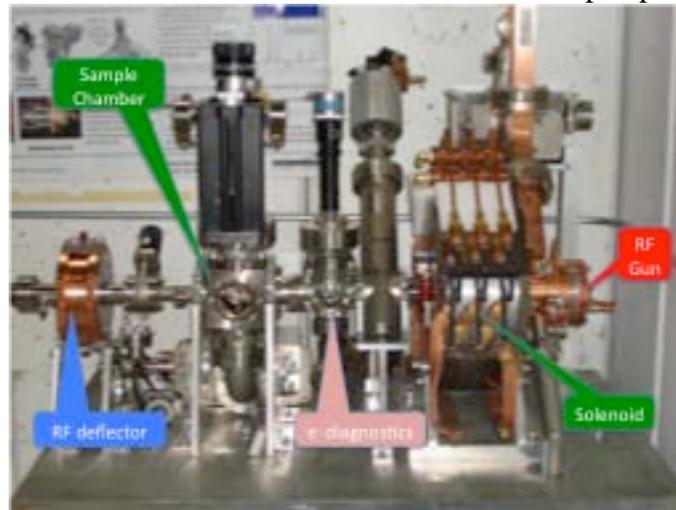


Fig. 1: The MeV UED system installed at the NSLS SDL.

TECHNICAL PROGRESS AND RESULTS:

The design of the proposed UED system has been optimized by tracking electrons from start (photocathode RF gun) to the end (detector), using both a particle tracking code PARMELA and a custom MATLAB code that calculates a scattering intensity distribution by an aluminum sample placed between the photocathode RF gun and the UED detector. We have completed the detailed engineering design of the MeV UED, and all major components are being installed at the NSLS SDL (figure 1).

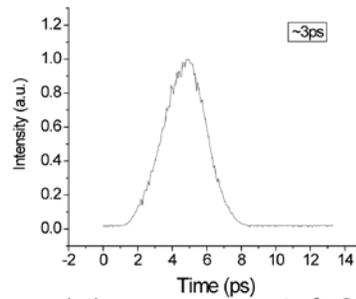
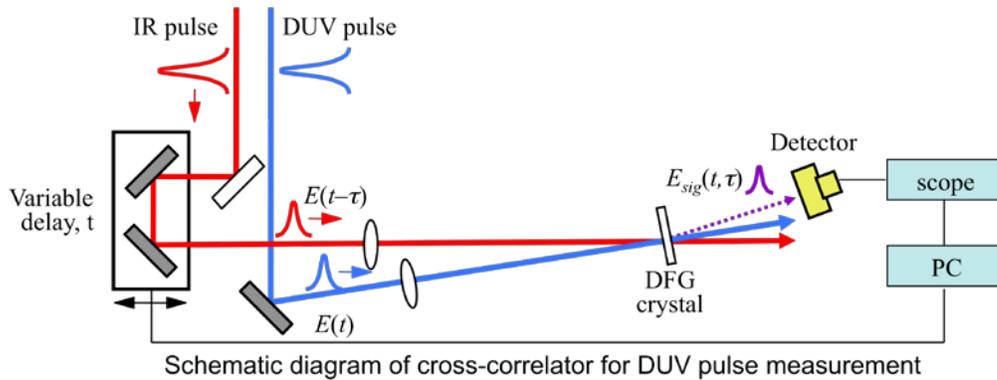


Fig. 2: the cross-correlator developed for the MeV UED. Other major achievements are the completion of the laser transport line and development of a DUV cross-correlator with 100 fs time resolution (figure 2).

Milestones for FY2010: September 2009 – March 2010: Installation of UED at the NSLS SDL. March-April, 2010: UED commissioning. May 2010: UED operational for ultrafast science.

The Development of a Laser Based Photoemission Facility for Studies of Strongly Correlated Electron Systems

LDRD Project 08-039

P.D. Johnson

PURPOSE:

The objective of this research program is to establish a photoemission facility based on the use of a laser as a source. The use of such a source has two objectives. Firstly, it is widely believed that the use of the lower photon energies available from a laser based source will result in a more sensitive PES experiment. This has never really been confirmed and needs to be investigated. Secondly the laser source is a high rep rate 75Mhz source that represents an ideal source for investigating the properties of a new high resolution time of flight (TOF) electron spectrometer developed at BNL. The latter represents a new type of electron spectrometer that may well see application at a variety of FEL type light sources.

APPROACH:

A laser based source that produces UV radiation by frequency doubling and quadrupling will be commissioned in the new laser laboratory in building 480. A new time of flight electron spectrometer, designed at BNL has been constructed and commissioned. These two separate components will be brought together to establish the laser based PES facility.

TECHNICAL PROGRESS AND RESULTS:

The TOF electron spectrometer has now been assembled and undergoing commissioning. The design involves the coupling of a parabolic collection mirror to a “velocity filter” that employs oscillating electrostatic fields to select electrons of particular energies. That such a system is capable of measuring the energies of electrons has now been demonstrated by firing the beam from an electron gun directly into the velocity filter. The arrangement for this experiment is shown in figure 1 below.

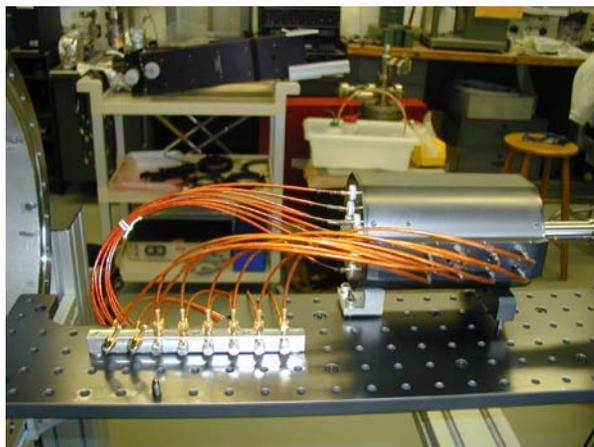


Fig. 1 *The velocity filter and associated cabling is shown with the nose of the electron gun entering the field of view from the right.*

The spectrometer has been installed in a vacuum vessel that has been especially designed to minimize magnetic and electrostatic fields that might interfere with the low energy electrons.

The latter chamber shown in figure 2 below has been designed constructed and tested for residual magnetic fields and vacuum tightness. The magnetic field was found to be less than 3 milligauss. In the course of testing the spectrometer, it became clear that the high frequency fields coupled to a number of the surrounding surfaces, a problem that could potentially limit the ultimate resolution of the instrument. With careful analysis this problem has been essentially mitigated by introducing appropriate filtering in the electronic circuits.

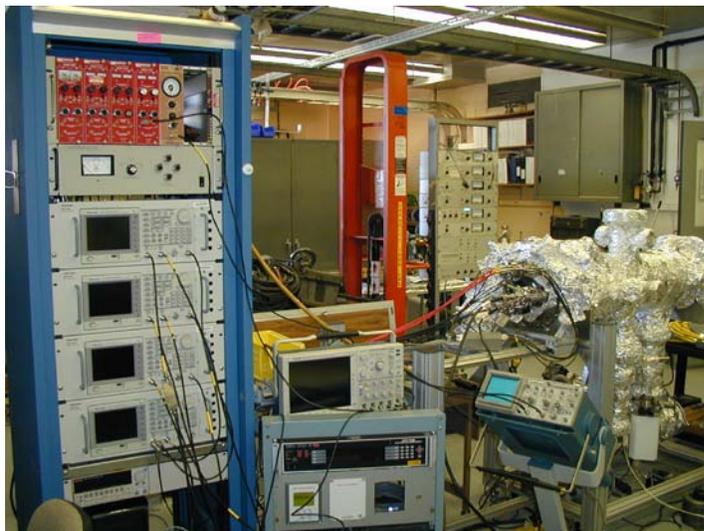


Figure 2. *The experimental system and associated electronics.*

An 80 MHz Mira Ti:S laser pumped from an 18 watt diode pumped solid state Nd:YVO laser that can produce femto or picosecond pulsewidths, a synchrolock to slave it to the spectrometer and a UHV monochromator/spectrometer have all been installed in building 480. A second femtosecond Mira laser, with the same rep rate, as well as a stretcher/compressor and a regenerative amplifier are also installed in the same laser laboratory. These different systems may be configured to allow direct photoemission experiments via the use of frequency doubling and quadrupling or 2ppe pump-probe type experiments.

A Labview based data acquisition system has also been developed to run the spectrometer.

Theory of Electronic Excited States in Heterogeneous Nanosystems

LDRD Project 08-042

Mark S Hybertsen

PURPOSE:

Understanding and predicting the energy level alignments in heterogeneous nanosystems are both important and very challenging for theory and computation. Predictive theories of electronic excitation energies are well established, but they are severely limited in the scale of systems that can be treated with present day computational capabilities. We plan to explore physically motivated approximations that may result in a significant improvement in the efficiency of these calculations for nanosystems and to implement these improved methods exploiting large scale parallel computing. If successful, this research could enable excited state calculations for systems comparable in size to those treated with conventional Density Functional Theory, a significant technical breakthrough. For BNL and the CFN specifically, this project will nucleate a new computational electronic structure research effort, attract external users to the CFN, and enable partnerships with key external groups.

APPROACH:

Prediction and understanding of the excited electronic states of nanomaterials are frequently essential to explain and modify their function. Examples include electron transfer through a molecular bridge, the active electronic states in novel photocatalytic nanocrystals, and resonant energy transfer in light harvesting structures. Large scale applications of Density Functional Theory (DFT) based computations enable theoretical understanding of chemical bonding and other important properties in such systems. However, the orbital energies from DFT calculations do not accurately model electronic excitation energies. For example, they are empirically found to poorly approximate key quantities such as the band gap in semiconductors or the ionization potential of molecules, although overall trends may well be useful. So-called hybrid functionals (e.g. B3LYP) give more accurate bond energies and are now widely used in quantum chemistry. A recent modification of this approach for solids resulted in improved band gaps for semiconductors [1]. However, this approach still misses essential physical processes, particularly the image potential effect that plays a critical role in heterogeneous nanosystems. Predictive theories of electronic excitation energies are well established, but entail substantially more complex calculations. As a consequence, while ground state calculations are now done for systems of order 1000 atoms, excited state calculations are limited to systems of order 100 atoms.

In our recent research in collaboration with Neaton and Louie (Molecular Foundry, LBNL), the well-established, full GW approach was applied to benzene on graphite, an example of a molecule coupled to a metal electrode [2]. The GW approach includes the image potential effects and we demonstrated the strong influence that the environment has on the benzene excitation energies [2]. However, the GW approach is computationally very demanding. Our treatment of the benzene on graphite was among the largest systems that can be treated today, of order 100 atoms. Many applications to interesting nanosystems are presently out of reach. Analysis of the benzene calculations showed that the change in electron correlation energy on the molecule due to interaction with the surface was largely due to static polarization effects [2]. This result suggests that a static approximation in the GW framework can be developed that will be broadly applicable to heterogeneous nanosystems. We envision an approximate treatment based on the GW framework for electronic excitation energies that can be applied broadly. In addition to the non-locality of exchange, it will account for polarization and screening explicitly. The latter is required to capture image potential effects. The feasibility and potential accuracy needs to be analyzed and the computational complexity must be explored.

We plan to investigate a new hierarchical analysis of the GW approach as a basis for a static approximation. This results in significant technical simplifications. The accuracy needs to be tested for prototype materials systems by direct comparison to complete GW calculations, e.g. for bulk materials like Si and for the interaction between small molecules to understand the applications to heterogeneous systems. Another critical issue concerns the necessary calculation of screening properties. A full calculation of the polarizability is equally as demanding as the evaluation of the full GW self energy. Research directed to identifying and implementing an efficient model screening approach will be undertaken. Candidate approaches include a model from our earlier research [3] and coarser grained solvation approaches [4]. In the first step, we require a model that adequately captures the local fields that most influence the electronic states of physical interest. Longer term, we seek a model that can be smoothly coarse grained to allow treatment of longer range environmental effects in heterogeneous nanosystems.

We plan to focus test calculations on a class of materials that are both technically challenging and more broadly significant for photocatalysis: N substituted titanates. The key physical question is the search for reduced band-gap oxynitrides that will both make better use of the solar spectrum and have frontier energy levels that properly align to the key electrochemical potentials for water splitting. The GW method will give a quantitative approach to this energy level alignment problem. This application will enable future collaboration with CFN users interested in photocatalysis, specifically Peter Khalifah (SBU and BNL Chemistry).

TECHNICAL PROGRESS AND RESULTS:

Research Associate, Wei Kang, who started in July, 2008, has carried out the research under the direction of Mark Hybertsen. In the first part, he has been investigating electronic and optical excitations in titanates and oxynitrides. This work uses conventional GW methodology, together with the Bethe-Salpeter methodology. The titanates proved to be a very challenging system so he has devoted significant time to implement the needed tools here at BNL, including porting the codes to the NY Blue facility, as well as implementing a full frequency approach that proved essential for quantitative results. His work focused on rutile and anatase will be submitted to Phys Rev B in February. Work on oxynitrides in collaboration with the Khalifah group is on-going.

In the second part of his work, he is investigating the new approximate treatments of the self energy operator in the GW framework. He has developed an approach to include local fields that is still under test for a suite of crystalline materials. This approach needs some refinement in order to generalize well to more inhomogeneous systems, e.g. heterointerfaces or nanowires.

March, 2010: complete analysis of new static approximation to the GW self energy operator.

July, 2010: more complete testing of new approaches & implementation of parallel codes. Completion of oxynitride research.

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Nanofabrication Methods Using Solution-Phase Nanomaterials

LDRD Project 08-043

C. T. Black and J. E. Allen

PURPOSE:

Our project involves creating and implementing a unique new fabrication method for uniform large-area assembly of nanostructured materials from solution, relying on self assembly of porous oxide templates. The objectives are to implement this technique first for studying photogenerated charge transport in devices composed of organic semiconductors. We will subsequently pursue new photovoltaic device designs incorporating multiple types of semiconductor nanocrystals to create heterojunction solar cells, and understand changes in their performance in response to systematic variation of nanometer-scale template dimensions.

APPROACH:

Processing materials from solution is a straightforward and efficient means for thin film device fabrication. Building *nanostructured* devices from solution is complicated by a lack of control of nanomaterial assembly over large-areas. This challenge is common to many areas of nanotechnology – the need for accurately positioning *nanometer-scale* elements across *centimeter-scale* areas.

Our project will create a wide-ranging fabrication technique for building complex solid-state electronic structures from solution-phase nanomaterials. The project will proceed along three specific directions focused on refining this innovative fabrication method; demonstrating its utility through device fabrication for study of photogenerated charge transport in *organic semiconductor* devices; and finally applying the technique toward formation of *inorganic* heterojunction solar cell devices.

Dr. Jonathan Allen, a Research Associate funded by this project, is primarily carrying out this research under the guidance of C. T. Black. Project collaborators include Dr. Chang-Yong Nam (CFN), Dr. Dan Johnston (CFN), Dr. Ben Ocko (CMPMS), and will include beginning this year Professor Chris Murray (UPenn).

TECHNICAL PROGRESS AND RESULTS:

In FY2009, we first established procedures for fabrication of highly ordered porous aluminum oxide templates — a capability not present at BNL previously. We designed, constructed, and tested a semi-automated system for electrochemical anodization of aluminum. A processing robot is remotely controlled by a computer in order to reduce the risk of exposure to strong acids. A custom designed Labview program provides flexibility for a wide range of experiments. We use this system to reproducibly create large area samples of highly ordered nanoporous templates, with close control over all dimensions (Fig. 1).

As-fabricated porous alumina templates consist of ordered nanoporous aluminum oxide on an aluminum substrate.

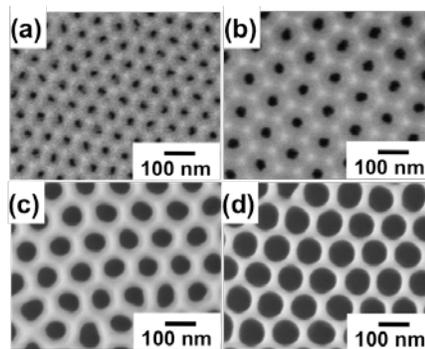


Fig 1. (a)-(d). Nanoporous aluminum oxide templates having pore diameters between (a) 20nm and (d) 85nm.

At each pore bottom is an oxide barrier roughly ~20-40 nm thick. Electronic device fabrication necessarily involves electrically contacting both top and bottom of the porous structure, and so we established a procedure for removing the oxide barrier at each pore bottom. Our process leaves an open pore structure useful for fabrication of nanostructured devices. A further benefit is that our procedure allows transfer of the aluminum oxide template to any substrate materials -- increasing the flexibility of this fabrication approach.

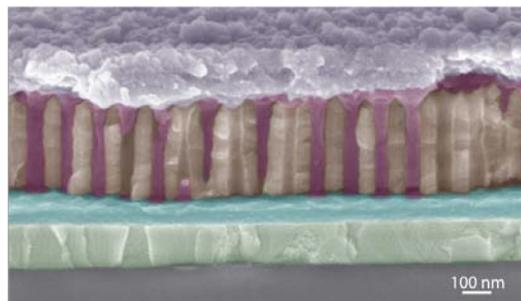


Fig. 2. Organic semiconductor solar cell with active layer confined to a nanoporous alumina template.

Our first target device demonstrations have involved templating solution-processed organic semiconductor materials using nanoporous alumina templates. The idea is that confining organic semiconductors in this way may enhance their electrical properties due to improvements in polymer chain conformation.

We have developed two promising methods for infiltrating nanoporous template patterns with organic semiconductor materials. The first is simply to spin coat the organic material on top of the template. Optimal pore filling is achieved by first cleaning the template using an oxygen plasma and depositing a monolayer of hexamethyldisilazane (a wetting agent) on the pore walls. The second method utilizes capillary force to ‘pull’ the organic material into the pores from below. After this process, the oxide template may be either removed or left in place before device fabrication.

We have successfully fabricated solar cell devices using the pore filling procedures for organic materials described above (Fig. 2). Device photovoltaic power conversion efficiencies have approached 1%, even with the porous aluminum oxide template occupying approximately 75% of the device active area. We estimate therefore that the confined organic semiconductor material outperforms an unconfined equivalent volume by roughly 2:1. We are presently correlating photovoltaic device performance with separate electrical mobility measurements and x-ray diffraction and transmission electron microscopy studies to illuminate the material structure.

In FY2009 we also developed an effective method for infiltrating nanoporous alumina templates with *inorganic* nanocrystal materials. Drops of solution containing highly concentrated nanoparticles of various materials (CdSe, PbSe, Au, Fe₃O₄) were applied to a template and the surface was then cleaned by physically using an elastomeric squeegee. This process both removes excess material from the sample top surface and also forces additional material into the template pores. Under appropriate conditions, nanoparticles enter the template pores and self assemble in the pore bottoms in a densely packed arrangement. This result is promising and confirms our ability to fabricate ordered, high aspect ratio inorganic structures by this method.

2010 Milestones:

- Correlate enhanced photovoltaic performance of confined organic semiconductor devices with improvements in material electronic and structural properties.
- Publish scientific results on organic semiconductor devices.
- Fabricate and characterize a new photovoltaic device architecture incorporating solution-phase processing of multi-component semiconductor nanocrystals and thin-film deposition by atomic layer deposition.
- Protect relevant intellectual property relating to new inorganic semiconductor nanocrystal device architecture.

Identification of Organic Aerosols and Their Effects on Radiative Forcing

LDRD Project 08-051

Yin-Nan Lee

PURPOSE:

The purpose of this research is to identify organic components present in ambient aerosol particles to improve understanding of their sources, formation mechanisms, distributions, and contributions to radiative forcing. Specifically, we focus on a class of compounds which is difficult to characterize at the molecular level but exhibits an ensemble property of semi-high molecular weight (MW~300 to 500 Da) containing possibly phenolic and carboxyl moieties similar to humic material, referred to as humic-like substances (HULIS). The sources (natural vs anthropogenic) and formation (primary vs secondary) of HULIS, which can account for up to 20% of the organic fraction, are largely unknown. This work attempts to identify their presence using a new sampling technique and to understand the conditions favoring their occurrence. This research is important to DOE's mission on quantifying the role aerosol radiative effects play on climate forcing of anthropogenic emissions. The explorative and high-risk nature of this work stems from the fact that HULIS are ill-defined and do not lend themselves to positive identification and method improvement with "standards", and are not consistently present in the atmosphere, making detection more challenging.

APPROACH:

Traditional techniques for analyzing aerosol organics involve filter sampling over extended periods (days to weeks) followed by extraction using organic solvents. The volume of the eluate is reduced by purging using inert gases from tens of a milliliter (mL) to a fraction of a mL to concentrate the analytes for analysis. Potential artifacts can result from long exposures, handling, and reactions of the myriad organic compounds during the extraction and concentration stages.

We employ a novel sampling technique which is on-line, continuous, and without concentration in organic solvents. This technique, developed at BNL, is referred to as Particle-into-Liquid Sampler (PILS) with which aerosol particles in the sample air are grown into droplets with water steam and collected using an inertial impactor. The liquid sample collected on the impactor is continuously washed off with a stream of purified water and passed through a suitable sorbent to retain the organic compounds. These compounds are eluted off the sorbent using a small portion of methanol or acetonitrile.

To appreciate and characterize the MW of the organics in the sample, we employ the High Performance Liquid Chromatography-Electrospray Ionization-Mass Spectrometry (HPLC-ESI-MS) technique capable of producing molecular ions. A reverse-phase column is used to separate the analytes in an order roughly corresponding to MW. Since the ESI ionization efficiency varies with the properties of the compounds (functional groups, acidities, etc), the ion signal is typically not a quantitative measure of the analytes. Without having standards for the myriad unidentified aerosol organic components, we employ in parallel an Evaporative Light Scattering Detector (ELSD), which atomizes the eluate, evaporates the solvent, and forms aerosol particles from the non-volatile analytes to be detected by light scattering, to provide an independent measure of mass loadings of the analytes against which the ion signals can be compared. To aid data interpretation, we make simultaneous determination of aerosol chemical composition, i.e., SO_4^{2-} , NO_3^- , NH_4^+ , and total organics (Org), using an Aerodyne aerosol mass spectrometer (AMS) to provide context of aerosol properties such as acidity and total organic mass loading. The primary disadvantage of the PILS technique has to do with its small sampling rate (i.e., 10 L/min for

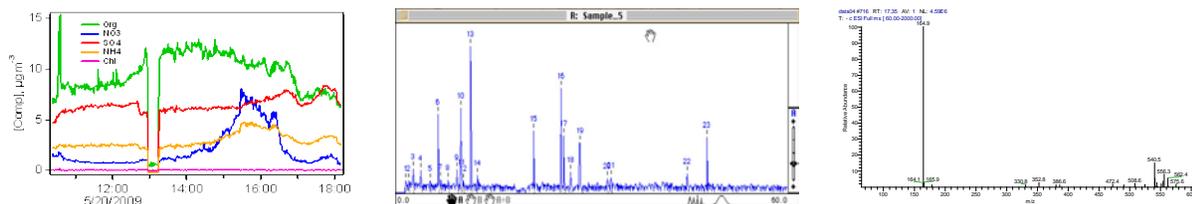
hours vs 2000 L/min for weeks with the filter technique), therefore requiring a high ambient organic aerosol loading (i.e., $>15 \mu\text{g m}^{-3}$) which was rarely met during the past summer at BNL.

Dr. L. Bowerman was a collaborator during the first year. She helped with the initial quartz filter preparation for the since abandoned filter sampling approach. Dr. C. Dodge joined the project as a replacement for Dr. Bowerman after she left the Division, and he helped with the operation of an HPLC-ESI-MS belonging to Environmental Research and Technology Division. Some delays were experienced due to these changes.

TECHNICAL PROGRESS AND RESULTS:

A complete sampling strategy and the arrangement of necessary instruments/apparatus needed for the project were in place after a year and a quarter into the program. These included the setup of an existing Thermo-Finnigan HPLC-ESI-MS (Model LCQ) system, acquiring and setup of an Agilent ELSD (Model 1200), and method development for the Solid Phase Extraction technique, as well as bringing the PILS and AMS instruments on line.

Aerosol sampling and analysis were performed during the second year of this project. In an experiment, aerosol sample in aqueous solution collected using the PILS was passed through a sorbent (Strata-X-AW, Phenomenex) appropriate for collecting carboxylic acid containing molecules (simultaneous AMS data shown, left figure). After 6-8 hours collection, the organics were eluted off the sorbent using 1 mL CH_3OH , and the sample was analyzed. Although the ELSD chromatograms (center figure) showed well separated peaks, the ESI-MS however did not exhibit corresponding ion chromatograms. Indeed, no dominating ion peaks were observed. On the other hand, analysis of model compounds (phthalic, hydroxylphenylacetic, protocatechuic acids, all containing an aromatic and carboxylic group) showed a reasonable detection (mass spectrum of phthalic acid, retention time 17.5 min, shown in the right figure). However, we were unable to see a distinctive mass spectrum for fulvic acid, the soluble fraction of humic acid.



Several possible explanations for the low response of the ESI-MS can be offered. The first being that none of the eluted organics were ionized because they don't mimic the model compounds. With that we may state that HULIS were absent in these samples. However, it is also conceivable that the ESI-MS sensitivity was insufficient for the low concentrations of organics eluted from the HPLC. Although the injected amounts of the model compounds and the aerosol organics sample were comparable, $\sim 100 \text{ ng}$, the organics in the sample are distributed across many species, each being present in a much smaller amount.

While the approach and the techniques established in this research is in principle sound, we need to have either an improved instrument sensitivity or an increased sample material to remove the ambiguity described above. Although funding for this project has ended, we can contemplate one more round of analysis in May 2010 when organic aerosol loading is high. However, it is evident that only a long term continuous analysis can provide meaningful data needed for gaining improved understanding of organic aerosols regarding sources and formation mechanisms.

Computational Climate Science

LDRD Project 08-060

Andrew Vogelmann

PURPOSE:

Assessments of the potential impacts of pollution on climate are hampered by an incomplete understanding of the atmospheric physical processes needed in climate models. Our objective is to assess and improve these physical processes via model simulations that will be run on the New York Blue (NYB) supercomputer by a team of researchers from BNL and the Institute for Terrestrial and Planetary Atmospheres at Stony Brook University (SBU). The follow-on implications of this research, in terms of new programs and BNL institutional strategy, are: (a) establish a climate science modeling institutional capability on NYB; (b) foster cross disciplinary collaborations within BNL, and between BNL and SBU; (c) support the EENS Strategic Initiative in Climate Research; and (d) support the FY08 Laboratory Strategic Initiative in Computational Science by expanding the range of scientific applications that would run on NYB.

APPROACH:

Accurate simulation of convection is an ongoing challenge that affects climate model transports of water vapor, cloud, and aerosol. We endeavor to improve our understanding by using the tropics as a convection testbed to determine whether explicit convection treatments are needed in global climate models to accurately simulate convection and aerosol transport. Simulations are run on the NYB supercomputer with successively high resolutions, and will be validated using newly available satellite observations and observational techniques developed at BNL.

- NYB atmospheric simulations use the Weather Research and Forecasting (WRF) Model, and its chemistry module extension WRF/Chem. WRF is a next-generation mesoscale model designed for atmospheric research that is ported to NYB as part of this project.
- WRF simulations are evaluated using new cloud and aerosol observations that provide constraints and insights into the model behavior: (a) a cloud identification and tracking algorithm; (b) an artificial neural network (ANN) being developed by BNL researchers that uses satellite data to characterize tropical cloud fields and their behavior; (c) new aerosol observations from the CALIPSO space-borne lidar that provides the first routine, global observations of aerosol vertical profiles and particle size.
- We target the most deficient physical processes by exploiting NYB computational power to perform ensemble runs to map the variances of the model solutions in a phase space that considers the uncertainties in the model parameters associated with convection.

The team is an interdisciplinary group of computer scientists and researchers at BNL and SBU that capitalizes on existing expertise. BNL units involved include the Atmospheric Sciences Division (Vogelmann, Guo, Luke, Daum, Jensen, Johnson, Liu, McGraw, Troyan), the Scientific Information Systems Group (Wagener, Cialella, Behrens, Gregory), and the Computational Science Center (Davenport, Efstathiadis, Slatest, Cortijo). The primary SBU faculty involved in this effort are Drs. Zhang, Colle, Lin, Jiao, Khairoutdinov, and Chang.

The novelty of this work is in the modeling approach that requires NYB computational power, and the use of newly available satellite observations. The risks are: (a) this level of WRF modeling (long simulations at high resolution for a large domain) has not been attempted before and could trigger instabilities, and (b) the core observational and modeling capabilities exist at BNL and SBU, but they have not worked together before on such a comprehensive study.

TECHNICAL PROGRESS AND RESULTS:

1. **Model and Software Installations:** Following our earlier success porting WRF to NYB with its software utilities and graphics packages, we endeavored to complete our model installations by porting WRF/Chem to NYB and conduct scaling tests. Owing to differences in the coding, this was more challenging than anticipated but was ultimately accomplished, completing this Milestone. Scaling studies indicate that WRF/Chem runs about 8x slower than WRF.
2. **Tropical Convective Cloud Simulations:** In the meantime, tropical simulations were initiated using WRF. These simulations exploited the computational power available from NYB by treating a broad swath across the Tropical Warm Pool (22°S-17°N, 100-162°E) at high resolution (4 km). To enable evaluation of the simulations using satellite observations, we developed a software module that converts WRF-simulated outgoing longwave radiation to satellite-comparable observations. A cloud tracking algorithm was applied to the observations and WRF simulations to assess the fidelity of the model via statistical comparisons of the size and longevity of tropical mesoscale convective systems (MCSs). Results indicate a paradox, where the simulated MCSs are smaller than those observed (by half) yet have similar longevities. Reasons for this paradox are under investigation. These results were presented at the 19th DOE Atmospheric Radiation Measurement Program Science Team Meeting. Overall, this block of research represents the accomplishment of multiple FY09 Milestones.
3. **Unanticipated progress** was made advancing joint research activities of the BNL-SBU climate science virtual institute (established in the prior FY), which involved the formation of two additional projects on NYB and submitting proposals. (1) BNL collaborated on a study (lead W. Lin, SBU) on the ability of WRF to simulate the chain of Atlantic hurricanes that occurred in the Atlantic in August and September 2008 (Gustov, Hanna, Ike). Results indicate a surprisingly good ability to simulate much of the hurricanes' lifetimes. (2) BNL collaborated on a study (lead W. Lin) of how mid-latitude storm track simulated by the NCAR Community Atmosphere Model (CAM) depends on horizontal resolution. Preliminary comparisons of high-resolution simulations to its typical T42 resolution and to global WRF indicate that CAM releases its moisture too early in the western Pacific regardless of resolution, but the WRF simulations are more realistic. Both results were presented at the SBU conference, "Changing Climates, Changing Minds – Storms, Trust and Public Perception." Further, two proposals were submitted and ultimately funded: the first (lead Y. Liu, BNL) with the objective of using Atmospheric System Research observations to evaluate and improve fast physical processes in climate models; the second (lead W. Lin, SBU) with the objective of developing a high-resolution climate modeling capability for regional climate change studies by interactively nesting a mesoscale model (WRF) in a global climate model (CAM).

4. Overall, activities this fiscal year have resulted in: (a) 2 publications; (b) 6 Meetings, proceedings and abstracts; (c) 1 project review; (d) 1 new hire, and (e) 2 successful proposals for follow-on funding.

MILESTONES

FY10: (a) Determine the explanation for the paradox in MCS simulations; (b) publish result; (c) complete development of an artificial neural network to determine precipitation regimes from satellite data for additional diagnostics of tropical convective storm simulations; (d) assist in the publication of the joint SBU-BNL research (hurricane simulations, and storm track resolution sensitivity).

A Novel Spintronic Room-Temperature High Purity Germanium X- and Gamma-Ray Spectrometer

LDRD Project 08-062

Giuseppe Camarda and Aleksey Bolotnikov

PURPOSE:

This proposal addresses the serious need for high-resolution, room-temperature X-ray and gamma radiation spectrometers for nuclear non-proliferation, homeland security, and synchrotron applications. High-Purity Germanium (HPGe) is the world's preeminent radiation detector material, because of its unique combination of material perfection, excellent charge transport properties and unsurpassed spectroscopic performance. However, the room-temperature band-gap of germanium is only 0.74 eV, and thermal charge generation must be suppressed by cooling the material to near liquid nitrogen temperatures, otherwise, the noise in the device is too large to provide spectral information. The necessity of cooling HPGe radiation detectors is both costly and cumbersome, and it has limited the utility of these devices. The energy resolution of HPGe detectors operated at liquid nitrogen temperatures is below 0.5%, and there has been an enormous push to develop a room-temperature detector that can provide the same energy resolution. The search has proven difficult and has recently focused on wide band-gap compound semiconductors, such as CZT, CdTe and HgI₂. These detectors currently can provide a room-temperature energy resolution near 1-2% @ 662keV, but the material imperfections have limited the size and corresponding detection efficiency of these devices. Therefore, none of the existing room-temperature radiation detectors have provided the combination of cost and performance necessary for security and synchrotron uses. A new spintronic high-purity germanium gamma-ray detector concept is proposed. Spintronic devices are based on the manipulation of an electron's spin state in addition to its charge, and have the potential to result in order-of-magnitude scale improvements in the performance of various semiconductor devices. In this project we are investigating the feasibility of applying spintronic principles to the production of a gamma-ray spectrometer based on HPGe that operates at elevated temperature.

APPROACH:

Semiconductor spin electronic devices offer great promise as a revolutionary technology for detecting radiation. Despite significant effort and investment worldwide, commercial semiconductor spintronic devices have not been realized. This fact highlights the challenge inherent in any semiconductor spintronics project.

We are undertaking initial steps towards constructing a spintronic gamma-ray detector using semiconductor material, such as High-Purity Germanium (HPGe) and Si.

We will test devices for unambiguous spin-transport signatures via nonlocal magnetoresistance measurements.

We anticipate realizing a measurable enhancement in resistance in the device structure compared to a non-magnetic-contacts reference one.

The success of our work under this project will afford proof-of-principle for the world's first spintronic gamma-ray spectrometer. Our development of the proposed spintronic detector could

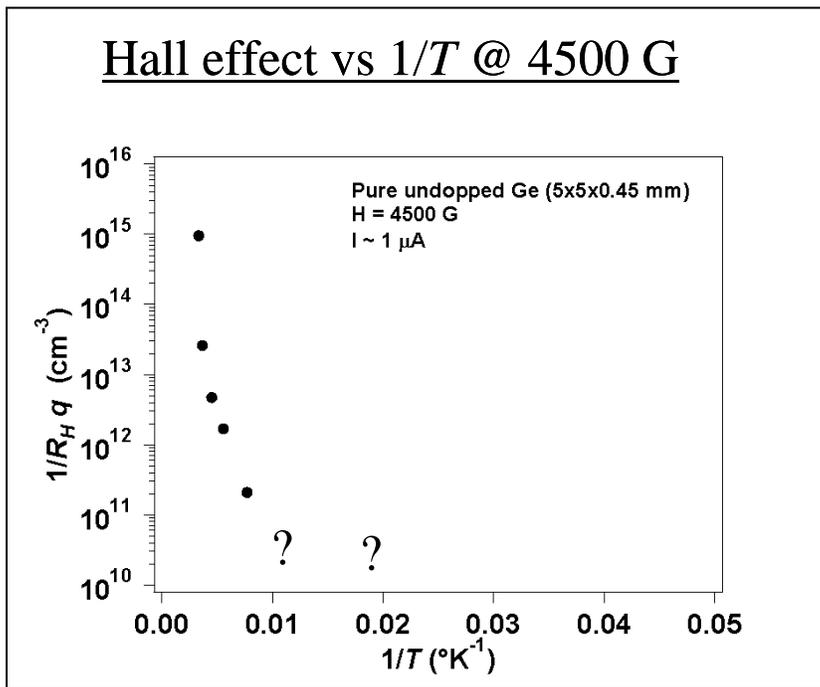
revolutionize the field of gamma-radiation detection and provide a room-temperature energy resolution far surpassing any existing instrument.

TECHNICAL PROGRESS AND RESULTS:

In FY08 the team has acquired the raw material needed for the structure fabrication and then sliced and polished it into wafers of 0.5mm, 1mm and 1.5mm thickness. The surface preparation/cleaning procedures were developed.

For FY09, we designed the photo-masks to fabricate a device structure with Ge to observe spin-transport. We anticipate realizing a measurable enhancement in resistance in the device structure compared to a non-magnetic-contacts reference one.

Hall Effect measurements were successful at elevated (>130 K) temperatures, where instead some contacts problems were encountered at lower temperatures. New measurements are planned in that range.



Tracer Development – Improving PET and MR Imaging

LDRD Project 08-080

Joanna Fowler

PURPOSE:

The next generation of tracers for medical imaging will require greater specificity in defining targets and in predicting and controlling the distribution and kinetics of labeled compounds. The goal of this proposal is to develop new classes of tracers for molecular imaging. This includes developing new synthetic and targeting strategies for both small molecules and nanoparticles aimed at increasing the specificity and targeting of radiotracers in the brain and in peripheral organs. Our approach is to develop new chemical reaction methodology for small molecules and for nanoparticles, to study targeting mechanisms in vivo using autoradiography, PET, microPET, microMRI (and in the future, using ratCAP and PET/MRI). These new probes will have the potential to serve as markers, identifying specific molecular targets. Ultimately, successful probes may serve as delivery agents that can carry cargo to specific tissues or cells in the form of drugs or radiotherapeutic agents. A long term goal is to lay the groundwork for creating targeted carriers that can cross the blood brain barrier and attach to specific classes of cells.

APPROACH:

Of major importance is the development of new synthetic methods for carbon-11 isotope incorporation so that molecules currently considered “un-labelable” or difficult to label can be synthesized and applied to problems in medicine and in drug development. For example, there are many drugs which cannot be easily labeled with current methods but for which knowledge of their biodistribution and kinetics is needed (e.g. drugs of abuse including new abused compounds like salvinorin A and certain solvents; tuberculosis drugs). Specific systems of interest include:

- The brain estrogen system including the enzyme aromatase (converts testosterone to estrogen and aromatase inhibitor drugs are used in cancer therapy and also abused by body builders)
- Nicotinic system (important in drug development for neurodegenerative disorders)
- Histone deacetylase which modifies DNA (important for epigenetic analysis and in understanding the relationship between genes and their protein products).
- Nanoparticles (synthesis, labeling, targeting, analysis and application). Of particular importance are studies changing the surface properties of the particles to alter their solubility and distribution and bioavailability.

Along with the development of synthetic methods, we also need to carry out mechanistic studies which will be facilitated by developing *series* of compounds with small structural changes for structure-activity studies. In addition, the development of the technology to

deliver labeled compounds and drugs by different routes of administration would be an important technical advance which would be of relevance in drug discovery where the measurement of bioavailability is a major bottleneck.

TECHNICAL PROGRESS AND RESULTS:

The initial efforts as detailed in the publication involved developing new methods to synthesize carbon -11 labeled compounds. This was very successful involving new methods to label formaldehyde with carbon-11 and use this as a building block for the synthesis of a wide variety of PET ligands previously, difficult or impossible to synthesize. This earned Jacob Hooker Inventor of the Year honors from Battelle. In addition radioactive nanoparticles were synthesized and used as tracers to track the distribution of nanoparticles in living animals using PET. This has resulted in valuable toxicological studies on nanoparticle distribution in the body and has resulted in a contract with Battelle for follow-on funding to continue this work. The detailed list of publications documents the advances including the initial synthesis of a new class of ligands aimed at the estrogen receptor aromatase was completed and shown to have specific and reproducible binding in the brain. Thus the results of this effort have opened up three areas for further research new synthesis methods for PET ligands, a new class of PET tracer, nanoparticles and finally a new class of receptor ligands aimed at estrogen receptors. Other specific accomplishments include:

- We have studied the brain pharmacokinetics and pharmacodynamics of the stimulant drugs methamphetamine and modafinil demonstrating relationships between brain kinetics and behavioral effects and showing shedding light on the molecular mechanism of action of the atypical stimulant modafinil.
- We have instituted a method to analyze for epigenetic patterns (DNA methylation) in DNA samples and we are applying it to DNA samples from human subjects in whom we also have genotyping and brain chemistry measures.
- We have initiated collaborations to transition into energy and environment applications. One of these is with Dr. Patricia Sobecky of the University of Georgia who is interested in using radiotracers to track uranium particle migration in soils. This has resulted in the hiring of a joint DOE funded post doctoral student at BNL.
- Through the implementation of GMP (good manufacturing processes), we have positioned ourselves to take on more pharmaceutical company projects and NIH projects to maintain and support our clinical neuroscience program. We have initiated contacts with Wyeth Pharmaceuticals and with Bristol Myers Squibb Pharmaceuticals to explore new CRADA projects at Brookhaven.

Development of MR Research at BNL

LDRD Project 08-081

Fritz Henn

PURPOSE:

The goal of the project is to make significant contributions to human MR imaging. This has involved both the application of new paradigms to fMR studies, the development of MRS methods and the use of trans-cranial magnetic stimulation to stimulate specific brain areas. The major effort in the past year has focused on the use of new paradigms for fMRI and the study of various mental states as well as the development of reliable trans-cranial magnetic stimulation paradigms and an analysis of which structures can be reliably stimulated with trans-cranial magnetic stimulation. The technology developed including multi-modal imaging using PET, MR and EEG to study the same paradigm has led to a detailed understanding of brain activation in addicted states compared to non addicted states. This has led to the development of a joint MR-PET scanner which has become a priority for the instrumentation group in PET.

APPROACH:

This project is aimed at developing paradigms to help understand the differences in cerebral processing between addicted brains and non-addicted brains. This work involves multi-modal imaging using paradigms to probe cerebral processing, such as pictures of drug related paraphernalia which illicit craving in addicts and no special response in non-addicted individuals. This allows an analysis of the pathways which underlie craving and a way to probe methods to reduce craving. This also involves looking at the dopamine activity in these states using PET, as well as the changes in EEG responses under these conditions. Since the time scale and spatial resolution of these methods is very different, combining them allows a much deeper understanding of brain mechanisms. Part of the effort of this program is to integrate the information from the three modalities using computational tools.

We also are continuing to develop sequences for MRS of glutamate and GABA which we are attempting to activate through specific activation of specialized brain pathways.

To date no group has been able to look at time dependent changes in glutamate or GABA activity as a function of brain activation and this is our goal.

TECHNICAL PROGRESS AND RESULTS:

The development of paradigms to measure salience resulted in 7 major publications in the last year and has led to a better understanding of the effect of addiction on attention and cognition. The methodology to put together data from various modalities has led to collaboration with computational science at Stony Brook and another NIH grant. The same general approach has been developed with studies of aggression, also involving genetic and epigenetic influences on aggression.

Milestone: A further grant in the area of aggression using MR imaging is anticipated in the coming year.

The area of TMS stimulation awaits further development of TMS coils to increase the depth of penetration to allow stimulation of areas related to mood and anxiety. Coil design is moving forward and this project should result in a viable coil for deep brain stimulation.

The area of MRS should lead to a study looking at the role of neurogenesis in depression and perhaps the ability to follow changes in GABA and glutamate in the brain as a function of regional activation.

Milestone: An NIH funded MRS project aimed at determining the role of neurogenesis in depression.

Biofuels and Nanotech for Improvement of Oil Heat Combustion Systems

LDRD Project 08-082

T. Butcher and M. Rafailovich

PURPOSE:

Condensing boilers achieve very high efficiency levels by recovering heat from the flue gas before it is discarded. The recovery of latent heat from the water vapor in the humid gas is a very important part of the total heat recovery but the condensate formed is corrosive – leading to the need for expensive alloys in the heat exchanger. This project is focused on the potential replacement of these alloys in the condensing section of home heating boilers with polymeric materials. The requirements for selecting the polymer are fairly rigorous and cannot be satisfied by any polymer alone; the polymer must withstand relatively high temperatures ($T \sim 250^\circ\text{C}$) and be resistant to degradation in the presence of the sulfuric acid environment found in condensates produced from conventional oil combustion. Furthermore, even though the polymer is not in contact with fire, its proximity to an open flame and to the ignition electronics found in boilers, OSHA and other building code regulations are expected to require that the materials must be flame retardant, and conform to UL94-V0 requirements. Since no single polymeric material can satisfy these criteria, the focus of this research was to develop organic-inorganic polymer blend nanocomposites, where the mechanical, chemical, and thermal properties could be tailored to meet the specific requirements for optimal boiler construction.

APPROACH:

Specific classes of polymers are known to be resistant to acid corrosion. These polymers include polypropylene, polycarbonate, Teflon, and other fluoro-polymers. The major drawback of these materials is their high degree of immiscibility, which makes it difficult to tailor their properties

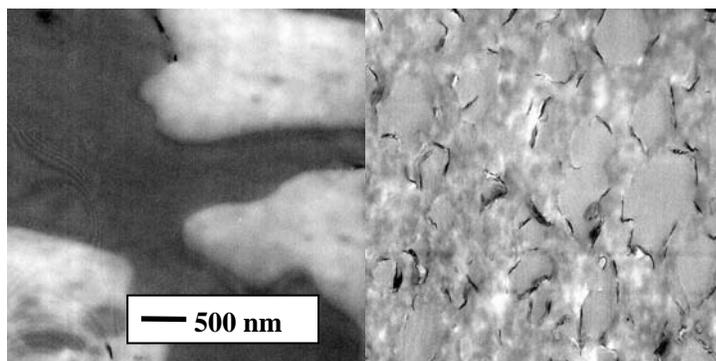


Figure 1: Effect of clay on flame retardant PC/SAN polymer blend. Compatibilization is achieved by forming in situ grafts on the clay and localizing the platelets at the interfaces.

for specific applications through blending. For example, polycarbonate, which has good thermal and corrosion resistance is too brittle, while polypropylene (PP), polyvinylchloride (PVC), or Teflon, which have the desirable impact toughness, deform easily when heated and therefore does not satisfy the UL-94 flame retardant criteria without further modification. We had previously demonstrated that it was possible to achieve compatibilization of a large group of polymers using exfoliated nano-clays [Compatibilizing bulk polymer blends by using organoclays Si M, Araki T, Ade H, Kilcoyne ALD, Fisher R, Sokolov JC, Rafailovich MH. *Macromolecules* 2006 39 (14): 4793-4801]. This enabled us to adopt an approach where different polymers are blended together, with specific flame retardant formulations to achieve the proper mechanical and thermal properties.

TECHNICAL PROGRESS AND RESULTS:

In the first phase we used polycarbonate, styrene, and acrylate polymers in order to establish proof of concept. We were able to demonstrate; (a) The addition of clays was able to stabilize the blends against further decomposition in the presence of heat or flame. Scanning Transmission X-ray Microscopy was performed at the Berkeley ALS in *collaboration with Harald Ade* (University of North Carolina) and electron microscopy was performed at Stony Brook

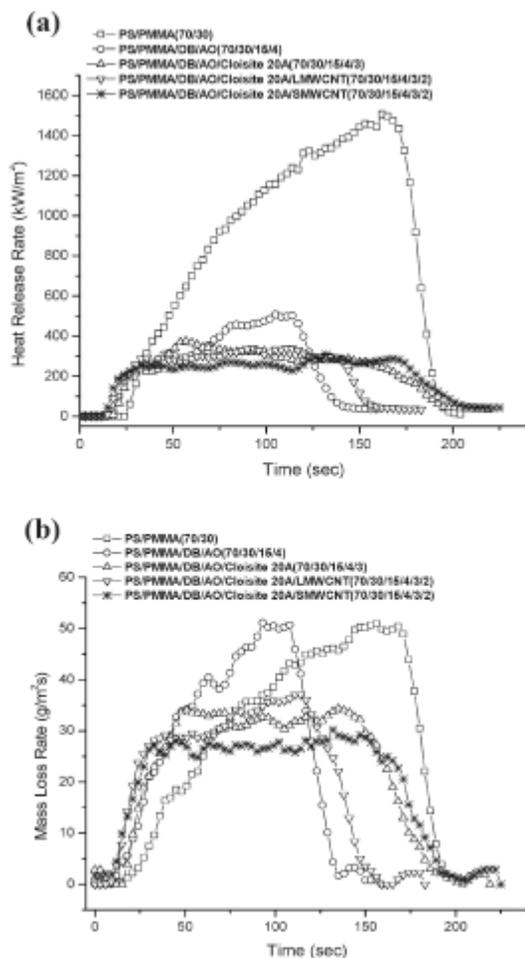


Figure 13. Effect of MWCNTs and clays additives in HRR and MLR. Figure 2 $\Delta A/DB/AO$ at 50 kW/m².

University on thin films obtained from cross sections of samples that were exposed to flame or high temperatures. The images clearly showed that the clays stabilized the phases, improved dispersion of the flame retardant formulation, and catalyzed conversion of the flame retardant component, increasing its efficiency in extinguishing the flame. (b) Cone calorimetry measurements performed in collaboration with *Dr. Takeshi Kashiwaga, from NIST* [figure 2] confirmed that the addition of the clays greatly decreased the heat and mass loss rates of the nanocomposites. Simulations of the UL-94 testing at Stony Brook University showed that the nanocomposites were able to pass the stringent V0 requirements for self-extinction within seconds after exposure to open flame.

es and Goals for the Future: The challenges that we wish to address in the future; (a) Even though the addition of clays improves the flame retardant behavior, the time to ignition is shortened. This was explained in terms of the lower heat capacity of the nanoparticles which can accelerate local combustion. We propose to solve this problem by using mixed nanoparticles. For example, we propose to use multiwall carbon nanotubes (MWCNT) in combination with clays. The MWCNT have been shown to be good dispersants of the flame retardant formulation, while at the same time providing a pathway for thermal conduction. This should prevent the local heating and combustion. (b) Thus far we have used halogenated flame retardant formulations in our blends. The increased efficiency imparted by the clays enabled us to use 75% less than the industry standard. Despite our success, concern is mounting regarding the environmental impact of these chemicals and reports that they can degrade into smaller molecules which may cause nerve damage. Hence a concerted effort is under way to develop formulations which degrade harmlessly. We have begun experimenting with phosphorylated compounds (RDP) and have achieved good flame retardant results in a number of polymer blends, including propylene and styrenics. Our future goal is to produce a polypropylene blend, with good impact and corrosion resistance, and rendered flame retardant using the new phosphorylated formulations.

Solar Water Splitting: Quantum Theory of Photocatalytic Processes at the Water/Semiconductor Interface

LDRD Project 08-083

P. B. Allen and M.-V. Fernandez-Serra

PURPOSE:

The aim of this project is to understand how sun-light might convert (“split”) water (H_2O) into molecules of its constituent gases H_2 and O_2 . The H_2 could then be collected, stored, and used as fuel (“solar fuel.”) The light is absorbed in a semiconductor (GaN/ZnO alloy) which is immersed in water. The questions are: (1) How should we understand the alloy structure and its light-absorbing properties? (2) What is the surface of the alloy like? (3) What is the nature of the interface between the water and the semiconductor alloy? (4) How do the chemical reactions proceed such that electronic excitations of the semiconductor (created by sun-light) cause the desired reactions that end up splitting the water?

APPROACH:

We use theoretical techniques of solid-state physics and quantum chemistry. Advanced computer codes and powerful computers make fairly reliable predictions about the lowest-energy states of atoms and molecules at interfaces. Also we have the ability to “simulate” the actual motions at room temperature of the semiconductor and water atoms in the interface region. We use these techniques to answer the questions listed above. The semiconductor absorbs sunlight, converting solar energy into electronic excitations. We predict what these excitations are, and how they alter the chemistry at the water-semiconductor interface. These problems are addressed by computational modeling on the BlueGene/L computer “NY Blue” and on the CFN computer cluster. The work is mainly done by two Stony Brook graduate students who are supported on this LDRD: Li Li (supervised by P. B. Allen) and Jue Wang (supervised by M.-V. Fernandez-Serra.) Their work is integrated with the Stony Brook/BNL working collaboration called SWaSSiT (the Solar Water Splitting Simulation Team). A third Stony Brook student, Xiao Shen, worked closely with this group on related projects, funded by a DOE grant to P. B. Allen. The SWaSSiT group met once a month at BNL and once a month at Stony Brook, to review progress, review the literature, and guide the work of the students.

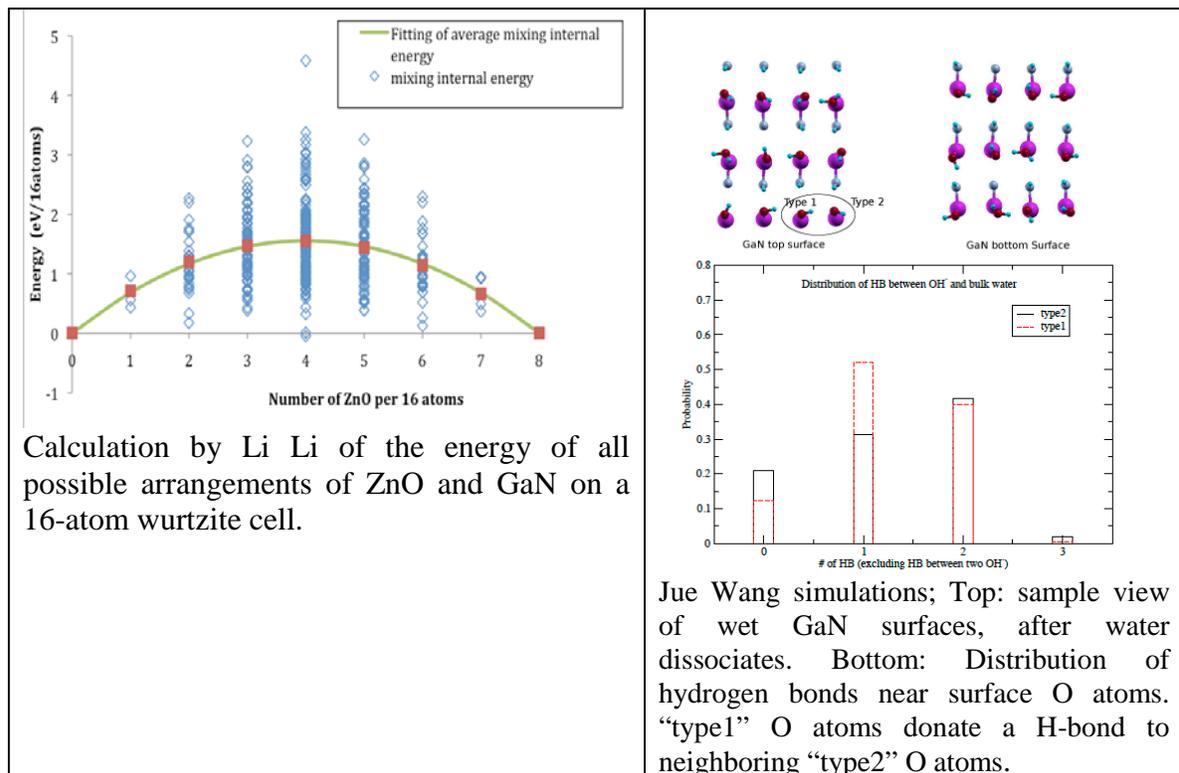
TECHNICAL PROGRESS AND RESULTS:

Li Li worked mainly on the theory of the semiconductor alloy and its light-absorbing properties. Jue Wang worked mainly on room temperature simulation of the interface between the semiconductor and the water.

Alloys of GaN and ZnO have not been systematically studied until very recently. It is a more complicated system than well-studied metallic alloys like copper/gold. We want to know what is the local structure in the interior of the alloy. Does the material separate into nuggets of GaN and nuggets of ZnO, or do the two constituents “dissolve” into each other? Both experiment and Li Li’s calculation show that “dissolving” is correct. However, experiments have difficulty producing alloys rich in ZnO. Li Li’s work shows that the “solution” of ZnO in GaN is not locally homogeneous. There is a strong local

tendency for “clustering.” Ga atoms try to retain N atoms as nearest neighbors. These N atoms in turn prefer Ga atoms around them, so that the resulting material contains regions rich in GaN and regions rich in ZnO. He is now making this description quantitative. He is also talking with three synthetic chemistry groups (directed respectively by Peter Khalifah, Etsuko Fujita, and Weiqiang Han) to combine theory and experiment to test his results and learn the detailed alloy structure. Li Li’s results also provide information about the “band gaps” of the alloys. It is important for the alloy to have a reduced gap relative to the pure GaN and ZnO materials. This is because a lower band gap is needed to increase the efficiency of absorption of sun-light. Li’s results indicate less likelihood of reduced band gaps than experiment so far indicates. He is working on several possible solutions to this problem. One possibility is that more advanced theoretical techniques are required, because the simpler techniques have limited reliability for band gaps. Another possibility is that experiments have not yet been well interpreted.

Jue Wang used massive computer simulation to explore kinetic properties of water near and at the semiconductor interface. Previous work by Xiao Shen had shown that water molecules dissociate on the surface of GaN, with H^+ ions attaching to surface N atoms and OH^- ions attaching to surface Ga atoms. Shen’s work was for the lowest energy structure at absolute zero of temperature. Wang’s work confirmed that not only is this still true at room temperature, but also that surface Ga or N atoms that happen not to be associated with corresponding ions, can rapidly acquire bonded ions from water molecules in the liquid above the interface. Also his results showed how the surface OH^- ions connect through hydrogen bonds with water molecules in the liquid above. Both of these insights were used by Xiao Shen in his thesis work in which a plausible reaction pathway for water oxidation was discovered.



Nanoscale Electrode Materials for Lithium Batteries

LDRD Project 09-001

Jason Graetz, Yimei Zhu, Xiao-Qing Yang and Weiqiang Han

PURPOSE:

The objective of this effort is to develop a fundamental understanding of how electrode nanostructure and morphology affect electrochemical performance (e.g. capacity, cycle life, rate capability) and how morphology and nanostructure are affected by lithiation and repeated cycling. Electrodes composed of nanoscale materials have been reported to exhibit higher capacities, faster cycling rates, and are believed to be less susceptible to particle deprecation.

The increase in energy generated from intermittent, renewable sources and the growing need for portable energy for transportation requires new, efficient means of storing energy. Lithium batteries are, and will likely be the primary battery chemistry for mobile energy storage applications. There is much interest in the development of new electrodes composed of inexpensive materials that can accommodate more lithium without compromising the system size, weight or cycle life. As a consequence, a number of opportunities are expected for follow-on funding from DOE (BES and EERE), NY State (NYBEST), and others.

APPROACH:

In this effort we will mitigate the particle deprecation that occurs in high capacity lithium electrodes during cycling by preparing electrodes from nanocrystalline powders. We expect these electrodes will exhibit improved reversibility as a result of their nanoscale dimensions, which circumvent conventional mechanisms of mechanical deterioration. In addition, the shorter lithium diffusion paths will promote fast cycling rates.

Nanoscale electrode materials were purchased from multiple chemical and lithium battery companies and synthesized via organometallic methods. Electrochemical testing was performed in half-cells (using a Li counter electrode) and used to measure capacity, cycle life (capacity fade) and rate capability. High-resolution electron microscopy was used to investigate nanostructure and morphology. Electron energy loss spectroscopy (EELS) was used to generate chemical maps in charged and discharged electrodes to identify the location/distribution of lithium.

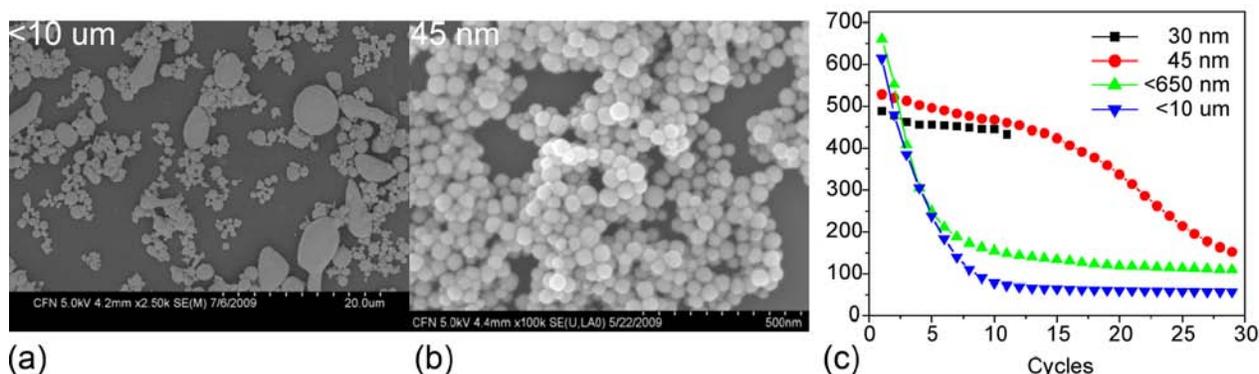


Figure 1. Tin electrode materials showing (a) bulk powder (b) synthesized nanopowder and (c) electrochemical capacity (mAh/g) as a function of particle size.

TECHNICAL PROGRESS AND RESULTS:

Tin nanoparticles were prepared using an organometallic synthesis and characterized using scanning electron microscopy (SEM) and electrochemical studies. The synthesis procedure was tailored to prepare samples with different particle sizes. Samples of 30 nm, 45 nm and 75 nm tin particles were prepared. Particle sizes were confirmed with SEM, which also showed a narrow particle size distribution for all three samples. Figure 1 shows an SEM image of the bulk tin powder (purchased from Aldrich) and the 45 nm synthesized material. Figure 1c shows the electrochemical performance for the nanoscale material and the bulk powders. The capacity of the bulk powder (<10 μm) falls to zero after 8 cycles, while the nanoscale tin shows improved cycle life. Although additional improvement is necessary, these results demonstrate improved cyclability of the nanoscale material. Future studies will investigate tin intermetallic compounds (e.g. FeSn_2 , Cu_6Sn_5 , Ni_3Sn_4) using a similar synthesis procedure.

The spatial distribution of lithium across a lithiated and a delithiated graphite anode was measured with nanometer resolution using energy filtered imaging in the TEM (figure 2).

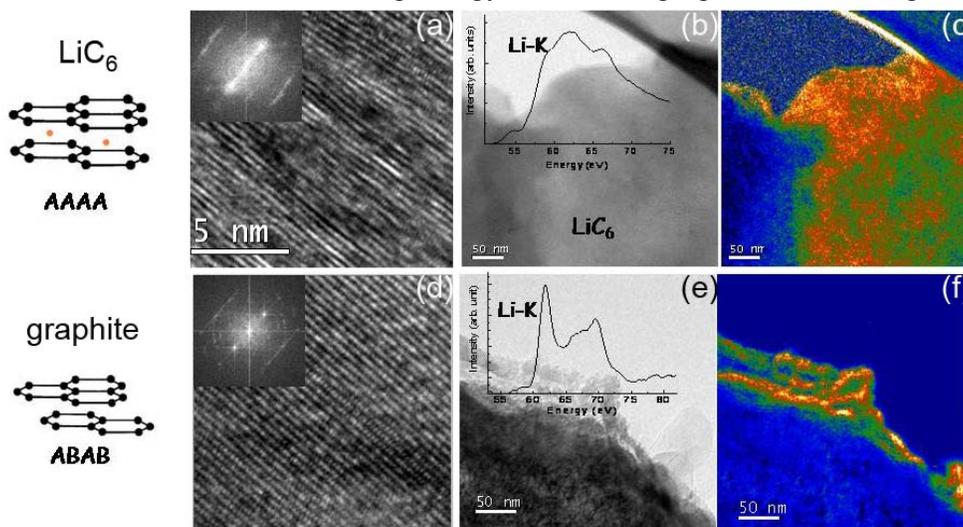


Figure 2. TEM and EELS images from LiC_6 showing a (a) high resolution image and FFT (inset) (b) Bright field image with EELS Li K-edge (inset) and (c) lithium map. A similar set of images are shown on the bottom (d-f) from the delithiated material (graphite).

High resolution images with simulated diffraction patterns (using a fast Fourier transform (FFT)) were used to determine the nanoscale structure of the electrode and this structure was compared with the lithium distribution. Li maps of the delithiated material revealed a surface layer replete with residual lithium. Our preliminary results suggest this is the surface electrolyte interphase (SEI) layer that typically forms on graphite during the first lithiation. The Li K-edge near-edge fine structure was used to determine the electronic environments of lithium and suggests one of the primary components of the SEI layer is LiF .

Milestones:

- FY10 Synthesis and electrochemical characterization of nanoscale silicon and tin intermetallic compounds; *in-situ* synchrotron studies (XRD, XAS, small angle)
- FY11 Synthesis and electrochemical characterization of novel olivine cathodes; *in-situ* electron microscopy of cycling lithium electrode.

Bioconversion of Lignocellulose to Ethanol and Butanol Facilitated by Ionic Liquid Preprocessing

LDRD Project 09-002

A.J. Francis, J. F. Wishart and J. Dunn

PURPOSE:

Lignocellulosic material is the most abundant renewable resource on earth and has attracted much attention as a source of the biofuels ethanol and butanol. However, lignocellulose is quite difficult to break down into its component parts, and therefore not efficiently converted to ethanol by hydrolysis and fermentation using current methods. The overall goal is to develop a comprehensive process for bioconversion of lignocelluloses to ethanol and butanol using ionic liquids as a pretreatment and fermentation by *Clostridia*. The specific objectives of this project are to (i) develop a simple and low cost pretreatment process using physical-, chemical- and biochemical- based methods to convert lignocellulose to fermentable substrates by the anaerobic fermentative bacteria *Clostridia*, and (ii) select *Clostridia* strains capable of fermenting a variety of simple and complex sugars, and modify their metabolic regulatory pathways to enhance the production of ethanol, butanol, and hydrogen as major end products. This is a multidisciplinary collaborative project involving microbiologists, molecular biologists, and physical, organic and analytical chemists. Other members include M. Thomas, C.J. Dodge and Y.V. Nancharaiah.

This project will advance the fundamental knowledge of potential application and development of environmentally benign new materials for biofuel production. We anticipate the outcomes of this research to include the following: (i) synthesis of new ILs with valuable properties for cellulose processing; (ii) correlations between structure and characteristics for the design of new ILs for biocatalysis; (iii) metabolically modified *Clostridia* strains suitable for effective production of ethanol and butanol; and (iv) development of a process for the conversion of underutilized biomass into ethanol, an important energy source, in keeping with the aims of the BNL bioenergy initiative.

APPROACH:

Ionic liquids (ILs), a new class of solvents with many useful properties, are known to solubilize cellulose and facilitate its separation from lignin. In this study we are developing materials and methods to use ionic liquids for the deconstruction of lignocellulose, yielding readily fermentable feedstocks for *Clostridia* to produce ethanol, butanol and hydrogen. This is a greener approach compared to the toxic and acidic chemicals used currently for pretreatment.

Specifically, we are investigating (i) the effect of IL composition (by variation of anions, cations, and functional groups) on the dissolution of cellulose and lignocellulose, (ii) the efficiency of separating cellulose from lignin using ILs, (iii) the effectiveness of IL recovery and recycling, (iv) the fermentability of the process-isolated cellulose, and (v) ways to direct the fermentation of multiple carbohydrate substrates by *Clostridia* to desired products by modifying the metabolic regulatory pathways. The structural characteristics of lignocellulose before and after treatment with ILs are analyzed by synchrotron-based Fourier transform infra-red analysis (FTIR) and scanning transmission electron microscopy (STXM) at the NSLS; transmission electron microscopy (TEM) at the CFN; and ¹³C nuclear magnetic resonance spectroscopy (NMR) and electro spray ionization-mass spectroscopy (ESI-MS) techniques.

TECHNICAL PROGRESS AND RESULTS:

Ionic Liquid (IL) synthesis and treatment of Wood Flour. We synthesized three ILs 1,3-dimethylimidazolium dimethyl phosphate [mmim][dmp], 1-ethyl-3-methylimidazolium diethylphosphate [emim][dep], and 1-butyl-3-methylimidazolium dibutylphosphate [bmim][dbp] and tested for their ability to dissolve microcrystalline cellulose (MCC) and cellulose from hard wood flour and corn cob. We found that IL [emim][dep] dissolves 24 wt% of MCC. Characterization of the extracted cellulose and the residual wood substrates by FTIR at the NSLS and CFN showed partial separation of cellulose from lignin.

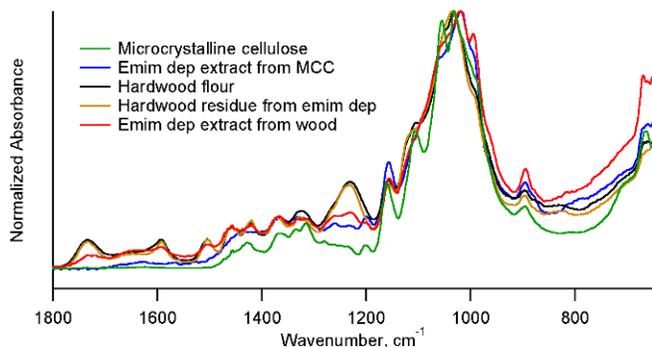
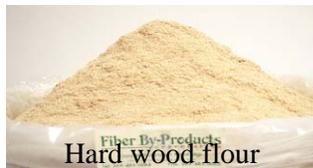


Figure 1. Comparison of FTIR spectra of samples before and after IL treatment.

FTIR indicates that lignin content is reduced in the wood extract compared to the starting material (Fig.1). The broader spectrum below 800 cm^{-1} implies larger structural heterogeneity. SEM analysis at the CFN showed conversion to amorphous materials (Fig.2), indicating the disruption of the recalcitrant fibrous structure. ILs with imidazolium cations were more effective in cellulose solubilization than those with pyridinium or pyrrolidinium cations, supporting the

Figure 2. SEM images of ILs treated hard wood samples.

hypothesis that the hydrogen-bond-donating properties of the imidazolium ring contribute solubilizing interactions with the heavily hydroxyl-functionalized biopolymer. Dialkyl phosphate ionic liquids, in particular [emim][dep], are effective in the extraction of cellulose.

Glucose Fermentation to Ethanol and Butanol by *Clostridium* sp. and Metabolic Engineering.

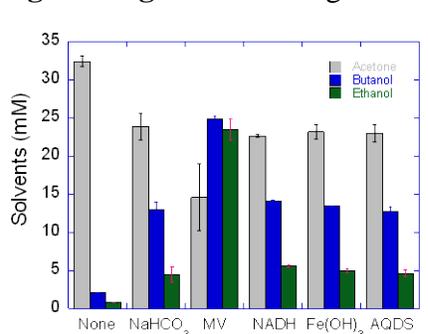


Figure 3. Effect of Electron shuttles on ethanol and butanol production from glucose by *Clostridium* sp.

We investigated the optimum conditions for *Clostridium* sp to shift from acetic and butyric acid production to ethanol and butanol production by manipulating the nutritional and growth conditions. Initial results show that the *Clostridium* sp produced ethanol and butanol by several folds in the modified medium supplemented with electron shuttle compounds (Fig.3). *Clostridium* sp is being sequenced for metabolic engineering studies to enhance ethanol and butanol production from IL pretreated lignocellulosics.

Milestones: 1. Optimize cellulose extraction from lignocellulosics by ILs and fermentation of extracted product to ethanol and butanol. 2. Determine the toxicity of ILs on Clostridia. 3. Metabolic engineering of Clostridia to enhance ethanol and butanol production.

Organic Photovoltaics: Nanostructure, Solvent Annealing and Performance

LDRD Project 09-003

B. Ocko, C.T. Black and R Grubbs

PURPOSE:

Organic photovoltaic devices (OPV) hold great promise as active elements in next-generation solar cells because of their low costs, environmental considerations and mechanical flexibility. Two significant factors - both largely structural in origin - limit the efficiency of organic photovoltaic devices, insufficient interfacial surface area between the donor and acceptor within the thin absorption region of the thin film and low charge mobility and high recombination rate. Understanding these issues may lead to improved OPV devices with efficiencies higher than the current best efficiency of 6%.

APPROACH:

Our approach to improving the performance of OPV devices involves (1) developing new materials with enhanced electronic and structural characteristics, (2) providing increased control of the nanoscale phase separation between donor and acceptor components, and (3) improving the internal microstructural characteristics of the material, including the molecular orientations and crystallinity. This is a team approach involving members of the Condensed Matter Physics and Materials Sciences Department and the Center for Functional Nanomaterials involving scientists with varying skill sets including organic synthesis, device fabrication, x-ray scattering and electronic device characterization. The synthesis effort is led by Barney Grubbs (CFN/SUSB), the electronic device characterization is led by Chuck Black (CFN), and the x-ray scattering effort is led by Ben Ocko (CMPMS). All team members are involved with device fabrication such as making test OPV cells, nanostructures, and stamping devices.

TECHNICAL PROGRESS AND RESULTS:

We have hired a team of three talented post-docs and a student, all with very different backgrounds and skill sets, who are now working closely on several projects. Progress is being made on several fronts, as detailed below. Whereas the first two projects attempt to control the nanoscale phase separation through thermal and chemical control, the latter projects attempt to use well-defined, nanostructured templates.

High Temperature and Pressure Solvent Annealing: We have developed a medium pressure cell to carry out these annealing measurements. This cell is composed of a beryllium cylinder and sealable temperature controlled caps. Using this cell at beamlines X22B and X21 at the NSLS we have carried out grazing incidence synchrotron x-ray scattering studies of the temperature dependent solvent annealing of polyhexylthiophene (P3HT) thin films in the presence of toluene vapor in a sealed cell at temperatures up to 130 °C. In addition to the room temperature swelling of the lamella spacing by 0.7 Å, after the introduction of the solvent, the spacing is expanded at all temperatures with respect to the dry sample. Further, the coherence length, related to the inverse scattering width, is larger in the presence of solvents than in the case of the dry sample. This improved order may help explain the improved performance of OPV devices after solvent annealing. Our results show that high pressure solvent annealing provides better order than in the absence of solvents. However, we have not been able to remove the solvents and maintain the improved order. We have prepared a draft manuscript.

High Temperature Annealing: The alkyl chains of conjugated polymers are vital to provide solubility. However, these same chains have a high coefficient of thermal expansion. We have carried out high-resolution in-situ x-ray scattering studies of the annealing of P3HT thin films and P3HT/PCBM blends to determine the lattice constants and diffraction widths. Our results show that the high thermal expansion coefficient of P3HT – a 10% expansion over a 150K temperature range - can be reasonably well described by a simple model using only the known thermal expansion coefficient of the alkyl chains. The large thermal expansion has implications for thermally annealing nanostructured devices and suggests that lower temperature processing should be used.

Nano-Structured Architectures: We are investigating the use of nano-structured architectures to better understand and improve the performance of organic photovoltaics. We are carrying out two parallel approaches. The first involves coating an organic surface with the OPV material and the second involves a hot stamping process using nano-grating stamps. At the CFN, we have developed the ability to fabricate nano-grating templates over large areas greater than 1mm x 1mm consisting of sub-50 nm lines with variable height on the order of 100 nm and variable pitch ranging from sub-100 nm to over 1 micron. Templates have been fabricated using state-of-the-art electron beam lithography on Si substrates with hydrogen silsesquioxane, an inorganic negative tone resist, as the template material. We have just started to investigate the best way to fill the templates and the role of surfactant coatings. By varying the lithographically defined pitch and wall height of the nano-grating template, it should be possible to control the stacking orientation of polymer chains deposited onto these gratings and to gain insight into structural correlation length scales. With the hot stamping approach, we have been able to successfully reproduce the fidelity of stamps with a 100nm pitch into thin P3HT films using a specially designed x-ray compatible stamping cell. We have also shown that the stamped P3HT films are stable to high temperature and that they are reasonably stable after solvent treatment with dichloromethane. This suggests that we should be able to deposit the acceptor material, PCBM, which is soluble in dichloromethane. Despite this success, we are still puzzled by the off-axis diffraction features of the stamped films. Future studies will correlate these geometries with optical and electronic properties. These early results point the way to future investigations.

Chemical Synthesis:

Our goal is to create polymers that can be cross-linked after patterning, this stabilizing nanopatterned films for further processing. A fully functional polymer synthesis and characterization laboratory has been established in the CFN in order to realize this goal. To date, pre-polymers have been synthesized for several projects, an important step to making the final polymer products. One project involves synthesizing azide functionalized poly(3-hexylthiophene) (P3HT) which can be cross-linked under UV irradiation in order to stabilize the nanostructured film. The resulting P3HT nano-structures should be rigid and robust and amenable to further solution processing in order to add electron acceptor macromolecules such as PCBM.

Surface Chemistry and Electrochemistry of Ethanol

LDRD Project 09-004

R. Adzic, J. Hanson, P. Liu, J. Muckerman, J. Rodriguez and M. White

PURPOSE:

The goals of this project are to understand the fundamental surface chemistry and catalysis of ethanol associated with its use as a source of renewable hydrogen (reforming), its direct synthesis as a liquid fuel from renewable sources of “syn gas” (CO/CO₂/H₂) and its use as a liquid fuel for direct electrooxidation in fuel cells. This effort is a response to the global need for an alternative fuel, e.g., ethanol, which can be generated from renewable sources, e.g., biomass, and can act as chemical source of stored energy for powering transportation vehicles or for generating electrical power. Developing a fundamental understanding of the reaction mechanisms and designing efficient and selective catalysts for reforming synthesis and electrooxidation of ethanol are the key outcomes of this project. This interdisciplinary program involves the close collaboration of scientists in surface science, catalysis electrochemistry and theory and is well-positioned to provide new approaches to alternative fuels that support BNL’s energy mission and respond to expected DOE-BES initiatives in catalysis for energy applications.

APPROACH:

Ethanol has been spotlighted as a source of clean, sustainable and readily used transportable fuel and it currently constitutes 99% of the biofuels produced in the United States. In addition to its use as a direct replacement for gasoline, ethanol holds significant potential for use in fuel cells for generating electrical power. Direct production of ethanol from fermentation of biomass or crops, however, suffers from poor efficiency such that bio-ethanol could at best only supplement current needs for liquid fuels. Moreover, the direct electrooxidation of ethanol ($C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$) suffers from complex and slow kinetics even with the best available catalysts in current fuel cell designs. Our approach to these issues is to develop new catalysts (1) for the synthesis of ethanol from renewable sources of “syn gas” that are more readily scalable for industrial production; (2) for the low temperature steam reforming of ethanol as an on-board source of hydrogen for powering fuel cells; (3) for improving the performance of the DEFC. In addition to identifying new catalytic materials, we need to understand the surface reaction mechanisms which could tell us how to selectively make (synthesis) or break (reforming and electrooxidation) the C-C bond in ethanol and avoid intermediates or products that act as catalyst poisons, rate-limiting traps or unwanted products.

The work is being accomplished through the coordinated efforts of several groups with expertise in the surface science of model nanocatalysts (Hrbek, Rodriguez White), in situ catalyst characterization (Rodriguez, Hanson, Adzic, Zhou), electrochemical methods (Adzic, Zhou) and ab initio theory (Liu, Muckerman). Catalyst materials to be studied will generally consist of nanoparticles of a metal (e.g., Rh, Pd, Pt) or metal alloy (e.g., Pt/Rh, Pt₃Sn, PtMo) deposited on a metal oxide support (e.g., CeO₂) or onto a metal electrode (Pt, Rh). Nanocatalysts will be prepared by a wide variety of techniques including vapor deposition, size-selected cluster deposition, electrodeposition and by “wet” chemical techniques. Our work will address the exact role of the metals and oxide in the catalytic processes and assess the importance of “ensemble” and “ligand” effects in metal alloy catalysts (e.g., Rh-Pt, Pt/SnO). Other aspects to be investigated include the importance of nanoparticle size, redox ability of the metal oxide components (CeO_x or SnO_x). This work builds on recent successes in the use of metal-ceria nanostructured catalysts for hydrogen production (water-gas-shift reaction) and the development of a novel ternary catalyst (Rh/Pt-SnO₂) for the electrooxidation of ethanol.

Characterization of the catalysts under reaction and electrocatalytic conditions will make extensive use of unique *in situ* x-ray probes at the NSLS (AP-XPS, XRD, XAS) and atomic imaging probes at the CFN (environmental TEM). In addition, a new instrument is being built as part of this project that will be able to link well-defined model nanocatalysts prepared under controlled UHV conditions with their performance under realistic reaction conditions.

TECHNICAL PROGRESS AND RESULTS: Listed below are highlights of technical progress made during the first year (FY09) of the LDRD project:

- The structure and stoichiometry of a promising new electrocatalyst for ethanol oxidation was characterized by XAS, XRD and HR-STEM. The results of this study showed that the catalytically active components are small nanoparticles (~1.5 nm) composed of a ternary mix of Pt/Rh-SnO₂.
- The reaction mechanism for C₂H₅OH decomposition on Rh(111) was investigated by density functional theory (DFT) calculations. In agreement with electrochemical experiments, Rh surfaces were found to be too active for ethanol decomposition which results in the formation of C atoms that likely poison the Rh(111) surface.
- DFT calculations and microkinetic modeling showed that modifying the Rh(111) surface with promoters (Fe) can improve the yield and selectivity for ethanol synthesis by suppressing methane formation and enhancing C-C bond formation.
- Discovery of a new catalyst for ethanol steam reforming (C₂H₅OH + 3 H₂O → 2 CO₂ + 6H₂) that is efficient, stable and composed of inexpensive earth-abundant materials (Ce_{1-x}Ni_xO₂). In situ studies showed that metallic Ni is the active phase under reaction conditions (400-500°C) and that Ni-Ce interactions are likely responsible for suppression of coke formation.
- Significant progress was made in the design and assembly of the new instrument for exploring the catalytic and electrocatalytic activity of model nanocatalysts. The main vacuum chambers, in situ electrocatalysis cell, transfer system, surface science instruments (electron analyzer, x-ray source, ion gun, LEED, mass spectrometer) and pumps were assembled and testing is currently underway.

Milestones

FY10

- Study reaction mechanism for ethanol steam reforming (C₂H₅OH + 3 H₂O → 2 CO₂ + 6H₂) on novel Ce_{1-x}Ni_xO₂ catalysts. Optimization of the performance of the oxide and metal phases.
- Explore the activity of NiMoO₄, Pt/CeO₂ and Pt-Ru/CeO₂ for ethanol steam reforming. Compare with the performance of Ce_{1-x}Ni_xO₂.
- Complete the assembly of the new instrument for nanocatalysis studies, including the addition of the gas-phase cluster source for size-selected cluster deposition.

FY11

- Perform experimental and theoretical studies on model nanocatalysts for the synthesis of ethanol from syn gas mixtures (CO/CO₂/H₂) and the electrooxidation of ethanol.

Synergistic Interactions Between Poplar and Endophytic Bacteria to Improve Plant Establishment and Feedstock Production on Marginal Soils

LDRD Project 09-005

Daniel van der Lelie, Lee Newman, Jorg Schwender, Safiyh Taghavi, Lisa Miller,
Richard Ferrieri, Alistair Rogers and Wei Zhu

PURPOSE:

This project forms an **integrated attempt by the BNL Biology Department** to develop and grow a multidisciplinary scientific team as part of a **Center of Excellence at BNL** that will use a systems biology approach to understand, model and improve the growth of bioenergy feedstock plants on marginal soils without competition for agricultural resources. The project is characterized by the following elements:

- New program, strategic hire to complement plant genetics expertise, team approach involving four departments plus Stony Brook University.
- Understanding the plant growth promoting effects that endophytic bacteria have on their poplar host plant, with special emphasis on root formation and its effect on nutrient acquisition and growth on marginal soil.
- Explore plant-endophyte interactions to make biomass production (feedstock and food) on marginal soils economically feasible.

APPROACH:

We are following an integrated research plan to understand at the level of the genome, transcriptome and metabolome the interactions between poplar and two well-characterized endophytic bacteria, *Enterobacter* sp. 638 and *Pseudomonas putida* W619. These two endophytes were chosen, as preliminary genome analysis reveals the existence of distinct mechanisms by which these bacteria can affect the growth of their host plant: IAA production by *P. putida* W619 and production of acetoin and 2,3-butanediol by *Enterobacter* sp. 638. Our hypothesis is that both strains will affect the expression of different regulatory pathways in poplar, but that their altered expression will ultimately result in the same beneficial effects on plant growth and development, and nutrient acquisition. The involvement of different regulatory pathways also opens the possibilities for synergistic effects.

TECHNICAL PROGRESS AND RESULTS:

The following approaches were used:

- **Comparative genomics** (Year 1): *Our hypothesis is that endophytic bacteria have acquired specific functions, which are absent in closely related, non-endophytic bacteria, and that help them thrive in a plant environment.* Annotation and manual curation of the genomes of *Enterobacter* sp. 638, *Pseudomonas putida* W619, *Stenotrophomonas maltophilia* and *Serratia proteamaculans* 568 was completed and showed the presence of several genomic islands that play a unique role in plant-endophyte interactions.
- **Metabolite analysis** (Years 1-2): *Our hypothesis is that the growth of Enterobacter sp. 638 and P. putida W619 in the presence or absence of poplar will result in changes in metabolite profiles, both for bacteria and plant, especially for compounds involved in plant-microbe signaling and plant growth promoting compounds.* The production of the plant growth promoting compounds acetoin and 2,3-butanediol was specifically induced by the presence of plant sugars in the medium. For instance metabolome analysis showed the production of acetoin and 2,3-butanediol by *Enterobacter* sp. 638 in the presence of sucrose, while these

phytohormones were not produced when lactate was used as a carbon source. On the other hand, the production of the antimicrobial compound 2-phenylethanol by *Enterobacter* sp. 638 was found to be constitutive.

- **Transcriptome analysis** (Years 1-3): *We expect changes in gene expression to be directly linked to changes in the plant's nutrient status, metabolite production, and altered plant growth and development.* An endophyte “microarray” was designed. Transcriptome analysis revealed changes induced by the presence of plant roots and root exudates, including that of the pathway for the synthesis of acetoin and 2,3-butanediol by *Enterobacter* sp. 638 when grown in medium with sucrose as the sole carbon source.
- **Plant growth promoting effects** of various endophytes were tested for other bioenergy feedstocks and food crops, including tomato, tobacco and sunflower. For all plant types, beneficial effects of plant growth and development were observed after inoculation with *Enterobacter* sp. 638.
- **Effects of endophytic colonization on the carbon and nitrogen status** of their poplar host. *Many of the signals for the plant's C and N status are well know regulators of gene expression (sugars, nitrate, amino acids). We expected to see changes in gene expression that are directly linked to changes in the plant's nutrient status, resulting from improved plant growth and development.* Using a high-throughput enzyme screening platform, we found that *Enterobacter* sp. 638 is impacting central C and N metabolism and increasing the availability of amino acids for protein synthesis.
- *Endophytic colonization is expected to constitute a new metabolic sink that will affect the flows of carbon and nitrogen to different plant parts.* Using real-time, non-destructive radiological techniques with ¹¹C (half-life 20.4 min) and ¹³N (half-life 10 min) - short-lived positron emitters, we showed that endophytic inoculation affected partitioning of ¹¹C carbon flow into new metabolites.

Milestones from the start date of project:

Month 6: List of candidate genes for *Enterobacter* sp. 638 and *Pseudomonas putida* W619 that are involved in endophytic colonization of poplar, including biosynthetic pathways for plant growth promoting compounds – completed.

Month 12: Microarrays to study the transcriptome of *Enterobacter* sp. 638 and *Pseudomonas putida* W619 – completed.

Month 18: Identify growth regulating compounds and other secondary metabolites that play a role in plant-microbe communication and plant growth regulation.

Month 18: Identify genes and pathways that are potentially involved in the regulation of plant growth and endophytic colonization.

Month 24: Description of the effects of endophytic colonization on the carbon and nitrogen status of their host plant

Month 30: Collection of endophytic strains mutated in genes involved in the synthesis of plant growth promoting compounds.

Month 30: Confirm the involvement of previously identified genes and pathways (based on transcriptome and metabolome data) in the regulation of plant growth and endophytic colonization.

Month 30: A series of comprehensive models that describe the genetic networks necessary for the successful symbiotic interaction between endophytic bacteria and their poplar host plant.

Development of Capability to Design State-of-the-Art Microelectronics

LDRD Project 09-006

Gianluigi De Geronimo

PURPOSE:

To maintain and enhance BNL's ability to develop state-of-the-art Application Specific Integrated Circuits (ASICs) in support of numerous DOE missions in the fields of Photon Science, High Energy & Nuclear Physics, Accelerator Development, Basic Energy Sciences, Life Sciences, Homeland Security and Industrial partnerships.

APPROACH:

Research programs such as NSLS II, RHIC, Medical Imaging, Detectors for Homeland Security, LHC, DUSEL and others have emphasized the need and reliance on advanced detectors. Such detectors are virtually impossible to develop without advanced low-noise mixed signal ASICs (e.g., RatCAP, various x-ray detectors, LEGS TPC, LSST, RHIC and LHC detectors). These ASICs integrate in a small area a large number of low-noise electronic signal channels capable of amplifying, processing and multiplexing a large number of sensing elements. The expertise required to design these specialized ASICs is unique and different than what is needed in the computer industry. Detector ASICs must be specifically optimized to a particular detector and application and are not available on the commercial market. The development of the ASIC design capability relies on a continuous R&D effort to keep pace with the increasingly stringent requirements of the applications and the rapid progress of the integrated circuit technologies. Over the past decade, the Instrumentation Division has provided several advanced ASICs for RHIC, ATLAS, NSLS, Medical Imaging and Homeland security initiatives.

With the advent of advanced detectors, the requirements on the performance, density, complexity and functionality of the ASICs have dramatically increased (e.g., transistor count on a single silicon chip is now exceeding one million). On the other side, the technology to fabricate the ASICs is rapidly progressing, imposing additional severe constraints (e.g., finer lithography layout, voltage limits decreasing to 1 Volt or less). These developments cannot be done using the existing low-cost and public domain design tools. These tools are not able to simulate more than a few thousand transistors, and do not have the model libraries and rule files associated with the commercially available technologies. With these dated tools, a reliable design of any more complex ASICs has become practically impossible. In order to design the ASICs for the BNL research programs, scientists and engineers in the Instrumentation Division must be provided with the appropriate industry standard design tools (CAD tools).

The work required for maintaining and enhancing BNL's ability to develop state-of-the-art ASICs has been organized in three phases. The *first phase* consists of comparing the available industry standard CAD tools in terms of performance and price and then selecting the ones that are most appropriate for ASIC designs in BNL. The *second phase* consists of selecting and purchasing the most appropriate set and number of licenses, software maintenance plans, and hardware (workstations) to cover the BNL ASIC design group. The *third phase* consists of progressively integrating the new CAD tools into our ASIC design flow. This is achieved by training our engineers, by migrating our basic sub-circuit designs, and by using the new tools for present and near future ASIC design.

TECHNICAL PROGRESS AND RESULTS:

In the *first phase*, completed in three months, it was found that the most appropriate toolset was a combination of CAD tools from Cadence Design Systems and Mentor Graphics Corporation, both considered industry standard providers. The former has the most appropriate tools for schematic entry, circuit simulation, physical layout and parasitic extraction. It also provides appropriate tools for design verification (layout-versus-schematic and design rule check) in some of the technologies and foundries that we adopt in our ASIC designs. The latter has the appropriate set of tools for design verification in the remaining technologies and foundries.

During the *second phase*, completed in three more months, the LDRD funding was largely used to purchase licenses from the two selected providers Cadence and Mentor. With the present LDRD funding level, it was possible to purchase licenses for two design seats (group of tools required by one ASIC engineer) plus one verification tool from each of the two vendors to be shared among our engineers. By adding another recent purchase of licenses, our current toolsets can cover a total of four engineers with some limitations due to the shared tool. This corresponds to our current workforce. On the other hand, our current computers are too limited in their computing capacity to fully benefit from the new CAD tools. The optimum configuration of computers and workstations is now being investigated.

Concerning the *third phase*, the effort has made significant progress. The new CAD tools are progressively being integrated in our ASIC design flow. They have already been used for a small design of a front-end prototype ASIC in SiGe 0.13 μm technology for the ATLAS Calorimeter upgrade and for a first prototype ASIC in CMOS 0.18 μm for the DUSEL LAr TPC. It must be emphasized that none of these designs would have been possible without industry-standard CAD tools. Test structures and advanced sub-circuits are also being designed, to be implemented in present and near future ASIC developments.

Additionally, the availability of the industry standard CAD tools to our design group made possible hiring and rapidly integrating two specialized and talented ASIC designers (both at Ph.D. level).