LEQSF(2007-12)-ENH-PKSFI-PRS-04

"A Center for Advanced Materials and Nanotechnology in AMRI at the University of New Orleans"

PI: Charles O'Connor

Lead Institution: University of New Orleans

Contents:

Proposal Narrative (without appendices)

COVER PAGE FOR POST-KATRINA SUPPORT FUND INITIATIVE
PRIMARILY RESEARCH SUBPROGRAM PROPOSALS
BOARD OF REGENTS SUPPORT FUND, FY 2006-07

032PKSFI-R-07

(For BoR Use Only)
Application Number:

1. Submission Discipline: ☐ Biological Sciences ☐ Information Technology ■ Materials Science
(check only one)

2. Name(s) of Lead Submitting Institution of Higher Education: University of New Orleans, Lakefront, New Orleans, LA
(Include Branch/Campus/Other Components)

3. Address of Lead Institution of Higher Education: University of New Orleans, Advanced Materials Research Institute, College of Sciences, 2000 Lakeshore Drive, New Orleans, LA 70148
(Include Dept/Unit, Street Address/P.O. Box Number, City, State, Zip Code)

4. Title of Proposed Project: A Center for Advanced Materials and Nanotechnology in AMRI at the University of New Orleans

5. Proposed Duration: (Circle # of Yrs.) 1 2 3 4 (5)

6. Funds Requested P-KSFI Year 1: $ 1,600,000 | ESIP: $ 800,000 | Project Total: $ 8,800,000

7. Name(s) of Partnering Institution(s) University of New Orleans; Children's Hospital-New Orleans-LSUHSC; Tulane University; Institute for Micromanufacturing-LA Tech University, LSU-CAMD; Communities in Schools

8. Does This Proposal Contain Confidential or Proprietary Information Which Falls Into a Category Described in R.S. 44:4(16)?
☐ YES ■ NO (NOTE: If YES, the proposal MUST be appropriately marked.)

By signing and submitting this proposal, the signators are certifying that: (1) the proposed project has not already been funded/is not currently being funded/has not been promised funding; (2) this proposal has been reviewed and approved by an Institutional Screening Committee; and (3) the institution and the proposed project are in compliance with all applicable Federal and State laws and regulations, including, but not limited to, the required certifications set forth in: (a) Grants for Research and Education in Science and Engineering, NSF Grant Proposals Guide (GPG), NSF 03-2, effective 10/1/02, and (b) 45CFR 620, Subpart F (Requirements for a Drug-Free Workplace).

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(Form 1-PKSFI-PRS, 1-2007)

PROJECT SUMMARY

Name of Lead Institution (Include Branch/Campus): University of New Orleans, Lakefront, New Orleans, LA

Name(s) of Partnering Institution(s) (Include Branch/Campus):
University of New Orleans; Children's Hospital-New Orleans-LSUHSC; Tulane University;
Institute for Micromanufacturing-LA Tech University; LSU-CAMD; Communities in Schools

Principal Investigators: Dr. Charles J. O'Connor

Title of Project: A Center for Advanced Materials and Nanotechnology in AMRI at the University of New Orleans

Abstract (DO NOT EXCEED 250 WORDS):

The ultimate goal of this proposal is to enhance the collaborative infrastructure that will allow the Advanced Materials Research Institute (AMRI) at the University of New Orleans to successfully compete for major centers grants (*e.g.*, NSF MRSEC, NSEC, ERC; DOD MURI, DOE, NIH, *etc.*). Since opening in 1996, AMRI has averaged over $3M/yr in grants and contracts. AMRI currently has over $6M in active funding and the funding for P-KSFI will be leveraged by current and subsequent grants. AMRI will recruit two faculty who will be charged with helping to organize the centers initiative; the UNO administration has allocated the new faculty to AMRI as cost-sharing for PKSFI. These positions are focused on projects that overlap with the research proposed here. Substantial startup funds are needed to be competitive when recruiting top notch faculty; the funds from P-KSFI combined with monies provided by UNO will afford a very attractive and competitive package that will increase the likelihood of landing first rate candidates. The premier research centers in the U.S. are defined by strong interdisciplinary research efforts. Towards this goal, this white paper is divided into four sections, three Focused Research Groups and Broader Impacts as follows:

1. *Nanomaterials for Biological Sensing and Imaging: FRG co-leaders – S. Pincus (Children's Hospital), W. Zhou (UNO)*
2. *Nanoscale Mechanical Devices: FRG leader - J. Wiley (UNO)*
3. *Nanomaterials for Energy Conversion and Storage: FRG co-leaders – Y. Lvov (LaTech), K. Stokes (UNO)*
4. *Broader Impacts (Educational and Commercial Outreach): FRG leader - M. Tarr (UNO)*

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4. GOALS AND OBJECTIVES:

The fundamental goal of this P-KSFI proposal is to establish a federally-funded center for advanced materials and nanoscience in Louisiana. We will focus our efforts on being the lead institution in an NSF-MRSEC.

For AMRI to be the lead institution in a major center, it is clear that a competitive and successful proposal must describe a center whose focus is precisely defined. In order to clearly define the focus of our programmatic goal, we have selected three research areas to develop. Using a MRSEC proposal as a guide, this P-KSFI proposal is divided into three Focused Research Groups and a Broader Impacts section.

To reach our goal, the team must build a significant body of collaborative successes in the fields of materials research for bio-sensing and imaging, nanoscale mechanical devices, energy conversion and storage, and outreach. Our primary performance metrics will be success in obtaining competitive federal research cluster funding (jointly with two or more PI's from this team) and production of intellectual property (IP). Secondary metrics will be those activities which increase our profile in the scientific community: publications in high-profile journals and presentations at meetings (particularly invited presentations and lectures). Again, these will be jointly-authored with other team members, outreach participants and industrial partners. The specific technical objectives of the focused research and outreach groups are described at the end of the Narrative section (pp. 18-19). The table below summarizes the objectives of the entire consortium for the five years; the fundamental project goal of developing a major federally funded center at AMRI.

Funding agencies (especially NSF) are directing an increasing component of their research budget towards funding of collaborative research programs for example in the Mathematics and Physical Sciences Directorate at NSF, especially in the Divisions of Materials Research (DMR) and Chemistry. In addition to the major centers grant, each year we will target several collaborative multi-investigator grants.

We expect to have at least 2-4 patent disclosures each year, with at least two patents issued and licensed by year 5. In addition to the two spin-off companies in existence (NanoPrism Technologies, Inc. and NSCR Biotechnologies LLC) we expect these companies to become more established commercial ventures and AMRI will spin-off at least two additional companies in the area of energy conversion and nano-mechanical devices.

Table 1. Goals for this research team for the PKSFI grant period. All outcomes listed will include two or more team members as principal authors.

PERFORMANCE METRIC	Year 1	Year 2	Year 3	Year 4	Year 5
Federal grant proposals (both major center and cluster)	2	4	4	4	4
Publications	5	10	15	29	20
Presentations	8	15	20	20	20
Patent Applications and Disclosures	0	2	3	4	4
Outreach Interns	17	17	17	17	17

5. Narrative and Bibliography

A. Project Rationale and Structure

(1) DESCRIPTION OF RESEARCH GROUP

The Advanced Materials Research Institute (AMRI) consortium includes 22 co-investigators from the following six partner institutions in Louisiana: University of New Orleans (AMRI and Center for Innovation), Children's Hospital, LSU (CAMD and Physics), Louisiana Tech (IfM), Tulane University (Chemical Engineering), and Communities In Schools of New Orleans, Inc.

The proposal is divided into three Focused Research Groups and a Broader Impacts section with 22 participating team leaders (co-P.I.'s) and co-investigators as follows:

1. ***Focused Research Group #1; Nanomaterials for Biosensing and Imaging:*** **S. Pincus** (co-Leader, Children's Hospital, LSUHSC), **W. Zhou** (co-Leader, UNO-AMRI), **C. O'Connor** (UNO-AMRI), **Z. Rosenzweig** (UNO-AMRI), **J. Goettert** (LSU-CAMD), **M. DeCoster** (LaTech-IfM)
2. ***Focused Research Group #2; Nanoscale Mechanical Devices*****: J. Wiley** (UNO-AMRI, Leader), **B. Gibb** (AMRI-UNO), **L. Spinu** (AMRI-UNO), **S. Whittenburg** (UNO-AMRI), **V. John** (Tulane–Chemical Engineering), **H. Ashbaugh** (Tulane–Chemical Engineering).
3. ***Focused Research Group #3 - Nanomaterials for Energy Conversion and Storage***; **Y. Lvov** (co-Leader, LaTech), **K. Stokes** (co-Leader, UNO-AMRI), **H. Gabrisch** (UNO-AMRI), **L. Malkinski** (UNO-AMRI), **K. Varahramyan** (LaTech-IfM), **D. Young** (LSU-Physics)
4. ***Broader Impacts - Educational Outreach and Commercial Outreach;*** **M. Tarr** (Leader, UNO-AMRI), **P. Hanson** (UNO-AMRI), **R. Bidwell** (Communities In Schools of New Orleans, Inc.), **N. Grace** (Vice Chancellor for Technology and Economic Development, UNO).

(2) CONTEXT FOR PROJECT:

Following the destruction of Hurricane Katrina, AMRI has resumed operations at the University of New Orleans. The devastation to AMRI was profound; many of our staff suffered immense loss and damage and the research infrastructure of the institute has taken many months of hard work to restore. In the days immediately following the hurricane, AMRI was able to form a virtual institute on the internet, coordinate communication between staff and the emerging university administration, and assist our displaced research staff to continue their programs at remote host institutions around the country. As we re-organize AMRI, we are building a better, more successful institute and have reclaimed our position as the region's premier institution in advanced materials and nanoscience.

The Advanced Materials Research Institute is a multidisciplinary research institute founded in 1996. AMRI provides a unique opportunity to develop novel research ideas that ultimately involve the government, private, and academic sectors in the conception and development of research programs. The interactions with corporate laboratories provide a synergistic pathway that promotes technology transfer and private sector involvement in the operation of AMRI.

The focus of this proposal is to enhance the collaborative infrastructure of AMRI to allow the AMRI consortium to successfully compete for major centers grants. AMRI has developed an international reputation for excellence in the 10 years since its inception and has averaged over

$3M per year in external grants and contracts. This project will be managed by the AMRI management team that is experienced in the administration of major grants.

(3) EXISTING SCIENTIFIC EXCELLENCE:

The consortium is lead by a group of outstanding Louisiana researchers, all of whom have significant federal funding and have experience leading productive interdisciplinary research teams. In addition, Profs. **O'Connor**, **Pincus** and **Lvov** are entrepreneurs and have each established spin-off companies using technologies developed in the course of their research.

Since its inception in 1996, AMRI has obtained over $30M in grants and contracts, most of these funds cane from the National Science Foundation, Department of Energy, and agencies of the Department of Defense. The AMRI research laboratories are located in the Science Building at the University of New Orleans, where it occupies more than 8,000 square feet of laboratory and office space. Over its 10 year history, AMRI has received over $30M in outside funding and has amassed an inventory of more than $4.0 million of specialized materials research instrumentation to carry out its research programs. The facilities available to AMRI researchers and collaborators are listed on the AMRI web page (http://amri.uno.edu/). In addition to occupying first rate facilities, AMRI is already well positioned for the transition to a federally funded center.

AMRI is a participant in a research cluster that is now applying for an NSF-ERC. Dr. Stuart Wolf was AMRI's first program director at DARPA. After about 10 years at DARPA, Dr. Wolf joined the Department of Materials Science and Engineering at the University of Virginia. Prof. Wolf is very much aware of our expertise and capabilities and he has asked AMRI to participate in an NSF-ERC Proposal. The name of the proposed center is: "*Spins in Quantum Electronic Systems and Technology (SpinQuEST)*". In addition to the University of Virginia, the partner universities include University of California at Santa Barbara (David Awschalom), Florida State University (S. von Molnar), University of California at Riverside (R. Haddon), Morgan State University (C. Williams/A. Lisfi), and the University of New Orleans (C. **O'Connor**, AMRI).

AMRI-UNO is also the lead institution for the Louisiana collaborative program funded under DARPA's BioMagnetic Interfacing Concepts (BioMagnetICs) initiative. The three partner institutions for that proposal were AMRI at UNO (lead institution), the Neurosciences Center at LSUHSC, and CAMD at LSU. This project was a three year collaborative program with total project funding of $6,115,538 from 2003 – 2006.

(4) MULTI-INSTITUTIONAL FOCUS:

AMRI has a history of multi institutional programs and has established a research consortium which includes academic, government, and industrial participants and their research laboratories. Together with the AMRI Technical Advisory Board (TAB), these institutions include:

Academic Laboratories

- University of New Orleans
- Louisiana State University
- LSU Health Sciences Center
- Tulane University
- Louisiana Tech

Industrial Laboratories

- NanoPrism Technologies, Inc.

- NSCR Biotechnologies LLC
- Parallel Synthesis Technologies (TAB)
- Lockheed Martin, Advanced Technology Center (TAB)
- Intel Corporation (TAB)
- Seagate Recording Media Operations

Government Laboratories

- Argonne National Laboratory (TAB)

B. RESEARCH PLAN

(1) PROPOSED WORK

a. FRG1: Nanomaterials for Biosensing and Imaging

Participants**: S. Pincus** (co-Leader, Children's Hospital, LSUHSC), **W. Zhou** (co-Leader, UNO-AMRI), **C. O'Connor** (UNO-AMRI), **Z. Rosenzweig** (UNO-AMRI), **Jost Goettert** (LSU-CAMD), **M. DeCoster** (LaTech-IfM)

Objectives: The objective of this research group is to develop nanomaterials to be used as biosensors and for clinical imaging. Specifically, we propose to develop highly sensitive nanowire-based biosensors and nanoparticle based real time imaging of biomolecules. The biosensors will be tested by detecting ricin toxin and secreted phospholipase A_2 ($sPLA_2$) enzyme, and through nanoparticle based real time imaging of biomolecules. The project will be led by **Seth Pincus** (LSUHSC, Children's Hospital, New Orleans) and co-led by **Weilie Zhou** (UNO-AMRI). The participants are **S. Pincus** (Biologist, LSUHSC, Children's Hospital, New Orleans), **W. Zhou** (Materials, scientist/physicist UNO-AMRI), **C.J. O'Connor** (Chemist, UNO-AMRI), **M. DeCoster** (Biologist, LaTech-IfM), **Z. Rosenzweig** (Biochemist, UNO-AMRI), and **J. Goettert** (Microfabrication specialist, LSU-CAMD) coupled with the expertise from four institutions and universities for nanomaterials synthesis, nanomaterials and biomaterials assembly, microfluid and sensor prototype fabrication, and biosensor and bioimage testing. Three sub-teams will be formed to accomplish three sub-projects associated with biodetection and clinical imaging.

Nanowire Biosensors

As binding of bio-agents to the surface of the nanowires can be detected at femtomolar (fM) concentration with millisecond response time,[1,2] developing highly sensitive nano-biosensors for biomedical research and pathogen monitoring has great potential for instant application. We will test the biosensors in two experimental systems that are well studied at our institutions and have considerable practical application: the detection of ricin toxin, a major biodefense concern, and secreted phospholipase A_2, an important clinical marker. Nanoscale biosensors can provide highly sensitive measurements, in real time and in extremely small volumes. Thus, they may have real application for in vivo sensing, distant monitoring, and the development of bioassays. Our test system will allow comparison to established bioassays.

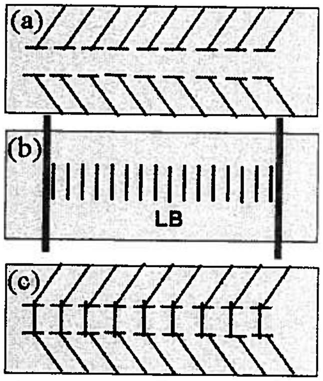


Fig.1 (a) pre-addressed electrode array (b) LB aligned NWs (c) NW FET array.

Ricin toxin, derived from the castor bean, is a major concern as a bioterrorist weapon. It is ubiquitous, reasonably easy to purify, and highly deadly. It is estimated that 1 million metric tons of castor beans are produced commercially each year.[3] In contrast, the lethal dose of ricin toxin for a human, by inhalation or injection, is estimated to be 0.5 mg.[4,5] In this sub-project, we will build multiplexed field effect transistors (FETs) for ricin toxin selective detection. This sub-team will accomplish the following tasks: 1. Nanowire synthesis (**Zhou** and **O'Connor**); 2. Patterning of micro- and nano- multiplexed electrodes (**Goettert** and **Zhou**); 3. Assembly of nanowires (**O'Connor** and **Zhou**); 4. Attachment of antibody and ricin toxin on nano-FETs (**Pincus** and **Zhou**); 5. Transport property measurement of FETs using a microfluid system (**Zhou** and **Goettert**); 6. Construction of a database for selective detection (**Zhou** and **Pincus**). Nanowires (Si and ZnO) will be fabricated through chemical and physical methods at AMRI (**Zhou** and **O'Connor**). In the past, AMRI has successfully fabricated all kinds of nanomaterials, such as one dimensional semiconductor nanowires[6] and magnetic[7] and luminescent[8] nanoparticles. A pre-addressed electrode array will be patterned on a Si/SiO_2 substrate by photolithography and e-beam nanolithography (Fig.1(a)) (**Goettert** and **Zhou**). Langmuir Blodgett techniques will be used to align ultra-thin semiconductor nanowires (Si or ZnO) (**O'Connor** and **Zhou**). By proper surfactant selection and controlled compression speed, evenly spaced aligned nanowires can be achieved (Fig.1(b)).[9] The aligned nanowire array can be transferred to the pre-patterned chip to form a nano-FET array (Fig.1(c)). We will then functionalize nano-FETs with different antibodies (**Pincus** and **Zhou**). A panel of 49 monoclonal antibodies that bind to ricin have been developed by the **Pincus** group.[10] We will first investigate the response of a single transistor to ricin toxin using different antibodies, buffer solutions, concentrations, etc. Then a series of antibodies will be attached to multiplexed nanowire FETs through a microfluid system (**Goettert** and **Zhou**). After collecting a series of data from each FET, a characteristic database for whole transistors will be generated for selective ricin toxin detection (**Pincus** and **Zhou**).

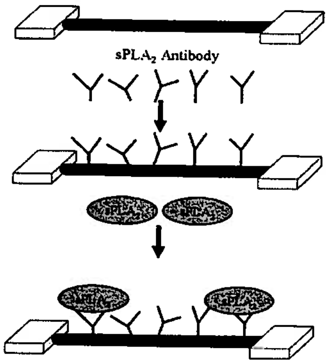


Fig.2 A FET Biosensor for sPLA$_2$ detection.

sPLA$_2$ is an endogenous component of the inflammatory response of mammalian cells, including humans, which has been detected in the clinically relevant conditions of cancer,[11] brain injury and disease,[12, 13] rheumatoid arthritis,[14] sepsis,[15] sickle cell disease, and acute chest syndrome.[16] Thus, the immediate detection of sPLA$_2$ from clinical (including blood) and cell samples is crucial. It is anticipated that detection will be much faster than the traditional methods of ELISA, Western blot, and enzyme assays currently used. Essentially similar tasks will be performed by this sub-team that parallel the ricin toxin detection. The fabrication process is shown in Fig. 2. Nanowires will be synthesized first (**O'Connor** and **Zhou**), which will be integrated into a patterned biochip detection device (**Goettert** and **Zhou**). Linkers and tails for sPLA$_2$ detection will be functionalized on the nanowires by using LBL technology (**DeCoster**). Transport properties will be measured, and a database will be established (**Zhou** and **DeCoster**). An additional goal of this project is to develop a cellular sensor that can detect responses to cell stress such as release of sPLA$_2$ from living cells and/or tissues (**DeCoster** and **Zhou**). Current methods for detecting sPLA$_2$ require more time for preparation and analysis than would nanowire-based biochips. Successful fabrication of these nanowire-based biochips could reduce the detection time to seconds or less for practical clinical application. **DeCoster** *et al.* have recently reported methods and conditions for eliciting sPLA$_2$ release from brain astrocytes after inflammatory stimulus.[17] We will utilize these methods as a starting point for developing a cell-based sensor to detect $sPLA_2$ release from living cells. Commercially available sources exist for both $sPLA_2$ antibodies and proteins (for example, Cayman Chemical), which will be utilized for device fabrication and testing.

Imaging

The development of in vivo imaging technologies is progressing rapidly. Imaging techniques cover a wide range of applications from the use of X-ray microscopy for cardiac imaging [18] to the employment of IR microscopy to study neuronal behavior.[19] In spite of many accomplishments, currently used imaging methods are limited in their spatial and temporal resolution and for the most part do not provide the information required to understand chemical and biological processes at the molecular level. A paradigm shift is needed to overcome the limit of diffraction in chemical and biological imaging techniques. The recent development of bio-nanotechnology[20] provides a unique opportunity to explore the use of nanomaterials as probes in imaging applications with temporal and spatial resolution superior to currently used state of the art imaging methods. The objective of the proposed study is to synthesize and utilize nanomaterials in imaging applications of chemical and biological systems. The hypothesis to be tested is that these nanomaterials could be targeted and placed selectively at sites of interest to provide dynamic information at the nanometer scale. The proposed study will focus on the synthesis of nanoparticles that are 50 times smaller than the limit of diffraction in optical imaging. The tasks will be carried out as follows. **O'Connor** and **Rosenzweig** will design and use nanomaterials as magnetic and luminescent vicinity probes with real time and sub-diffraction limit spatial resolution capabilities in magnetic and optical imaging applications. **DeCoster** will employ magnetic nanoparticles as magnetic resonance imaging (MRI) contrast agents and functionalized luminescent quantum dots to study signaling processes in neuron cells to demonstrate the capabilities of these materials. **Pincus** will derivatize these materials using antibodies to well established tumor antigens and test their ability to localize to tumors implanted into immunodeficient mice, thus testing the ability of these materials to function in vivo.

The proposed group represents a broad variety of established institutions and expertise from a cross-section of this state, with prior and on-going collaboration.[21,22] Collaboration on this project would repair and solidify these ties that were disrupted by Katrina, and would help foster new ideas and approaches that could lead to national and regional scientific impact, funding, and possible commercialization of technology.

It should also be noted that the research activities of **O'Connor** and **Rosenzweig** have already resulted in the formation of two startup companies, **NanoPrism Technologies Inc**. and **NSCR Biotechnologies LLC**. Both companies rely on intellectual property developed by UNO researchers at UNO. The proposed study will increase the property base of these companies and support their growth. It is worth mentioning that while the Biotechnology sector in Louisiana has been an area of targeted growth, there have been very few Biotechnology companies in the city of New Orleans before Katrina. This number decreased even more in the aftermath of Katrina. The proposed study will support the growth of the two Biotechnology companies and provide high paying jobs to scientists in the city of New Orleans.

b. FRG2: Nanoscale Mechanical Devices

Participants: **J. Wiley** (UNO-Chem-AMRI), **V. John** (Tulane-Chem. Eng.), **B. Gibb** (UNO-Chem-AMRI), **L. Spinu** (UNO-Physics-AMRI), **S. Whittenburg** (UNO-Chem-AMRI), **H. Ashbaugh** (Tulane-Chem. Eng.)

Objectives: The objectives of this program will be to design and fabricate a series of nanoscale mechanical devices. Combinations of nanocomponents will be assembled to make structures with specific functions. Applications for such systems will be widespread including fluidics, medicine, tools for nanocomponent manipulation, communications, data storage, and sensors. The program will also tackle fundamental issues pertinent to the scaled up production of such nanoscale mechanical devices and the fabrication of motorized components.

Program: To realize the targeted nanoscale mechanical devices, this program will require the coordination of many activities. These include the fabrication of nanocomponents (**Wiley, John**), the assembly of the components (**Wiley, Gibb**), the design and fabrication of platforms via nanolithography for assembly and testing of devices (**Wiley, Whittenburg, Spinu**), testing of the devices (**Spinu**), and the modeling of the devices (**Whittenburg**) and their assembly (**Ashbaugh**). Subsets of these efforts are molecular directed assembly, actuation methodologies, and motorization.

Nanocomponents (**Wiley, John**). Team members have extensive experience in the fabrication of nanocomponents via template methods.[23-31] They will be able to routinely provide various nanoscale wires (simple wires, superlattice, core-shell, porous, etc.), tubes, or spheres. Samples are typically prepared by chemical or electrochemical methods and can be made of metallic, magnetic, and/or polymeric materials. Further efforts will involve the formation of gel nanocomponents that are to be used as actuators (see below).

Nanolithography (**Wiley, Whittenburg, Spinu**). AMRI is well equipped to carry out in-house e-beam nanolithographic preparations and thin film depositions. Platforms, designed by **Spinu, Wiley and Whittenburg**, will be routinely fabricated. Photolithographic preparation of larger features, such as macroscopic interface components, can also be carried out in-house; photolithographic masks can be obtained commercially or prepared through the facilities at CAMD.

Assembly (**Wiley, Gibb, Ashbaugh**). The assembly of nanocomponents will be directed either through physical or chemical methods. Physical methods will utilize nanolithographically patterned substrates where clefts in the substrates will be used to align and contain nanocomponents.[32-34] Insertion into these clefts will be carried out by hydrodynamic and/or magnetic methods or via the nanomanipulator available in AMRI. Chemically-directed assembly methods will also be explored. Sets of specific binding pairs of host-guest molecules[35,36] will be used to direct the assembly of nanocomponents – either for placement of components onto surfaces or for the combining of sets of components. Modeling of assembly processes will be carried out (see below) to help refine this approach.

Actuation (**Wiley, Spinu, John**). The movement of the nanocomponents in these devices will be critical to their success. Here we will utilize electrostatic or magnetic interactions to direct the movement of the components. Interconnects will be positioned adjacent to nanocomponents to direct them up-down, left-right, etc. depending on the device (see example devices below). Further efforts will investigate the use of gel-based actuator systems. Various gels can exhibit significant volume expansions with different stimuli such as solvent uptake, pH change, thermal variation or electrical stimulation.[37] Some response times in terms of volume expansions are slow, while others are in the millisecond range. Further volume changes can also vary greatly with some values exceeding 1000% being reported. While the electromagnetic components will be integrated during the fabrication of the platform, the gel components may be integrated during the nanocomponents fabrication step.

Testing of components (**Spinu**). Once assembled, device testing will be carried out. Visualization of the active components during testing will be highly desirable. Since the components will be in the nanometer-to-micron scale (50 - 1000 nm), simple optical microscopy will not be effective. Therefore we will work to characterize devices in an electron microscope (SEM or FESEM) or with probe microscopy. Due to the interactive nature of each of these techniques, we may not necessarily be able to follow the movement within the device continuously, but instead would monitor the process at each endpoint. In those cases where the devices are switches (see below), we can also measure the output of the device before and after the circuit is complete.

Modeling (**Whittenburg, Ashbaugh**). Modeling of various aspects of these devices will be important to understanding their response and sustainability. Factors such as the electromagnetic field strengths needed to move components, the impact surface roughness on movement from the nanocomponents and the platforms, structural fatigue in repetitive processes, response times, and in the case of gel expansions, variations needed to effect desired movement, will all be studied. Further, directed assembly of nanocomponents will also be an important part of this study; here we will model assembly processes controlled by complementary host-guest (HG) pairs based on organic capsule structures. The effectiveness of sets of HG pairs in directing assembly, the importance of surface coverage and topology on HG-directed nanocomponent interactions, and ease of orientational control will all be considered over multiple length scales.

Devices – Specific examples of the types of devices targeted in this program are shown in Figures 3 and 4. An on/off switch will be prepared (Fig. 3a); these switches can then be used in parallel or series to make nanoscale logic devices (e.g. AND or OR gates), in simple data storage architectures or as part of sensor arrays. The second device (Fig. 3b) will allow control of fluidics in the nanoscale. The valve is 2-way where fluid flow direction (left or right) will be controlled via the positioning of a nanosphere. The third targeted device is a nanopump system (Fig. 3c). It combines some ball valves with a plunger system; as the valves are alternately opened and closed, the plunger is moved in and out to drive the flow of fluid from the lower part of the pump to the upper part. Both the valve and pump assemblies will allow for significant advances in drug delivery, medical implants, separations, chemical synthesis, chemical analysis, etc. Finally, architectures for the propulsion of small mechanical devices will be developed (Fig. 4); these motors will be based on electromagnetic or chemical propulsion and can serve as the foundation for the fabrication of a set of active and potentially mobile nanodevices (see below).

Motors – The switch, valves, and pump will be designed such that they are mostly run in an on/off mode. Alternatively, we wish to design and fabricate devices that can operate in a more continuous fashion. These motorized devices will be used to drive a simple cog assembly. One propulsion technique will be based on an electromagnetic system where the cog will have a magnet piece attached and will be turned by sequentially activating a series of pads. A second propulsion method will be based on the chemical system recently reported by Mallouk and coworkers;[38] they found that a platinum-gold segmented wire was drawn through a peroxide solution. If a similar component can be tethered to the cog (Fig. 4), it too could be driven (motorized) in the presence of a peroxide solution.

Economic Impact – This grant will allow our team to then pursue major grants such as the NSF NIRT or MRSEC center grant. Further, patents will be sought on processes and devices; these will then lead to licensing agreements and/or the development of small businesses putting Louisiana in a leadership role with respect to nanotechnology and nanodevice development.

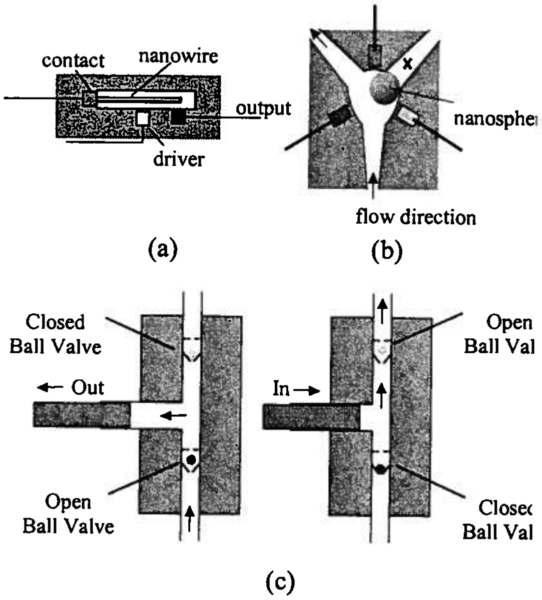
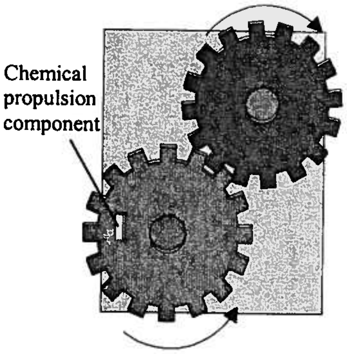


Figure 3. Top views of nanomechanical devices will be prepared that consist of one or more nanocomponents assembled into nanolithographically patterned arrays. The active structures will be driven by either magnetic or chemical means. The devices shown here consist of a (a) simple electric on/off switch, (b) 2-way ball valve where nanosphere controls flow direction (drivers shown as colored pads). (c) A pump system consisting of two one-way valves that will be controlled independently of each other. The red plunger works as the pump, pulling fluid from below (left) with an outward stoke and expelling it above (right) as the plunger moves inward.

Figure 4. Chemically driven mechanical device; the chemical propulsion unit (motor) on top of one cog will be used to drive the second cog – this is important in the fabrication of active nanomechanical devices.



c. *FRG3:* Nanomaterials for Energy Conversion and Storage

***Participants*:** **Y. Lvov** (co-Leader, LaTech-IfM), **Kevin Stokes** (co-Leader, UNO-AMRI), **Heike Gabrisch** (UNO-AMRI), **Leszek Malkinski** (UNO-AMRI), **Kody Varahramyan** (LaTech-IfM), **David Young** (LSU-Physics)

The world demand for energy is projected to increase to 28 TW (terawatts) by 2050, almost double what it is today.[39] As the finite supply of fossil-fuel is being consumed at an ever increasing rate, the search for alternative energy sources and more efficient energy storage and distribution materials is critical. Engineered nanomaterials are key enablers in the development of next-generation energy conversion and storage technologies.[39] Nanomaterials are attractive since, in nanostructures, it is possible to manipulate and control electron transport, phonon transport and chemical reactions at nanometer-scale interfaces. To accomplish this goal, we have assembled a team which combines expertise in chemical synthesis, thin film deposition, solid-state materials synthesis, and micro- and nano-fabrication. This team will apply the fundamental science of nanometer-scale materials and engineering architectures to four key areas: 1. Thermoelectric materials (**Stokes, Varahramyan** and **Young**), 2. Electrochemical storage materials (**Gabrisch**), 3. Ferroic composites for magnetostrictive and electrostrictive materials (**Malkinski and Varahramyan**) and 4. Nanomaterials for hydrogen storage (**Lvov**).

THERMOELECTRICS

Objective - Our objective is to design and engineer highly efficient thermoelectric materials that can be used in microdevices or to directly replace existing thermoelectric materials. Direct thermal to electrical energy conversion can be accomplished using compact, solid-state thermoelectric devices. The engineering applications of these devices have been limited by the relatively low intrinsic efficiency of the constituent semiconductor materials. This efficiency is directly related to figure of merit, *Z,* for the materials and is given by $Z = S^2\sigma/(\kappa_e + \kappa_p)$ where S is the Seebeck coefficient, σ is the electrical conductivity and κ_e and κ_g, are the electronic and lattice components of the thermal conductivity.[40] High thermoelectric efficiency then requires materials with large Seebeck coefficient and electrical conductivity, but small thermal conductivity. While these properties are strongly coupled in bulk materials, material structures in which at least one dimension is on the nanometer scale dramatically alter the carrier transport properties due the confinement of the carriers inside the material and provide possibilities to increase the figure of merit. [41]

Engineered nanometer-scale materials have been shown to provide an increase in the thermoelectric figure of merit of semiconductor materials.[42] At present, these materials are fabricated using thin-film deposition technology. The challenge is now to use the enhancements provided by nanometer-scale materials on both a larger scale and in a three-dimensional geometry. We believe that to address this challenge, other nanoscale architectures and manufacturing avenues will have to be developed. To this end, we propose to fabricate high-efficiency thermoelectric composites composed of binary assemblies of nanoparticles and conducting polymer/nanoparticle composites. These architectures are designed to take advantage of the intrinsic quantum confinement effects associated with increased Seebeck coefficient as well as increased phonon scattering.

Nanoscale semiconductor structures and/or conducting polymers will be combined to design and fabricate composites. In these nanocomposites, the electron and phonon transport is decoupled, allowing disruption of heat transport by phonons while retaining high electrical conductivity. In addition, quantum confinement of electrons enhances the Seebeck coefficient (thermal-to-electrical energy conversion capability) of the constituent semiconductor. We will also explore binary assemblies of nanoparticles[43] and bulk-like, complex compounds which have intrinsic nanostructure.[44] For proof-of-concept, we will incorporate the materials into MEMS-like device structures to develop small-scale energy conversion modules.[45]

TASKS: Synthesize semiconducting lead telluride and lead sellenide nanoparticles with controlled surface chemistry (**Stokes**); Form the nanoparticle materials into composites (**Stokes**); Measure thermophysical properties of the composites (**Stokes** and **Young**); Synthesize "bulk" materials with intrinsic nanostructure (**Young**); Investigate novel high-temperature oxide materials (**Young**); Incorporate the materials into a prototype microdevice structure demonstrating high efficiency (**Varahramyan**).

ADVANCED BATTERY MATERIALS

Objective - Our objective is to create characterization techniques to study micro-structural details in Li-intercalation compounds on sub-particle size-scale and apply these techniques to the study of new electrode materials.

Rechargeable batteries (e.g. Li-ion) currently suffer from several limitations including the amount of retrievable capacity at a given discharge rate, capacity retention in the charged state, and stability over a high number of charge discharge cycles. While electrochemical characterization of assembled batteries accompanied by x-ray diffraction studies are traditional investigation techniques in battery research, it has become evident that investigations on the sub-particle size scale will advance the understanding of failure in the battery electrode materials. Examples are the role of the interface between heterosite and tryphelite in $LiFePO_4$ or the role and details of cation ordering in layered manganese oxides [46-50]. The proposed research is aimed at understanding the fundamental electrochemical processes in the battery electrodes in order to improve battery performance.

Various intercalation compounds will be synthesized and subjected to charge/discharge cycling and/or chemical delithiation in collaboration with LIFCO, Inc. (see the attached support letter). The micron and nanometer-scale structure of the materials will be characterized with advanced transmission electron microscopy (TEM) techniques (convergent beam electron diffraction) complemented by x-ray diffraction.

TASKS: Choose suitable candidates for the study synthesis methods; develop techniques to assemble and cycle batteries; characterize structural and chemical changes **(Gabrisch)**.

FERROIC COMPOSITES

Objective - The objective is to design ferroic composites consisting of electrostrictive ferroelectrics and magnetostrictive ferromagnetics that both produce small, usable power for micro and nanodevices and provide control of magnetic properties using electric field.

Present magnetoelectronic devices such as magnetoresistive random access memories (MRAMs) and nanomechanical devices use relatively high currents to switch magnetization of memory elements or actuators.[51] High currents result in high energy consumption and heat dissipation which can be significant considering the density of nanoscale magneto-electronic elements (for example, ~Gigabit/in^2 density for information storage). This problem can be solved using electric potential instead of current to switch magnetization of the memory elements, provided a suitable electrical to magnetic conversion material can be created. In addition, micro and nanoscale magnetoelectronics require reliable, sustainable power supplies, particularly for those devices used in remote or in-situ operation. Replacement of traditional power sources (miniature magnetic coils and batteries) by microscopic magnetic-to-electrical power conversion devices would lower the cost, reduce energy consumption and expand the applications of microelectronic devices. Further, the principle of operation (stress induced magnetic anisotropy by piezoelectric component) can be used to tune radio-frequency and microwave responses in the devices for wireless communications. In addition, the magnetoelectric effect can be used to provide galvanic isolation of electric circuits in a similar manner as optoelectronic isolators.

Piezoelectric materials exhibit mutual coupling between their electric and elastic properties and a similar relation exists between magnetic and elastic properties in piezomagnetic materials. Materials which consist of combined piezoelectric and piezomagnetic materials make it possible to convert electric into magnetic energy (or vice versa) through the stresses produced in both materials by the electric or magnetic fields. The application of electric field (or potential) will result in the change of the magnetization of the composite, and application of magnetic field will change the electric properties of the material (magnetoelectric effect). Two different approaches will be used to fabricate granular and multilayered ferroic composites. 1. Thin film materials which consist of alternating layers of magnetostrictive and piezoelectric materials and 2. Composites made from nanoscale piezoelectric and giant magnetostrictive materials.

TASKS: Produce multilayer piezoelectric-magnetorestrictive films using both magnetron sputtering and pulsed laser deposition **(Malkinski)**; Create nanocomposites from piezoelectric-magnetorestrictive nanoparticles (chemically or mechanically derived) **(Malkinski)**; Systematically investigate the magnetic-electrical coupling in the films and composites as a function of nanosctrure and processing parameters **(Malkinski)**; Develop a prototype device structure demonstrating electronic control of magnetic fields and/or conversion of magnetic to electric power. **(Varahramyan)**

NANOMATERIALS FOR HYDROGEN STORAGE

Objective - We aim to develop "smart" nanofilms for the protection of metal hydrides against air and moisture, while permitting release of hydrogen gas through these semi-permeable protective nanofilms. Future generations of these films will have catalytic metal nanoparticles (like TiO_2)-known to enhance the dehydrogenation reaction-embedded within for the purpose of controlled release of catalyst to the hydride particle surface.

The increased need for energy requires that viable alternatives to fossil fuels be explored. Hydrogen may provide an alternative but will require a significant research effort in production, storage and distribution if hydrogen is to become economically competitive with fossil fuels.[52] This research impacts on the hydrogen energy economy through the nanoparticles and molecular assembly procedures to create next-generation hydrogen storage materials.

Metal hydrides are compounds comprised of metals which crystallize with anionic hydrogen in their lattice. There are a vast number of metal hydrides that can be synthesized, but the prevalent scope of interest is in the lighter metal hydrides. Of these light metal hydrides - sodium aluminum hydride, lithium aluminum hydride, lithium hydride, and sodium hydride have high gravimetric storage capacity for hydrogen, but are also reactive in air and moisture-rich environments.

Our nanofilms for encapsulating metal hydrides are formed using layer-by-layer electrostatic self-assembly. Layer-by-layer (LbL) thin films are comprised of polyelectrolyte layers each on the order of 2 nm thickness. The LbL self-assembly technique can be used to deposit conformal, multilayer nanofilms onto planar surfaces and colloidal particles. The working medium for LbL self-assembly is always a polar solvent and has, typically, been water. However, water as a solvent cannot be used to coat the water sensitive metal hydrides. For metal hydrides, pure formamide will be used as a solvent for the LbL self-assembly of nanofilms by alternate adsorption of montmorillonite clay and polycations. In preliminary studies, we have already produced protective nanocoating for $NaAlH_4$ microparticle material.

TASKS: Create protocols for the synthesis of semi-permeable nanofilm coatings for a variety of metal hydrides; Systematically investigate the hydrogen storage/release capability of these nanostructures **(Lvov)**.

d. Broader Impacts

Matthew A. Tarr (Educational Outreach Leader, UNO-AMRI), **Paul Hanson** (UNO-AMRI), **Rebecca Bidwell** (Communities In Schools of New Orleans, Inc.), Collaborating High Schools in New Orleans, **Norma Grace** (Commercial Outreach Leader, Vice Chancellor for Technology and Economic Development, UNO, Coordinator – Center for Innovation)

Educational Outreach Group

Objectives and Background

Objectives of this component are: 1) To provide summer research opportunities in nanoscale science for secondary educators and high school students; 2) To develop academic-year programs to expose students and teachers to nanoscale science and technology; and 3) To provide undergraduate and graduate training in materials science and nanoscale science. Based on programs in this project, we expect to receive sustained funding through the National Science Foundation GK-12 program as well as through center grants such as the NSF MRSEC program.

The United States is facing a critical shortage of qualified workers in science and technology, while demand for skilled workers in nanotechnology is growing rapidly. Furthermore, basic science skills among US students are very weak.[53] Effective development of technology based business in Louisiana requires an investment in human resource development. We include an extensive education outreach program to stimulate science education as well as to attract young students into careers in science and technology. We have a strong history of effective training of high school students and teachers, including conference presentations and research publications[54-58] with high school co-authors. We also have a strong history of providing research opportunities for undergraduate students, and our NSF supported Research Experiences for Undergraduates (REU) program has focused on providing opportunities for students from Historically Black Colleges and Universities (HBCUs). REU participants have been co-authors on numerous presentations at local, regional, or national meetings.[59-77] Program participants are also co-authors on several published, submitted, or in preparation journal articles.[58,59,78-87]

Outreach Plan

The education outreach program will include several components: 1) a summer research and training program for secondary teachers, high school students, and undergraduate students from HBCUs; 2) an intensive pre-matriculation training program for incoming UNO freshman chemistry and physics majors; 3) implementation of available nanoscale science modules at participating secondary schools in New Orleans, including teacher training; 4) a comprehensive pre-college mentoring and training program for high school students in New Orleans; and 5) training of graduate students in materials and nanoscale science.

Summer Research Training. Each summer we will provide research experiences for high school students (12/year), secondary educators (2/year), and undergraduate students from collaborating HBCUs (3/year). These interns will be joined by 4-6 additional teachers and 9-12 additional undergraduates supported through separate programs. High school interns will participate for 7 weeks of research and undergraduates for 9 weeks. Each intern will be assigned to an AMRI research group and a semi-independent research project. Interns will work alongside graduate students and post doctoral fellows. Interns will gain a first hand understanding of cutting edge research and facilities, gain substantial self confidence, and gain access to future opportunities through their research experience and contact with faculty mentors. Secondary educators will gain insight and perspective that are uncommon among teachers; their personal and professional growth will be passed on to the hundreds of students they teach each year. During the summer, weekly meetings will familiarize interns with materials science and nanoscale science and provide training on specific skills (such as using the scientific literature). Interns will also interact with professors during informal sessions designed to build relationships among participants and faculty members. Each intern will prepare and present an end of summer poster reporting the results of their summer research projects.

Pre-Matriculation Training Program. Major barriers for entering freshman students include poor reading skills, writing skills, math skills, and time management/study skills. To overcome these barriers, we will provide an intensive immersion program for entering UNO chemistry and physics majors, including several of our high school research interns. These students will participate in a five week chemistry and physics immersion program designed to improve their chances of success in college. The program will address important weaknesses among entering students through structured programs in an active learning environment. Math and writing skills will be presented in context of nanoscale science and materials science. Important chemistry and physics concepts will also be introduced. Strong emphasis will be placed on developing critical thinking skills and good study skills.

Implementation of Available Nanoscale Science Modules. Summer teacher participants will also attend a graduate level course. This class will provide guidance on how to incorporate scientific inquiry and research concepts into secondary classrooms. These teachers will be expected to incorporate into their classes at least one new teaching module focusing on nanoscale science or materials science.[88-94] Support for such activities will be provided by graduate students and professors during the academic year. This support will include classroom visits as well as periodic workshops. Communities In Schools will involve other teachers through already established contacts and will provide assistance with correlation to grade level expectations established by the state Board of Elementary and Secondary Education.

Comprehensive Pre-College Mentoring and Supportive Guidance Program. High school students who complete the summer research program will be provided ongoing pre-college mentoring and supportive guidance by the staff of Communities In Schools. Regular mentoring will be conducted with individuals and small groups of students attending the same school in order to provide follow-up and guidance related to study skills, college investigation, the college admissions process, and financial aid. Each student in grades 9-11 will participate in 3-4 mentoring sessions per month. Graduating seniors will be offered additional mentoring sessions, as well as family information sessions. Communities In Schools will also complete an individual and family needs assessment for each student so that appropriate referrals can be made to overcome barriers to college admissions and success related to health/human services, educational enhancement, enrichment, and other support services.

Training of Graduate Students in Materials Science and Nanoscale Science. Focused Research Groups 1-3 will each involve graduate students in materials science and nanoscale science research. These graduate students will serve as a base of highly skilled scientists who will be ready to enter the workforce in roles that require advanced training. In addition, each of these graduate students will be integrally involved in our outreach programs by mentoring summer research interns and by working with teachers and students during the academic year.

Partnership with Communities in Schools

We will team with Communities In Schools (CIS) of New Orleans, Inc., a local non-profit affiliated with the Communities In Schools national network. The CIS network specializes in providing resources to help at-risk students across the country learn, stay in school, and prepare for life. This national network is recognized as a leader in dropout prevention. CIS will serve two roles by: 1) coordinating interactions between UNO and several high schools in New Orleans and 2) providing mentoring and supportive guidance for high school students who are potential undergraduate students in science, technology, engineering, and math (STEM) fields.

Coordinating Interactions Between UNO and High Schools. Most high schools in New Orleans lack the appropriate resources to encourage students to pursue careers in STEM fields.

The University of New Orleans is able to provide important assistance in this regard. However, high school teachers and administrators are currently overwhelmed and lack the ability to coordinate such interactions. At the same time, UNO personnel lack the necessary familiarity with the needs of high school students, but are able to provide a number of important resources (access to research opportunities, formal and informal training for teachers, mentoring of students and teachers). Communities In Schools has a substantial history of working with New Orleans high schools and can readily coordinate UNO resources with high school needs. Specific tasks will include: identifying students and teachers for participation in summer programs at UNO, coordinating UNO professors and graduate students to provide classroom assistance (mentoring teachers) and student mentoring (e.g. science fair projects), and coordinating UNO run workshops for teacher training in nanoscale science.

Providing Supportive Guidance for Students. Many high school students in New Orleans do not have the necessary skills to successfully apply to and attend college. For example, students are often unaware of the expected length or content of a college application essay or deadlines for application. Without these basic skills, many otherwise qualified students are at a severe disadvantage and are not likely to succeed in college. Furthermore, most students are unaware of career opportunities in STEM fields. Communities In Schools will provide mentoring and supportive guidance for high school students at six targeted high schools (Edna Karr Secondary School, Capdau Early College High School, New Orleans Math and Science High School, McDonough 35 High School, McMain Secondary School, Warren Easton High School). These schools were chosen because they have a large population of students with reasonable academic skills but a lack of other basic skills needed for college entry. In addition, these schools are currently involved with other CIS programs. The Capdau Early College High School is a charter school that is administered by UNO.

In this project CIS will 1) Provide UNO faculty, staff, and students inroads into Orleans Parish high schools; 2) Schedule and coordinate information session/recruitment events at each of the identified schools; 3) Provide ongoing college/career mentoring for students after their summer research experience; 4) Work with the Office of Financial Aid at UNO to assist students; 5) Provide referrals to health/human services, educational enhancement, enrichment, and other programs; and 6) Coach UNO personnel for outreach exercises at local schools.

The roles of each member of this FRG are: **Tarr** (team leader) will coordinate student/teacher research opportunities, develop/implement curriculum materials and teacher training; **Hanson** will run the 5-week pre-matriculation training program and will assist with academic year workshops for teachers as well as on-site school visits by UNO personnel; **Bidwell** will coordinate all Communities In Schools participation.

Economic Impact

Short term impacts will result from strengthening schools in Katrina impacted neighborhoods. Providing strong primary and secondary academic options will facilitate repopulation of these impacted neighborhoods, stimulating economic redevelopment. Long term economic growth will be developed by building strong links between K-12 educational institutions and nanoscale research teams. A culture of nanoscale literate students will result. These students will fill future jobs in nanotechnology businesses. The availability of trained workers and the academic/research culture will encourage nanotechnology companies to locate in the region.

Commercial Outreach Group

The National Science Foundation awarded a Center for Innovation (CFI) grant to the University of New Orleans in September, 2005. The mission of the CFI is to 1) develop and manage a process to facilitate the transformation of innovation into viable businesses for the creation of wealth for the region, and 2) develop a core of entrepreneurs to sustain the regional economy. In pursuit of its mission the Center will achieve the following objectives:

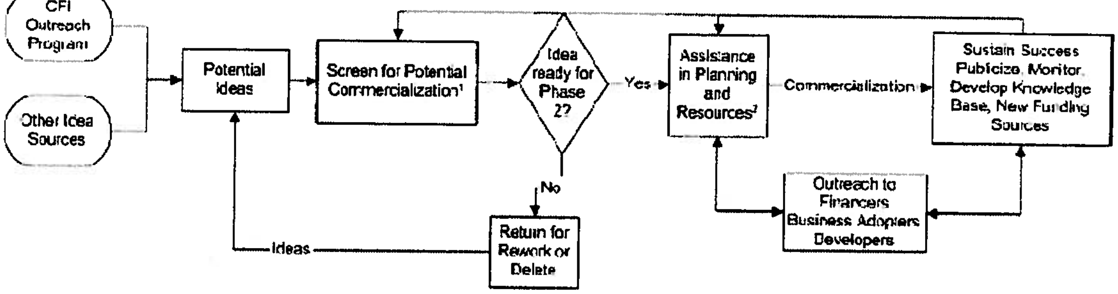
- emphasize industry-based and university-based translational research in the region and the Gulf Coast as a source for potential business concepts;
- focus primarily on developing products and services that include applied materials, nanotechnology, marine technology, and software and information technology; and,
- target projects with the potential to generate a regional impact of $5M within 5 years.

To achieve this mission, CFI will identify innovative technologies using its "Community of Practice" partners:

CFI will work with the inventor through the intellectual property protection process and analyze potential for commercialization. It will use its industry advisory board to assist with screening of commercially viable outcomes. It will then help create the business plan, provide access to capital and assist in the growth of a business or license agreement, whichever best fits and promotes the outcomes for the inventor, institution and organizations.

One of the goals of sustainability is to develop a template for discovering potential ideas from research centers and to transform them into viable products and processes in industry and government organizations. The CFI team has developed a process that will be the initial step in developing a template. The process flowchart is depicted below.

Figure 1
CFI Process Flowchart



1. Screen for Potential Commercialization
Receive, Route, Integrate, Facilitate

2. Assistance in Planning and Resources
Business Planning - Marketing Research
Legal
Funding Sources - Startup Funding
Assistance from State and Local Government

The best indicator of success will be the creation of jobs and new start-up companies. However other important indicators are patents granted, licenses granted, royalties received, start-up loans and investments, and increase in average incomes.

The University of New Orleans Center for Innovation will work with the Center for Advanced Materials to identify potential commercial applications for business growth and development. CFI is currently working with NanoPrism Technologies, Inc., and AMRI spin off established in 2005. **Norma Grace** and the CFI team will engage a specialist in technology development and commercialization to concentrate specifically on the innovative technology coming out of the research of this grant. It would also support intellectual property protection -- attorneys and market research -- appropriate to the inventions.

(2) PROJECT IMPACT

The President's nearly $1 billion budget proposal for nanotechnology R&D in 2005, a doubling over levels in 2001, reflects how fast nanotechnology is growing (http://www.nano.gov/). Since last year, more companies associated with nanotechnology products have been established, such as First Nano, Inc, NanoSys, Inc., Zevex, Inc, Quantum Dot Corp., The Nanotech Company, LLC, NanoPrism Technologies, Inc, *etc*. This trend indicates the growing market for nanotechnology products in the next ten years. Our proposed project targets areas of nanotechnology in which individual Louisiana researchers are already making significant contributions. Collectively, the group of researchers in this proposal will leverage their individual research programs and strengths of their respective institutions to create a state-wide consortium for nanomaterials research and technology development. This consortium will impact the local economy architecture, providing a high technology platform for start-up companies and/or stimulating investments of larger corporations. Specific impacts in four key areas of nanotechnology research and education are listed below.

Biotechnology - The project will impact the biotechnology sector in Louisiana, which has been an area of targeted growth, especially after Katrina. It will spur the application of nanomaterials in clinical procedures. It will bring a revolution of biosensors for detecting bio-agents at shorter times and higher sensitivities. And it will open a new regime for real time imaging of biomolecules in vivo. Fast detection nanosensors for ricin toxin and $sPLA_2$ could provide commercially important alternatives to traditional detection methods. Development of a functional nanowire based biodetection sensor will have direct commercial value for diagnostic purposes and bio-defense applications. Magnetic and luminescent nanoparticles integrated with chemical and biological systems will help to connect the application of nanoscale materials to clinical applications.

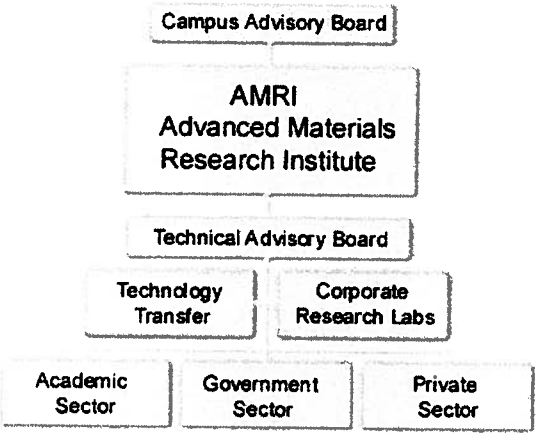
Nanodevices - Advances in the area of nanoscale mechanical device fabrication will also greatly impact nanotechnology. Various device constructs will be useful in electronic, fluidics, medicine, etc. Our team is uniquely positioned to become a leader in this area. Industry will be greatly interested commercializing our technology, routinely licensing the patents generated on our products. This will positively impact our state's economy as well as raise revenue for the associated universities. Also, extended success in this area will likely lead to spin off companies in Louisiana, further impacting the state's economy.

Energy - Louisiana is a national leader in the production of fossil fuels and this industry drives much of our economy. However, to build our economy, we require research programs which investigate affordable, renewable energy conversion technologies and technologies which make more efficient use of available energy. This proposed research is focused on developing the materials which will enable these next-generation technologies. Expected outcomes will be high efficiency thermoelectric materials which would produce electrical energy using the waste heat from a power plant or an automobile engine. Practical, low cost, low power thermoelectric generators which use temperature gradients from the environment will be possible for powering remote sensors or in military applications. Battery research would impact both low power (consumer and military portable electronics and medical devices) and high power applications (back-up power supplies, and automobiles, for example). High efficiency, high power density batteries are required to support renewable energy technologies like solar and wind power conversion by storing energy for use during those times when wind or solar energy is not available. Micropower sources based on novel electro- or magneto-strictive nanostructures could be used in conjunction with microelectromechanical (MEMS) devices to provide power for microelectronic circuits. Finally, novel materials for hydrogen storage will developed enabling economically-feassible hydrogen distribution and storage for pollution-free energy production, safe on-board vehicle storage and use in proton exchange membrane fuel cells, and micro/nano scale fuel cells having energy density exceeding present-day rechargeable batteries.

Science and Technology Workforce - Not just within Louisiana but throughout the United States, there is a critical shortage of workers in emerging high tech fields such as nanoscale science. In order to reverse this trend, it is essential that institutions of higher education interact extensively with primary and secondary education programs in order to attract more students into science and technology fields. Over the past five years, our efforts with high school students, secondary educators, and undergraduates have been extremely successful. We have multiple peer reviewed publications with these participants. Furthermore, we have shown many students how they can succeed in science and technology fields. The current project builds upon and strengthens our previous efforts at levels from secondary education through graduate school. Furthermore, the components of this project will serve as models that can be readily copied by other institutions. Successful implementation of this project will make substantial progress toward the goal of building Louisiana into a state that can educate, employ, and retain highly skilled workers for new and growing economic sectors such as nanotechnology and materials science.

(3) MANAGEMENT PLAN

This project will be managed by the Advanced Materials Research Institute (AMRI) at the University of New Orleans. AMRI was formed to meet the research needs of the University of New Orleans in the area of materials science. An organizational diagram of the components of AMRI is shown below.



The administration of AMRI is structured to involve two advisory boards, the Campus Advisory Board (CAB) and the Technical Advisory Board (TAB). The Director of AMRI reports to the Dean of the College of Sciences (Dr. Joe King) who consults the CAB on matters pertaining to the administration of AMRI (*e.g.*, appointments to the senior staff of AMRI, ratification of nominations for membership on the Technical Advisory Board, *etc.*). Although AMRI has a multi-disciplinary research mission, it is sponsored jointly by the Departments of Chemistry and Physics in the College of Sciences and the College of Engineering at the University of New Orleans and the composition of the Campus Advisory Board reflects this authority. The CAB consists of the following members:

- Dr. Joe M. King, Dean of the College of Sciences and Chairman of the CAB
- Dr. Charles J. O'Connor, Director of AMRI
- Dr. Robert C. Cashner, Vice Chancellor for Research
- Dr. Russ Trahan, Dean, College of Engineering
- Dr. Edwin D. Stevens, Chairman, Department of Chemistry
- Dr. Greg Seab, Chairman, Department of Physics

Industrial and government involvement is crucial to the development of AMRI. A Technical Advisory Board (TAB) oversees the operation of AMRI. The duties of the TAB are to provide expertise and insight as AMRI projects are initially developed and to ensure the value and utility of the research to both the private sector and government agencies. The TAB oversees the development of research initiatives at AMRI, directs the addition and distribution of personnel, conducts a yearly review of the operation and performance of the Institute, and makes recommendations on reallocation of AMRI resources. The TAB consists of the following members:

- Dr. Robert Haushalter, Parallel Synthesis Technologies
- Dr. Gary Bush, Lockheed Martin, Advanced Technology Center
- Dr. John T. Vaughey, Argonne National Laboratory
- Dr. Youren Xu, Intel Corporation, Components Manufacturing Quality & Reliability
- Dr. Dieter Weller, Seagate Recording Media Operations

The overall project management will be melded into AMRI's existing management and review structure as follows. Each year, all P-KSFI teams will hold a comprehensive annual review of its funded programs in conjunction with the Annual AMRI Mardi Gras Review and Symposium. Invited to participate in this review are the members of the TAB and review teams from the funding agencies. In addition to this meeting, there are one day AMRI review meetings for the other three quarters in the year where the teams and investigators will present their research and discuss strategies.

Each Focused Research Group team will hold meetings once a month and all researchers in the consortium are encouraged to attend these meetings even when other FRG's are being presented. This will promote cross-fertilization of ideas and help to further expand the pool of expertise available within these groups. The basic management tasks at this level (FRG) is to facilitate communication, minimize the administrative burden on the faculty and to mentor the junior faculty in writing large, multi-PI grant proposals and effectively handling intellectual property (IP) issues. This will be accomplished using video conferencing facilities and coordinating the quarterly meetings with the lead PI. The AMRI multi-investigator meetings are currently held on each Thursday afternoon with a different multi-investigator group each week.

The research groups of all co-investigators will also hold their group meetings, usually once a week.

(4) PERFORMANCE MEASURES AND OBJECTIVES

The fundamental goal of this P-KSFI proposal is to establish a federally-funded center for advanced materials and nanoscience in Louisiana. To reach that goal, the team must build a significant body of collaborative successes in the fields of materials research for bio-sensing and imaging, nanoscale mechanical devices, energy conversion and storage, and outreach. Our primary milestones and objectives for the AMRI consortium are listed in section *4. Goals and Objectives* (p. iv). In this section we will concentrate on technical milestones and deliverables for the four sections of the proposal.

FRG#1: Technical Milestones:

- Assemble and pattern bio-nanosensor prototypes
- Fabricate biosensors for ricin toxin and $sPLA_2$ detection
- Attach the magnetic nanoparticles and photoluminous nanoparticles on biomolecules and mice for signaling processes and bioimaging in vivo.

FRG#2: Technical Milestones

- Develop schemes based on specific binding pairs of host-guest molecules to direct the assembly of nanocomponents
- Use gel-nanocomponent systems to create new actuators
- Create devices where the mechanical properties are used to control a switch or a valve can be used in switch and valve to control

FRG#3: Technical Milestones

- Create nanocomposite demonstrating enhanced thermal and electrical transport properties.
- Create nanocomposite material which allows electrical control of magnetization.
- Develop prototype, microscale energy conversion devices using novel nanocomposites.

Broader impacts:

Educational Outreach Milestones

- Secondary teachers in this project (funded by this and other programs) will impact at least 600 secondary students per year; grow to at least 3000 per year by project end.
- Obtain NSF funding through the GK-12 mechanism.

Commercial Outreach Milestones

- Finalize the business plan for NanoPrism Technologies, Inc. and establish it as a viable company in the UNO Research and Technology Park small business incubator.
- Find customers and secure licensing agreements for patents that arise from this project.

(5) SUSTAINABILITY

Our P-KSFI program will be sustained by industrial and federal funding. AMRI has already achieved the funding momentum necessary to sustain its research programs. We are now focused on reaching the level of a federally funded major research center. The main agencies that fund such fundamental materials-related research are the National Science Foundation (NSF), the Department of Defense (DOD), the Department of Energy (DOE), and the National Institutes of Health (NIH). Within each of these agencies, there are several interdisciplinary programs we will take advantage of. The AMRI cluster of co-investigators will lead to strong teams for applying for multi-PI (2-5 members) grants from the funding agencies. Recently, both the Division of Chemistry and Division of Materials Research have promoted such efforts. For example, we will apply to the Nanoscale Interdisciplinary Research Team (NIRT) program at NSF. In fact J. Wiley (AMRI) already heads an existing NIRT program at AMRI and proposals will be submitted by the Energy and Biomaterials groups. By the end of year two (summer 2009) we will submit at least one NIRT using researchers from this consortium as the core. Also, we will target the Grant Opportunities for Academic Liaison with Industry (GOALI) program which is a joint industry/university program sponsored by the NSF. We will continue to work with small businesses to obtain SBIR/STTR funding in the near term in order to build a platform with which to apply for larger federal grants, in partnership with industry.

C. Leveraging of Resources:

As part of its cost sharing for this proposal, the University of New Orleans has agreed to the addition of two faculty positions to AMRI to strengthen its P-KSFI proposal. The UNO administration has also agreed to provide $125K for start-up for each position. This $125K will be matched by AMRI's existing grants and contracts for a total start-up package of $250K for each position. The new faculty will join the P-KSFI projects as well as AMRI's other programs. An additional leveraging of this proposal by AMRI is a promise to cover tuition expenses of all graduate students that are funded by this proposal through a rebudgeting of its existing grants and contracts,

Part of AMRI's success has been its educational outreach program. This program leverages the P-KSFI educational outreach component. Each summer, AMRI brings 20-25 high school teachers and students and undergraduates to its outreach programs supported by the Board of Regents and NSF (REU). A majority of AMRI's outreach participants come from under-represented minorities. With the addition of the P-KSFI educational outreach component, we plan to expand this program to a year round effort that includes UNO directed charter schools in the revamped post-Katrina New Orleans public school system.

AMRI is also active in commercial outreach. To maintain commercial viability of its research programs, AMRI has recruited 4 researchers from corporate research labs for membership on its Technical Advisory Board. Also two start-up companies, NanoPrism Technologies, Inc and NSCR Biotechnologies LLC., have grown from research that has been conducted at AMRI with assistance from UNO's Center for Innovation. NanoPrism Technologies focuses on the synthesis of functionalized nanoparticles for various applications. NSCR Biotechnologies develops clinical assays based on the use of bio-functionalized luminescent nanoparticles. The development of these companies will be assisted by this project. NanoPrism Technologies will provide nanoparticles for biomedical research. Advances in luminescent nanomaterials used in studies proposed here will be further developed and commercialized by NSCR Biotechnologies, LLC. The commercial outreach component will be leveraged by the NSF funding for the Center for Innovation.

The ultimate goal of this program is to successfully compete for a federally funded major centers grant. Furthermore, NSF is directing an increasing component of its research effort towards funding of collaborative research programs in the Mathematics and Physical Sciences Directorate, especially in the Divisions of Materials Research (DMR) and Chemistry. AMRI's successes in these programs will be further leveraged by the program proposed here.

AMRI will be starting two projects with DARPA this summer with a total of $4.5M in new funding; the two projects are on Nano-Sensors and Quantum Computing. The Nano-Sensors project has a direct positive overlap with the research in FRG1 and will significantly impact and leverage the progress of this project. In addition, other AMRI grants will bring consultants and seminar speakers to the consortium. There is a minimum of management expense in the budget because the existing AMRI management team is experience in administering large collaborative programs and will oversee the day to day execution of this proposal.

Contract Work Plan

Project Work Plan

"A Center for Advanced Materials and Nanotechnology in AMRI at the University of New Orleans"

LEQSF(2007-12)-ENH-PKSFI-PRS-04

PI: Charles J. O'Connor
University of New Orleans
June 21, 2007

a. Goals and Objectives

The **goals** of this project are to:

1) Enhance the collaborative infrastructure that will allow the participating institutions to successfully compete for major center grants (*e.g.*, NSF MRSEC, NSEC, ERC; DOD MURI; DOE; NIH; *etc*);
2) Build opportunities to translate research success into economic development through patents, licensing, and start-up companies; and
3) Strengthen the secondary educational infrastructure to increase the number of undergraduate and graduate students pursuing science and technology careers.

The **objectives** of the project are to:

1) Develop nanomaterials for application as biosensors and for clinical imaging;
2) Design and fabricate nanoscale mechanical devices for use in fluidics, medicine, communications, data storage, and sensors;
3) Create highly efficient materials for energy conversion (thermoelectric and ferroic composites), advanced batteries, and hydrogen storage;
4) Provide summer research opportunities in nanoscale science for high school students;
5) Develop academic-year programs to expose secondary students and teachers to nanoscale science and technology;
6) Provide undergraduate and graduate training in materials science and nanoscale science;
7) Create opportunities for international recognition in advanced materials;
8) Increase translational research in advanced materials; and
9) Create opportunities for patents, licensing, and potential start-up companies.

b. Deliverables

Deliverables will include annual reports and a final end of project report. Dissemination of results through publications in top scientific journals, and presentations at professional conferences including American Chemical Society, Materials Research Society, and American Physics Society. Grant applications for center grants to Federal agencies (e.g. NSF, DOE, etc.).

c. Performance Measures

The fundamental goal of this P-KSFI proposal is to establish a federally-funded center for advanced materials and nanoscience in Louisiana. To reach that goal, the team must build a significant body of collaborative successes in the fields of materials research for bio-sensing and imaging, nanoscale mechanical devices, energy conversion and storage, and outreach. Project milestones for this project are listed below. Accomplishment of these milestones can be evaluated through documentation in annual reports as well as publications resulting from and acknowledging this project. Specific performance indicators will include: number of federal research proposals submitted and awarded, number of publications, number of presentations at professional conferences, number of patent applications and disclosures, number of high school interns participating in summer research, and number of high school students served during academic year outreach programs.

- Assemble and pattern bio-nanosensor prototypes
- Fabricate biosensors for ricin toxin and $sPLA_2$ detection
- Attach the magnetic nanoparticles and photoluminous nanoparticles on biomolecules and mice for signaling processes and bioimaging in vivo.
- Develop schemes based on specific binding pairs of host-guest molecules to direct the assembly of nanocomponents
- Use gel-nanocomponent systems to create new actuators
- Create devices where the mechanical properties are used to control a switch or a valve can be used in switch and valve to control
- Create nanocomposite demonstrating enhanced thermal and electrical transport properties.
- Create nanocomposite material which allows electrical control of magnetization.
- Develop prototype, microscale energy conversion devices using novel nanocomposites.
- Secondary teachers in this project (funded by this and other programs) will impact at least 600 secondary students per year; grow to at least 3000 per year by project end.
- Obtain NSF funding through the GK-12 mechanism.
- Finalize the business plan for NanoPrism Technologies, Inc. and establish it as a viable company in the UNO Research and Technology Park small business incubator.
- Find customers and secure licensing agreements for patents that arise from this project.

d. Monitoring Plan

The services to be undertaken by the Contractor (University of New Orleans) under this contract shall commence promptly after the execution of the contract. The Board of Regents (Board) and its representatives shall have the right to inspect the progress of the work, as well as financial records pertaining to the work. Upon expiration of the contract term, the Board reserves the right of future inspection.

These reports will be reviewed, at a minimum, by the Commissioner of Higher Education, acting for the Board. As deemed appropriate, the Board will engage the services of out-of-state consultants to evaluate these reports and other pertinent documentation and to conduct on-site visits. The consultants' assessment will guide the Board in determining the effectiveness of the Contractor in fulfilling objectives of the project.

In addition to written reports, a comprehensive mid-course evaluation will be conducted by external consultants, selected by and acting under the auspices of the Board, during the third project year. Continued funding beyond the third project year will depend upon the external review's evaluation of the quality and success of project activities and the project team's ability to meet benchmarks identified in Appendix B of this contract and/or adapt project activities to unforeseen circumstances.

d. Utility of the Final Product

This project will build a significant body of collaborative successes in the fields of materials research for bio-sensing and imaging, nanoscale mechanical devices, energy conversion and storage, and educational and commercial outreach. The resulting successes will lead to development of a nationally competitive center in materials science. Such a center will increase Louisiana's stature in materials science and nanotechnology and will eventually lead to increased commercialization and increased economic prosperity within the state. The project will build intellectual property, scientific expertise, human resources, and new small businesses.

Time Line

Time Frame	Activity or Milestone
June 2007	Project start; subcontracts initiated
June – July 2007	Design and planning of academic year high school outreach program
June '07 – May '08	The 3 FRG's will initiate research activities.
Aug '07 – May '08	Implement academic year high school outreach program
June '08 – July '08	Summer research internships for high school students
June '08 – May '09	Initial dissemination of research results from FRG's; pursuit of patents when appropriate
Aug '08 – May '09	Academic year high school outreach program
June '09 – July '09	Summer research internships for high school students
June '09 – May '10	Further dissemination of research results from FRG's and pursuit of patents
Aug '09 – May '10	Academic year high school outreach program
June '10 – July '10	Summer research internships for high school students
June '10 – May '11	Develop and execute strategy, including determining focus (foci) and teaming, for federal center grant
Aug '10 – May '11	Academic year high school outreach program
June '11 – July '11	Summer research internships for high school students
June '11 – May '12	Pursue Federal research center grant(s)
Aug '11 – May '12	Academic year high school outreach program
June '12 – July '12	Summer research internships for high school students

Annual Report for Year 3 (ending 6/30/2010)

A Center for Advanced Materials and Nanotechnology in AMRI at the University of New Orleans

Louisiana Board of Regents Contract
LEQSF(2007-12)-ENH-PKSFI-PRS-04

Annual Progress Report - 2010

June 30, 2010

SUMMARY

The purpose of this report is to provide an annual progress report for the LA Board of Regents funded project entitled: "A Center for Advanced Materials and Nanotechnology in AMRI at the University of New Orleans" through LA Board of Regents Contract LEQSF(2007-12)-ENH-PKSFI-PRS-04 during the third year of the project from July 1, 2009, through June 30, 2010. Included are progress reports from the three Focus Research Groups (FRGs) and the Broader Impacts group which comprise the organization of the overall project, plus a progress report on the Clean Room Project for which received ESIP funds for development of a Nanodevice Processing Laboratory to support ongoing research projects in nanotechnology at UNO.

The third year of this project was very productive and has been successfully completed. A research consortium organization for this project continues in place and includes as participants the University of New Orleans and the following five partner institutions: Louisiana State University, Tulane University, Louisiana Tech University, Children's Hospital, and Communities in Schools of New Orleans, Inc. The subcontracts from the University of New Orleans to the five collaborating partner institutions continue in place and the work at these institutions is progressing well. The overall effort of the project is organized into three FRGs based on technical areas and one Broader Impacts group, which provides community outreach support for the project. These groups are: FRG-1: Nanomaterials for Biological Sensing and Imaging; FRG-2: Nanoscale Mechanical Devices; FRG-3: Nanomaterials for Energy Conversion and Storage; and the Broader Impacts (Educational and Commercial Outreach) group. All research activities within each group are progressing well.

The overall project management for this program is melded into AMRI's existing management and review structure as follows. Each year, all P-KSFI teams hold a comprehensive annual review in conjunction with the Annual AMRI Mardi Gras Review and Symposium. Invited to participate in this review are the members of the AMRI Technical Advisory Board (TAB) and review teams from the funding agencies. In addition to this meeting, there are one-day AMRI review meetings for the other three quarters in the year where the teams and investigators present their research and discuss strategies.

Once a month one of the Focused Research Groups (FRGs) in this program holds a meeting and all researchers in the consortium are encouraged to attend these meetings so that all are aware of what each group is doing. This promotes cross-fertilization of ideas and helps to further expand the pool of expertise available within these groups. The basic management tasks at this level (FRG) is to facilitate communication, minimize the administrative burden on the faculty and to mentor the junior faculty in writing large, multi-PI grant proposals and effectively handling intellectual property (IP) issues. This is accomplished using video conferencing facilities and coordinating the quarterly meetings with the lead PI. The AMRI multi-investigator meetings are currently held on each Thursday afternoon with a different multi-investigator group presenting their work each week. The research groups of all co-investigators also hold their own group meetings, usually once a week.

The PKSFI researchers participate in a monthly meeting where research progress, issues and potential collaborations are discussed. The responsibility for the meeting rotates between the individual Focused Research Groups (FRGs) and the Broader Impacts group. A researcher (co-PI, post-doc or student) typically gives a 20-40 min presentation followed by discussion. All AMRI researchers are encouraged to attend the meetings including those not part of the PKSFI program. Table 1 below lists the meetings held in year 3 (2009-2010).

Table 1. PKSFI Monthly UNO group Meetings for 2009-2010.

DATE	GROUP	SPEAKER	TOPIC
June 25, 2009	FRG 3	K. Stokes	Progress in Nanophase Bismuth Telluride
August 27, 2009	FRG 2	L. Spinu/V.J. John	Novel Fe-Carbon Composites with Applications to Environmental Remediation, Bioseparation and Magnetic Materials
September 24, 2009	Broader Impacts	M. Tarr	Outreach Programs in Development
October 22, 2009	FRG 3	L. Malkinski	Bulk Multiferroic Composites and New approaches to Voltage-Controlled Magnetism
January 28, 2010	FRG 1	S.Rai	Synthesis and Characterization of PC/PMMA Blend Nanocomposite
February 25, 2010	FRG 2	J. Wiley	Recent Results in Polymer Nanowires
March 25, 2010	FRG 3	N. Henderson	Chemical Synthesis of Ag and Ag_2Te Nanoparticles for Thermoelectric Nanocomposites
April 22, 2010	FRG 1	H.Qu	Synthesis of Fe3O4 nanoparticles with different surface functionality
May 27, 2010	Broader Impacts	M. Tarr/K. Stokes	A First-Hand Look at the Gulf of Mexico Oil Spill
June 24, 2010	FRG 2	J. Wiley	Curls and Swirls in Polymer Wires

Report for LEQSF(2010-06)-ENH-PKSFI-PRS-04

Weilie Zhou

(PKSFI FRG 1, 2009-2010)

FRG-1: Nanomaterials for Biological Sensing and Imaging

UNO-AMRI

1. Personnel: personnel involves with this project

- **Weilie Zhou**- co-Leader of FRG 1. He is mainly responsible for overall management for biosensor part and coordination of AMRI tasks with other partners
- **Kun Yao**-Postdoctoral Research Associate. He is in charge of nanowire FET design, fabrication, and detection of antigen fabricated from Children Hospital of LSUHSC.
- **Hui Ma**-Ph.D student. She is fabricating magnetic nanocarriers for drug delivery and meanwhile she is in charge of modifying the nanowire surface for bio-detection.

2. Activities and Findings:

I. Nanowire FET fabrication for biosensor application

We have shown the In_2O_3 nanowire field-effect transistors (FET) by bottom-up method in the last report. We also worked on Si nanowire FET by top-down method this year, because it is more compatible with modern semiconductor manufacturing techniques and potential for large scale integration. Furthermore, we can precisely design the position of the nanowire without imperfect alignment issue which most happens in bottom-up method.

Figure 1 illustrates the process of top-down approach to fabricate Si nanowire, summarized as follows: a) Starting with silicon-on-insulator (SOI) wafer that consists of a 380nm buried oxide layer and a 100~280 nm silicon layer on insulator; b) Cr mask fabrication

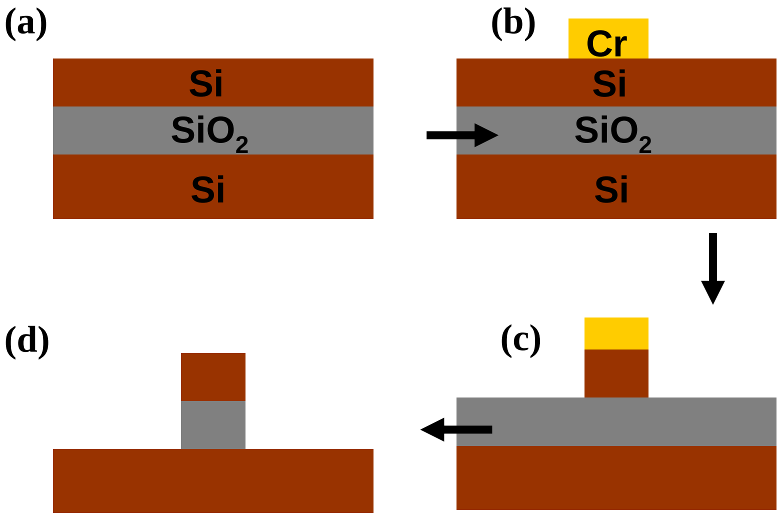


Fig. 1. Schematic diagram of Si nanowire device fabrication process through top-down method.

by e-beam patterning, Cr metal deposition and liftoff process; c) Silicon etching by a reactive ion etching (RIE) system; d) Cr mask remove by Cr etching solution.

Figure 2a shows SEM image of a Si nanowire between two predefined electrodes and Figure 2b shows the magnified SEM image from a tilt view. The roughness of the Si surface comes from the etching processes. However, we found obvious current leakage from test between Si nanowire and the bottom Si layer, which might result from the residues during RIE etching process and definitely degraded the performance of Si nanowire FET.

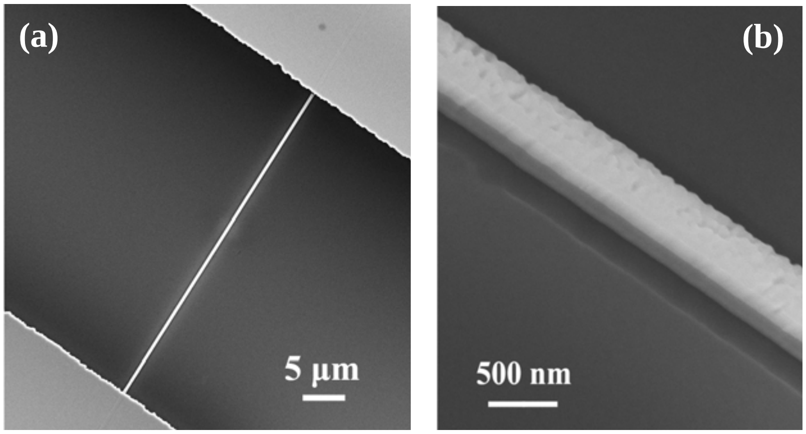


Fig. 2 (a) SEM image of a Si nanowire between electrodes. (b) Magnified SEM image from a tilt view.

Jointly with researchers at CAMD initial efforts optimizing the etching procedures have been started. If the etching time is not enough, the Si layer would etch incompletely. In contrast the insulator layer (SiO_2) may remove partially, worsening the dielectric properties of nanowire devices. Initial etching conditions were using an ICP power of 600 W, an Rf power of 15W, and a pressure of 20mtorr with CF_4 as etch gas. The results are shown in Figs. 3 clearly stating that more process optimization is required to achieve smooth sidewalls of the channel/wire structures.

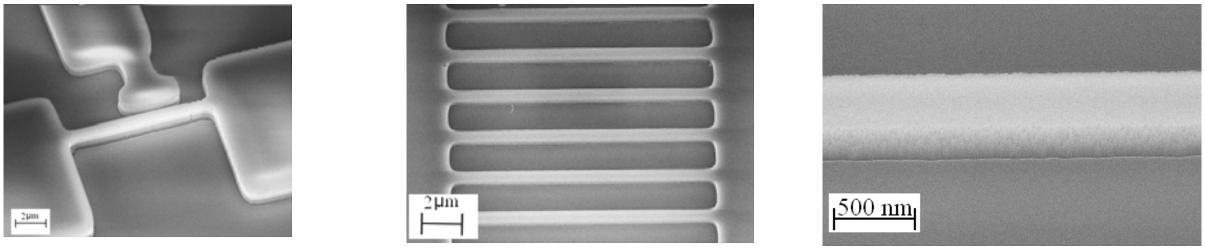


Fig. 3: Examples of etched nanowires and channels, the Cr layer was nearly etched away allowing the gas to attack the covered silicon layer and also partly the SiO_2 layer.

Further improvement in the etching process is illustrated in Figures 4 showing different surface conditions after DRIE etching between the photoresist (PR) etch mask and an optimized Cr mask on Au/Cr/SOI wafer. In Fig 4, left even though a very thick PR (~1.5μm) etch mask was used the surface showed surface charging on SEM picture indicating oxidation and potentially influencing the Si NW characteristics. Fig. 4, right shows a much higher etch selectivity for the Cr mask compared to the PR mask. The selectivity was > 80:1 of Si: Cr.

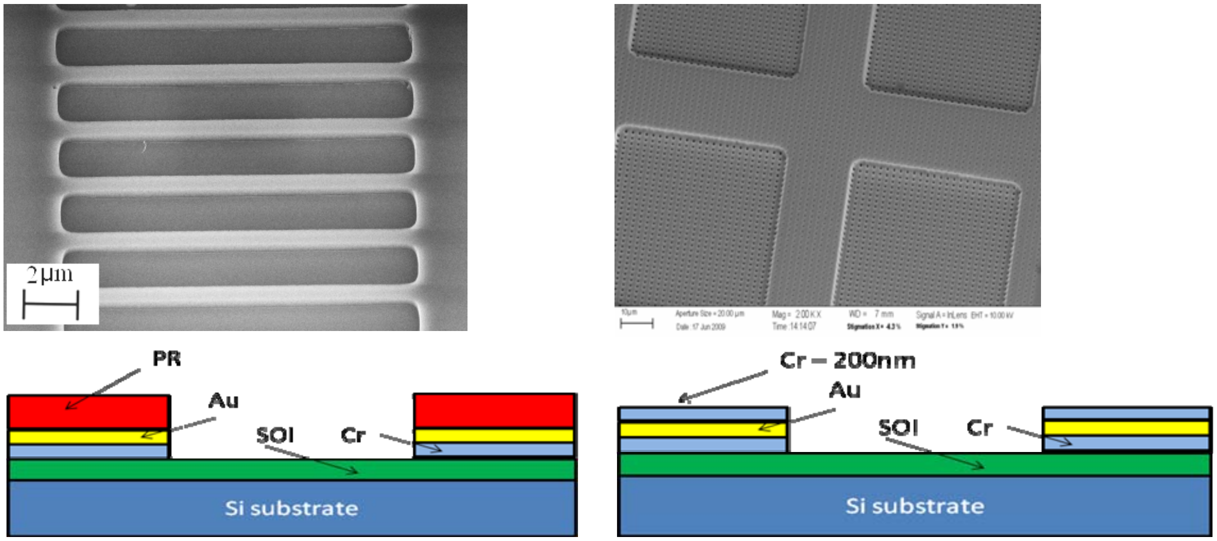


Figure 4: Surface condition difference after DRIE between the photoresist mask (left) and the Cr mask (right) on Au/Cr/SOI wafer. The schematic illustrates the respective etch mask configuration.

Another issue associated with the etching process is the non-uniformity of DRIE etching due to different feature-scales on a typical etch sample ranging from millimeters to nanometers (Fig.5).

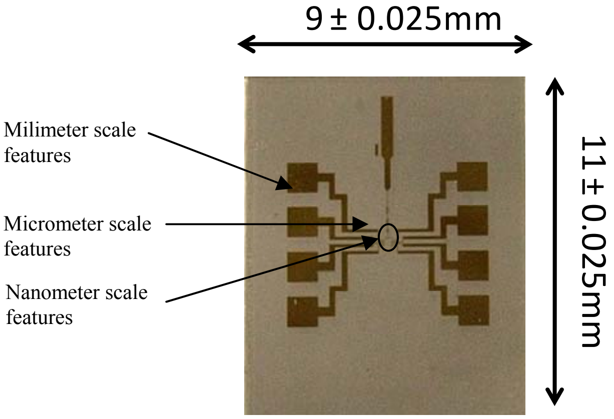


Fig. 5: Typical electrodes patterns

As a preliminary result optimum process results has been achieved using alternative process recipes of two different rf powers of 15W and 50W, respectively. The other etching conditions are ICP power of 400 W, substrate temperature of 35 °C and pressure of 20 mtorr with etch-gas CF_4 of 30 sccm. Pictures in Fig. 6 show the etching uniformity controlling by alternating rf power 15W to 50W for 1 minute respectively. Total etching time was 6 minutes.

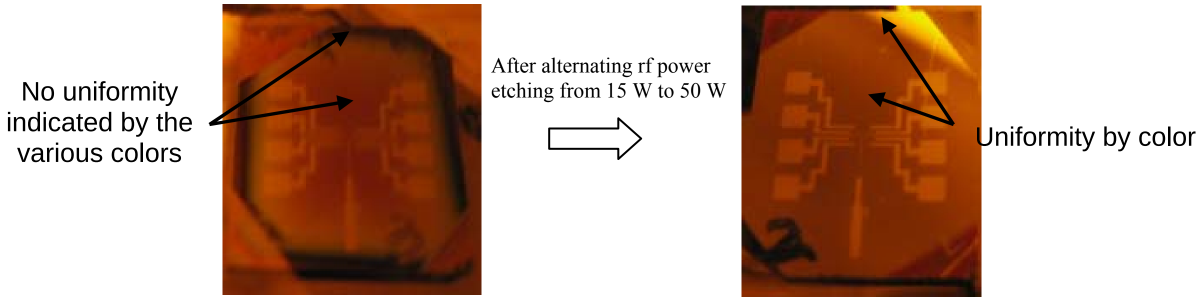


Fig. 6 DRIE etching SOI samples

In future work, we will further address the process related issues and optimize the etching procedure.

Ⅱ. Surface modification engineering

The simple concept and mechanism of nanowire FET based biosensor is shown in Figure 7, where the current flowing through the nanowire channel (orange part), as the sensing signal, can be modulated by the electric field derived from the attached molecules (pink part). For bonding the target bio-molecules to the nanowire, medium molecules (blue part) are usually needed, consisting of one kind of molecule or several kinds of molecules connecting one by one. Such binding process should also be reversible by buffer solutions [1].

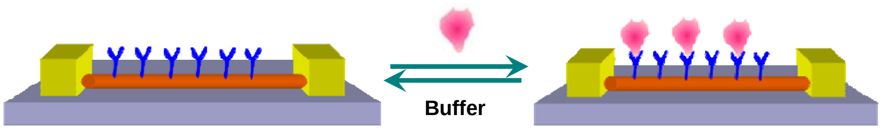


Fig. 7 Schematic illustration of a nanowire FET configured as biosensor with medium receptors.

Figure 8 shows an example structure of the medium molecules (blue part in Fig 3) with backbone, variable portion for binding to bio-molecules and engineered tag for binding to nanowire [2]. So far we consider several candidates for the engineered tag such as lysine, histidine, cysteine.

The surface modification engineering work is based on In_2O_3 nanowire FET which we have studied for a long time. In our design, 6-Phosphonohexanoic acid will binding on In_2O_3 nanowire surface by stirring in aqueous solution, followed by attaching medium molecules (mostly lysine tagged antibody). To ensure the series of binding, we need to figure out some methods to monitor them step by step. For the first step to verify the binding of 6-Phosphonohexanoic acid, 4-aminobenzoic acid (PABA) were linked to the tip of 6-Phosphonohexanoic acid under catalysis (EDC) because PABA can be detected by UV absorbance, which is shown in Figure 9a. Figure 9b demonstrates the UV absorbance of contrastive samples, where both the position and intensity of the peak from PABA attached nanowire matches PABA solution very well and proves the successful binding.

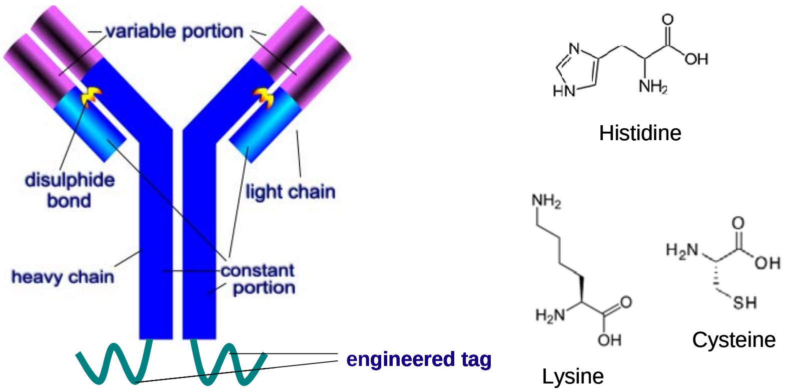


Fig. 8. Example structure of the medium molecules.

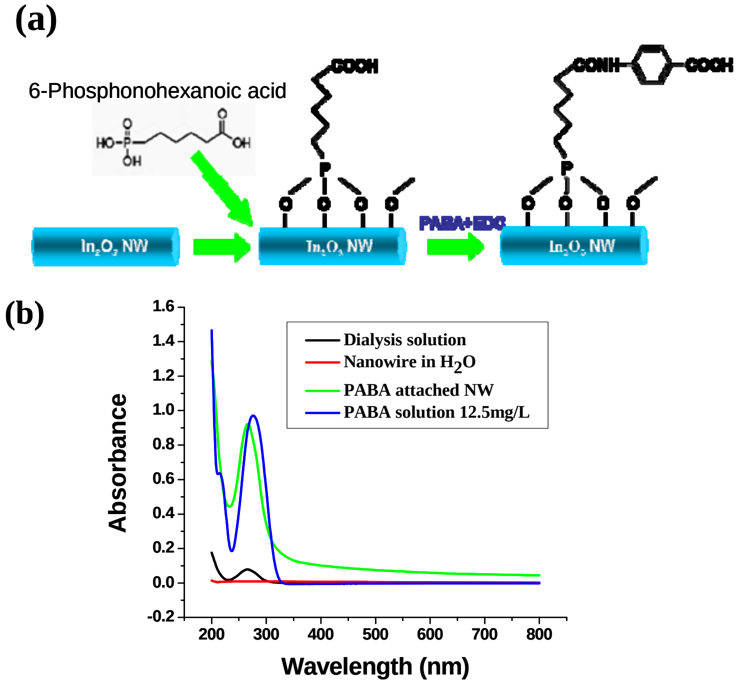


Fig. 9 (a) Schematic illustration of In_2O_3 nanowire attached with 6-Phosphonohexanoic acid and then PABA. (b) UV absorbance of contrastive samples showing the successful binding.

Reference

[1] Patolsky, F.; Zheng, G.; Lieber, C. M. *Nanomedicine* **2006**, *1*, 51

[2]http://upload.wikimedia.org/wikipedia/commons/thumb/f/f6/Antibody_svg.svg/339px-Antibody_svg.svg. png

Publication

1. Kun Yao, Daniela Caruntu, Zhongming Zeng, Jiajun Chen, Charles J. O'Connor, Weilie Zhou, **J. Phys. Chem. C** 113, 14812, 2009, "Ppb level H_2S Detection at Room Temperature Based on Self-Assembled In_2O_3 Nanoparticles".
2. Kun Yao, Daniela Caruntu, Baobao Cao, Charles J. O'Connor, Weilie Zhou, accepted by **IEEE Trans. Nanotechnol**, 2010, "Investigation of Gas Sensing Performance of SnO_2 Nanoparticles with Different Morphologies".
3. Daniela Caruntu, Kun Yao, Zengxing Zhang, Tabitha Austin, Weilie Zhou, Charles J. O'Connor, **J. Phys. Chem. C** 114, 4875, 2010, "One-Step Synthesis of Nearly Monodisperse, Variable-Shaped In_2O_3 Nanocrystals in Long Chain Alcohol Solutions".

Presentation

1. Kun Yao, Daniela Caruntu, Charles J. O'Connor, Weilie Zhou, "Ppb Level Gas Detection at Room Temperature Based on Self-Assembled Indium Oxide Nanoparticles", **2009 Nanoelectronic Devices for Defense & Security (NANO-DDS) Conference,** Ft. Lauderdale, Florida, USA, Sept. 28~ Oct. 2. (Oral Presentation)
2. Hui Ma, Zhongming Zeng, Yoon Young Jin, Jost S. Goettert, Seth Pincus, and Weilie Zhou, "Semiconductor Nanowire Transistor for Biosensor Detection", **2009 Nanoelectronic Devices for Defense & Security (NANO-DDS) Conference,** Ft. Lauderdale, Florida, USA, Sept. 28~ Oct. 2. (Poster Presentation)
3. Kun Yao, Zhijie Li, and Weilie Zhou, "Synthesis and sensing investigation of new coordination compounds nanowires", **The 3rd International Conference on One-dimensional Nanomaterials**, Atlanta, Georgia, USA, December 7-9, 2009. (Poster Presentation)
4. Hui Ma, Zhongming Zeng, Yoon Young Jin, Jost S. Goettert, Seth Pincus, and Weilie Zhou, "Surface modification of silicon nanowire array for selective biosensor detection", **The 3rd International Conference on One-dimensional Nanomaterials**, Atlanta, Georgia, USA, December 7-9, 2009. (Poster Presentation)
5. Kun Yao, Daniela Caruntu, Zhongming Zeng, Jiajun Chen, Baobao Cao, Charles J. O'Connor, and Weilie Zhou, "Parts per Billion-Level Gas Detection at Room Temperature Based on Self-Assembled Nanoparticles", **Annual AMRI Mardi Gras Review and Symposium**, New Orleans, Louisiana, USA, February 11-12, 2010. (Poster Presentation)
6. Hui Ma, Zhongming Zeng, Yoon Young Jin, Jost S. Goettert, Seth Pincus, and Weilie Zhou, "In_2O_3 Nanowire Based Field-Effect Transistor for Ricin Detection", **Annual AMRI Mardi Gras Review and Symposium**, New Orleans, Louisiana, USA, February 11-12, 2010. (Poster Presentation)

LSU-CAMD

1. Personnel:

Senior staff (entire time)

- Jost Goettert
- Yoonyoung Jin

Student support (entire time)

- Kyung-Nam Kang (thin-film deposition, Si etching, optical lithography)

Part time on this project

- Proyag Datta (until 10/2010)
- Niklas Frische (until 9/2010)
- Sital Tiwari (part time, molding support since 10/2010)
- Jeonghwan Kim (part time, microfluidic, since 10/2010)

Summary

The efforts in the past year were focusing on three areas. Two areas were related to further develop the microfluidic stack and expand its potential while the other effort was a close collaboration with AMRI researchers to develop top-down nanowire sensor modules.

Fluidic stack solution for cell sorting application

This effort was aimed to bring together all previous efforts and build a complete module that controls a fluidic flow and detects cells passing across the electrode area. The idea for cell sorting is based on the fact that a cell can be represented by resistivity and capacity and that electrodes embedded in a fluidic channel experience a change of impedence when a cell is passing by. This impedence change generates an electrical signal characteristic for the particular cell (for example size) and can be used to trigger a fluidic flow manipulation allowing to selectively extracting the cell. Fig. 1 summarizes the fundamental idea and illustrates that sensing with high frequencies in the kHz to MHz range allows using different cell properties for selection while Fig. 2 presents the basic idea of how the cell sorting in a continuous flow is realized.

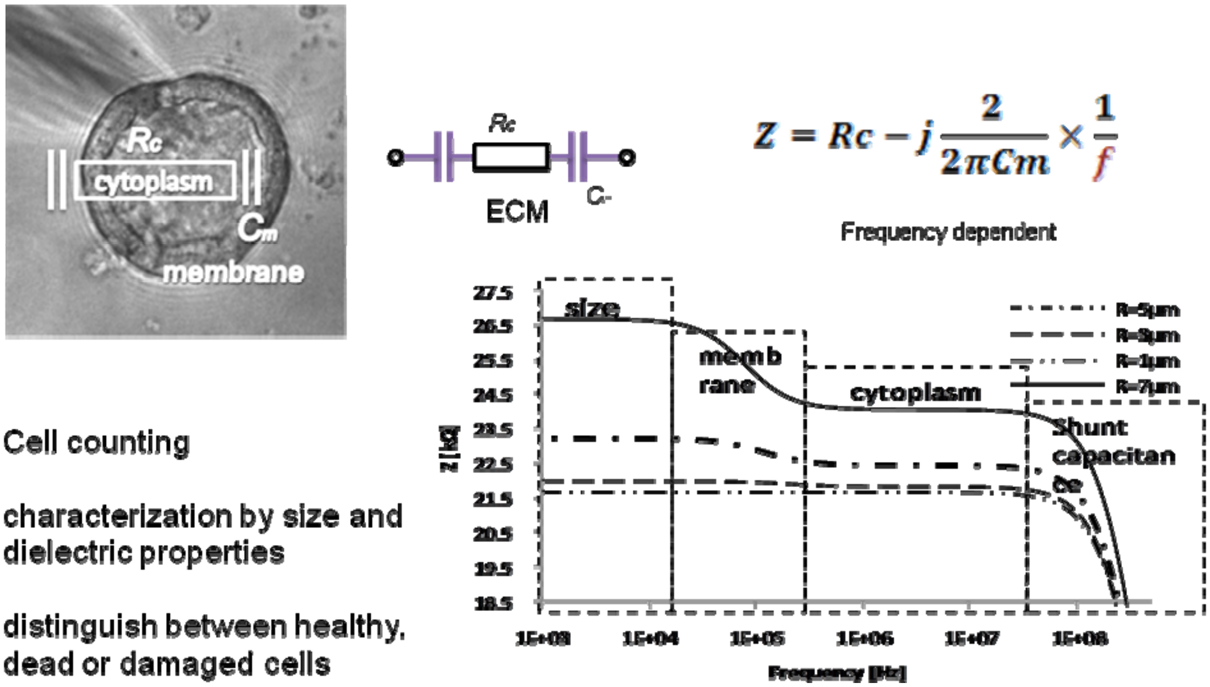


Fig. 1: Electrical representation of a cell and calculated impedence change for different frequencies representing different cell characteristics suitable for cell selection.

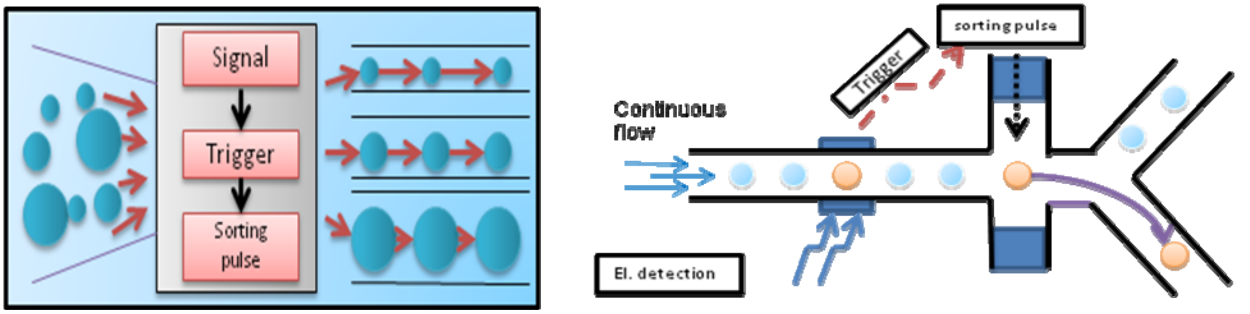


Fig. 2: Representation of the basic sorting concept – a continuous of cells with different size/properties is passing the electrode setup and generates a trigger pulse that will be used to sort out the cells with pre-defined characteristics.

The experimental setup used in this experiment is illustrated in Fig. 3. The fluidic stack was assembled, connected to the electrical and fluid control units, and placed under an optical microscope for in-situ inspection allowing correlating the electrical signal with a visual impression. While the stack is truly a MEMS size device all peripheral equipment like syringe pumps, electrical signal generator, and data acquisition unit have not been miniaturized at this point.

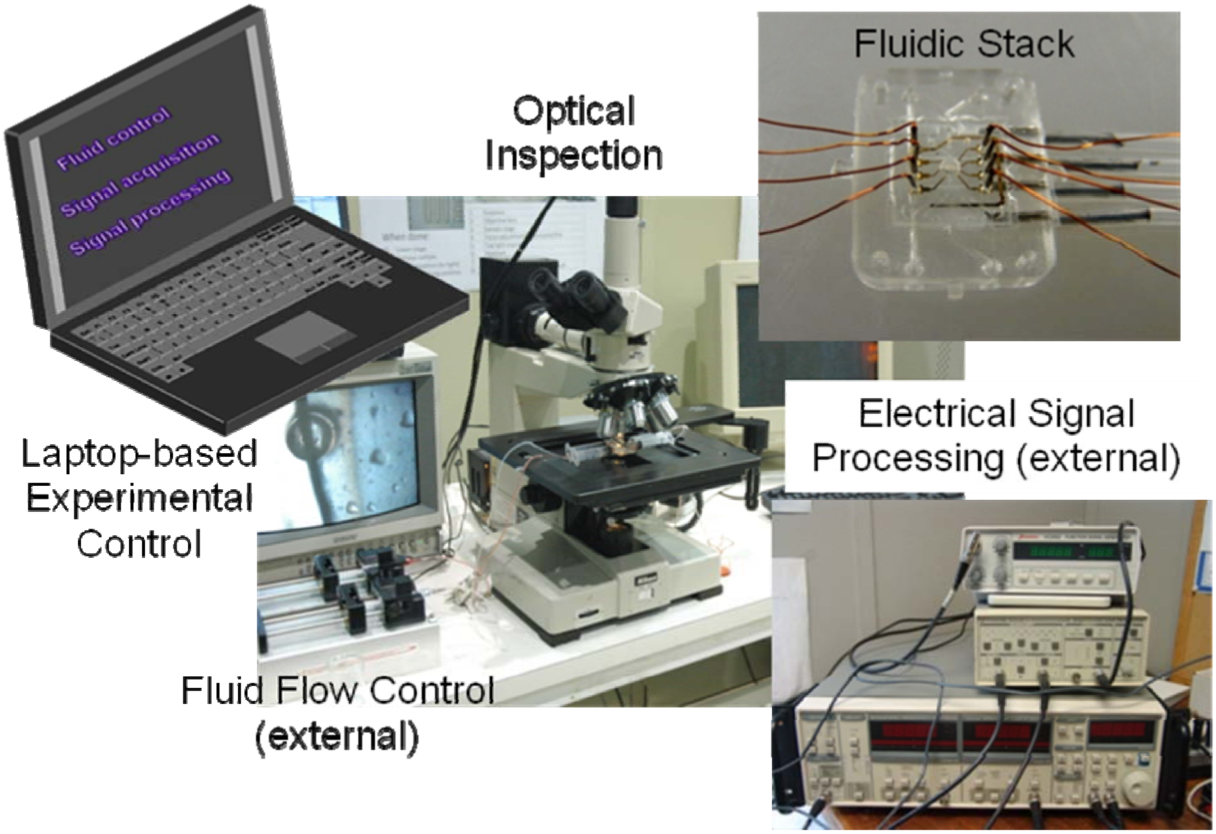


Fig. 3: Experimental setup for initial cell sorting experiments.

The fluidic stack consists of different functional modules described in last year's reports. One important fluidic module is a hydrodynamic focusing module which allows focusing and manipulating the sample carrying liquid (see Fig. 4). This prevents agglomeration of cells by sticking to the channel sidewalls and ultimately clogging it (see Fig. 5).

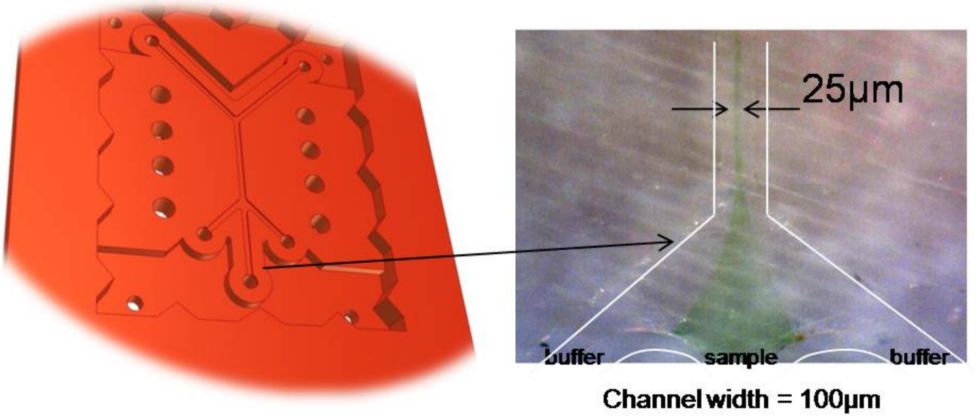


Fig. 4: Design of the hydrodynamic focusing module (left) and successful focusing the sample stream (made visible by green food color) to about 25µm width while flowing through a ~100µm wide channel (right).

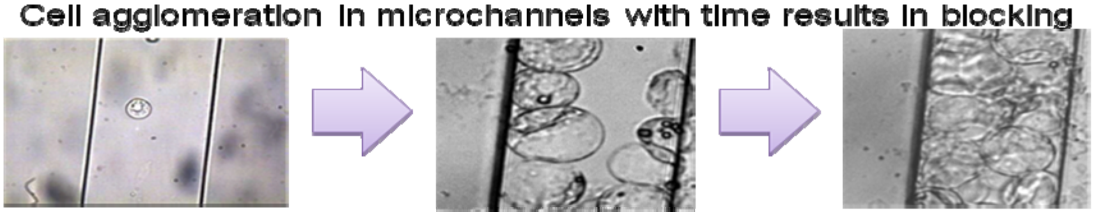


Fig. 5: Example of channel clogging over time when running typical cell samples through the ~~100µm wide channel.

A test run using polystyrene microspheres of different sizes was conducted illustrating the successful generation of characteristic electrical signals for spheres of different sizes (see Fig. 6).

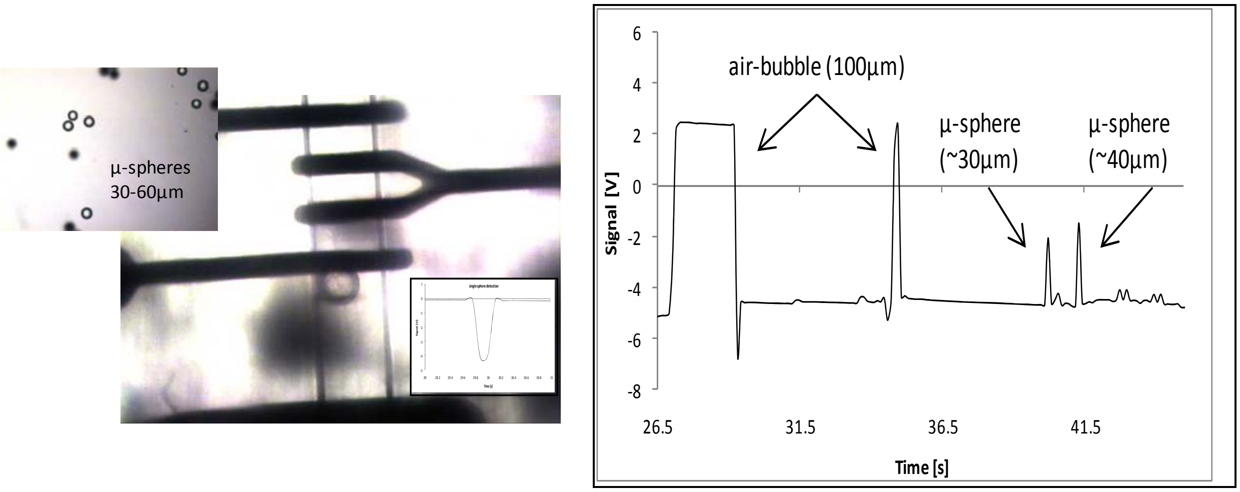


Fig. 6: The picture to the left shows the electrode arrangement inside a fluidic channel with a sphere of ~60µm width passing by and measured signals generated by spheres of different size (right). A problem still to be addressed are air bubbles that cover the entire channel width and cause a maximum signal of about 7V.

Achieving an electrical signal using laboratory-size electronic and fluidic control equipment demonstrates that in principle all key functions of the stack are working and allow detection of electrical signals generated within the microfluidic stack. Research described in more detail in the thesis from Niklas Frische (N. Frische, “Microfluidic impedance spectroscopy module for label-free particle sensing and counting, Bachelor Thesis Fachhochschule Gelsenkirchen, June 2009) shows, however that much more efforts need to be invested in the development of miniaturized, customized, printed-circuit board size electronic solutions before the entire sensor can be packaged into a small, handheld instrument. In the interest of focusing our efforts on integrating nanowire and biological sensing into the stack we shifted our efforts away from an overall small sensor device.

Development of a micropump module to the fluidic stack

In past efforts CAMD researchers jointly with partners at AMRI/UNO have optimized the design and fabrication of customized fluidic stacks. However, the current solution is far from perfect due to relatively big peripheral equipment such as syringe pumps which do not allow good local control of fluid flow conditions because of large dead volumes. Size is also an obstacle for realization of fully miniaturized micro-total analysis system (µTASs) and lab-on-a-chip (LOCs) devices, and we have therefore started to design a pumping module compatible with the fluidic stack - the multi-fluidic-speed-modulating micropump (MSM-micropump). Fig. 7 shows the concept of adding a pump module to the fluidic stack assembly.

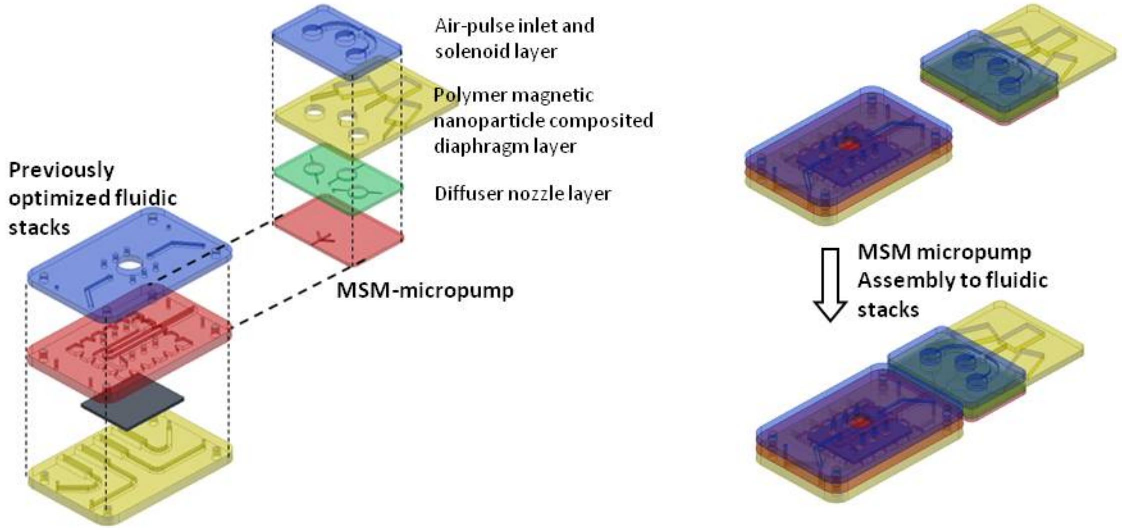


Fig. 7: left: Microfludic biosensor chip and MSM-micropump illustrated layer-by-layer, right: assembled MSM-micropump platform mounted to the microfluidic biosensor stack.

The MSM-micropump is a membrane pump. The basic components of this pump illustrated in Fig. 8 are diaphragms, drivers or actuators, and diffuser/nozzle chamber. As described in more detail in our quarterly reports the multi-fluidic-speed-modulating micropump (MSM-micropump) is driven by one external source (oscillating compressed air) and offers local, electrical control of the fluid flow using an embedded solenoid and magnetic force exerted onto the diaphragm. The diaphragm is made from a polymer filled with magnetic nanoparticles which can be preloaded using an external magnetic field generated by a solenoid operating against a certain external air pressure (pulsed) applied via the hole of the air-pulse inlet layer. During micropump operation, the air pressure acts on the diaphragm to decrease and flatten periodically the chamber volume pushing fluid out of the chamber or drawing it into it. Flow control is realized via the valve-less nozzle and diffuser structures which are connected to the inlet and outlet of the chamber to rectify the flow. The flow rate can be controlled by solenoid magnetic force acting upon the magnetic nanoparticles filled polymer diaphragm.

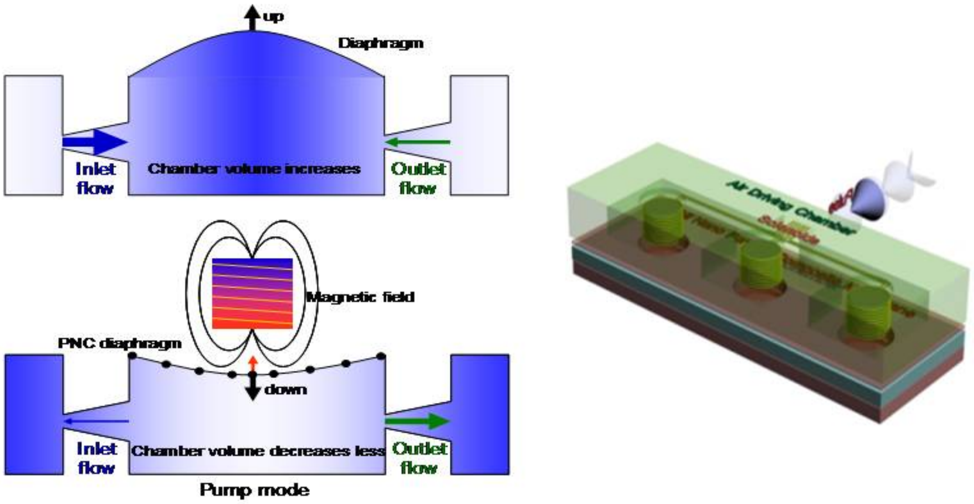


Fig. 8: Concept of operation of the MSM-micropump, left: preloading of diaphragm using an external magnetic field exerting a force onto the magnetic nanoparticles embedded in the membrane; right: assembled pump module with three pumps to regulate flow in a hydrodynamic focusing test structure.

Simulation helped with better understanding the relationship of design parameters and pump performance. In our simulation the diaphragm was actuated assuming a certain external force and calculating the correlated displacement. In addition, the magnetic force between solenoid and nanoparticles filled polymer diaphragm was calculated for a range of characteristic displacements (see Fig. 9).

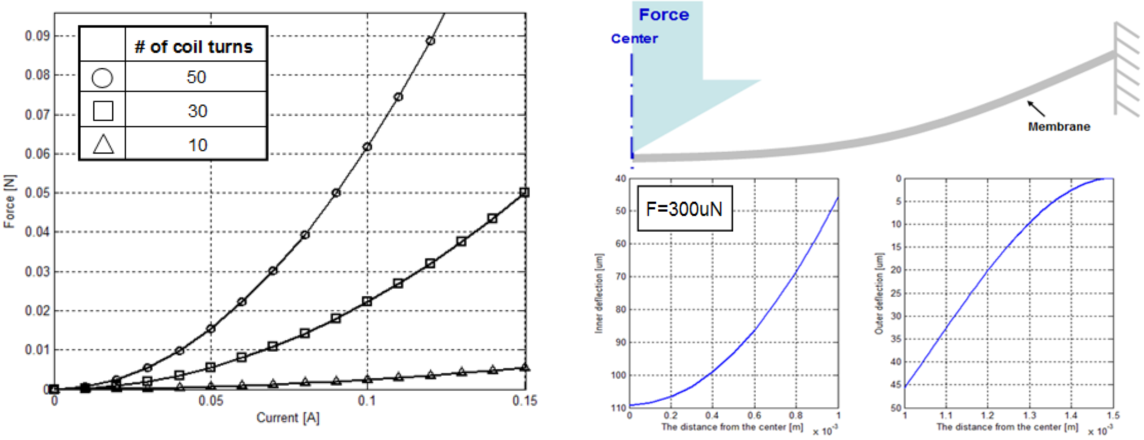


Fig. 9: Solenoids magnetic force by specifications of current, sizes, and number of turns; and a Nano particle composited diaphragm displacement by the driving force.

Given these numbers simulation of the flow rate is calculated around 10μ/min when the solenoids are turned off and much less for preloaded diaphragms.

The diaphragm was made from PDMS loaded with Ni-nanoparticles. Diaphragms were formed by mixing the particles into the liquid PDMS and spin-coating uniform layers of the composite material onto glass or polymer substrates preconditioned with a plasma treatment (100mW RF, Oxygen, 1 min) for improved bonding. Fig. 10 shows the diaphragm thickness as a function of spin speed for diaphragms with different Ni nanoparticles content. The optical micrographs show that the particles are uniformly mixed into the diaphragm ensuring a predictable operation.

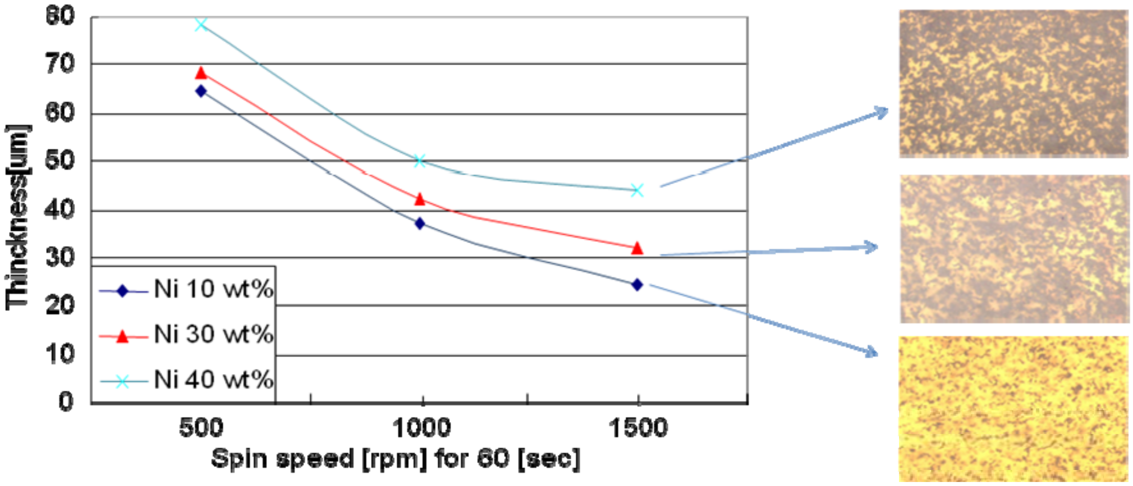


Fig. 10: PDMS-Ni diaphragm thickness as a function of spinning speed for three samples of different Ni particle weights and optical micrographs of Ni nanoparticles in the composite diaphragm.

Diaphragm operation was visualized using the setup shown in Fig. 11a. The diaphragm was bonded to a pre-structured PMMA chip and upon applying air pressure the diaphragm was stretched and a focused light beam was deflected accordingly monitored with a CCD camera (Fig. 11b).

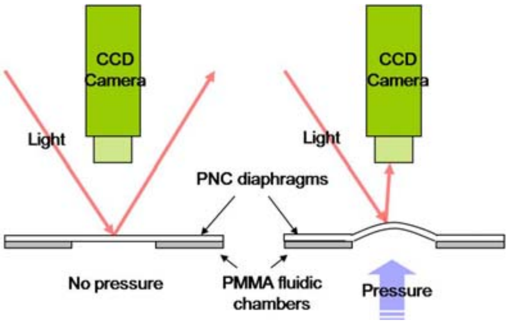
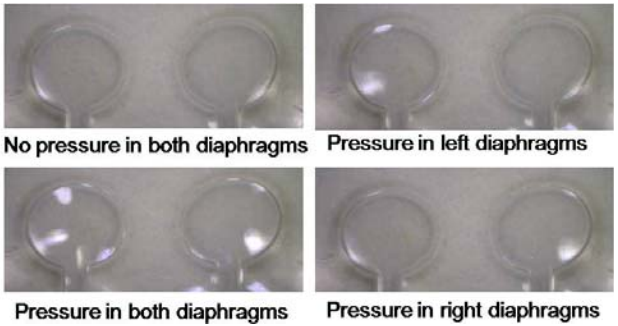


Fig. 11a: Experimental setup for monitoringmembrane deflection.



No pressure in both diaphragms

Pressure in left diaphragms

Pressure in both diaphragms

Pressure in right diaphragms

Fig. 11b: Observation of deflection indicated by abright spot on the actuated membrane.

These initial tests demonstrate successful fabrication of diaphragms and their suitability as actuator for a micropump.

Fabrication has started by designing the bottom chamber layer including inlet/outlet. MSM-micropump design was drawn in AutoCAD considering the simulation results (Fig. 12). Several possible designs meeting different pumping requirements have been realized including changes of chamber size and channel width. Initially, a simple nozzle/diffuser was used in the simulation as fixed geometry valve. Supported by literature study it was decided to use more complex Tesla valves instead promising a better performance. As a result, the prototype design chip size was a little larger than the standard fluidic stack chip.

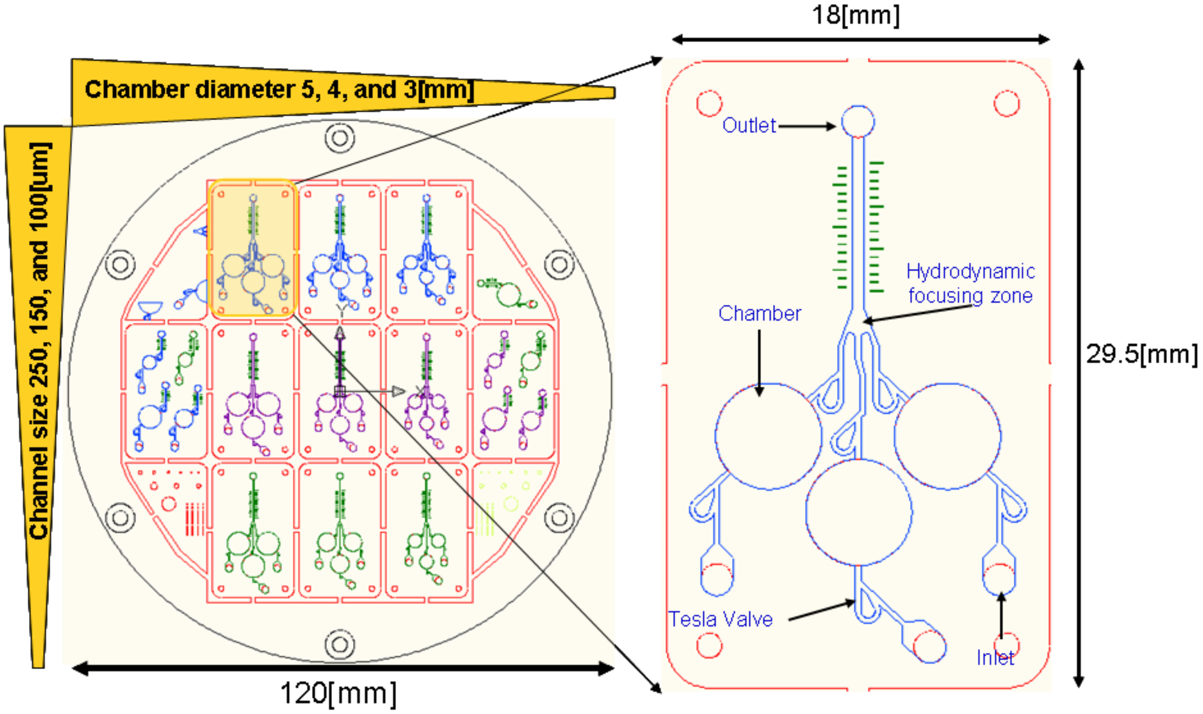


Fig. 12: MSM-micropump - AutoCAD design with variations in channel size and chamber diameter.

Precision micromilling was employed to fabricate a brass mold insert from the AUTOCAD design. Though this process is well-suited for rapid prototyping the use of drill tools with finite size and aspect ratio is limiting the quality of some structure details. Nevertheless it's appropriate for first tests and can be replaced later by a lithography-based LIGA mold insert if needed. The first generation MSM-pump mold insert is shown in Fig. 13.

Using hot embossing the insert pattern was transferred into a PMMA sheet. The different process steps are illustrated in Fig. 14. Initial tests used 1.8 mm thick PMMA sheets and a molding temperature of about 160°C. Further improvement is necessary as not all details were transferred accurately and also the molded parts showed some thermal stress/warping making the assembly difficult/nearly impossible.

Due to equipment failure (precision milling machine was done for about 2 months) the fabrication of a first pump prototype is behind schedule and results of its performance as well as suggestion for further improvement will reported in the coming quarterly reports.

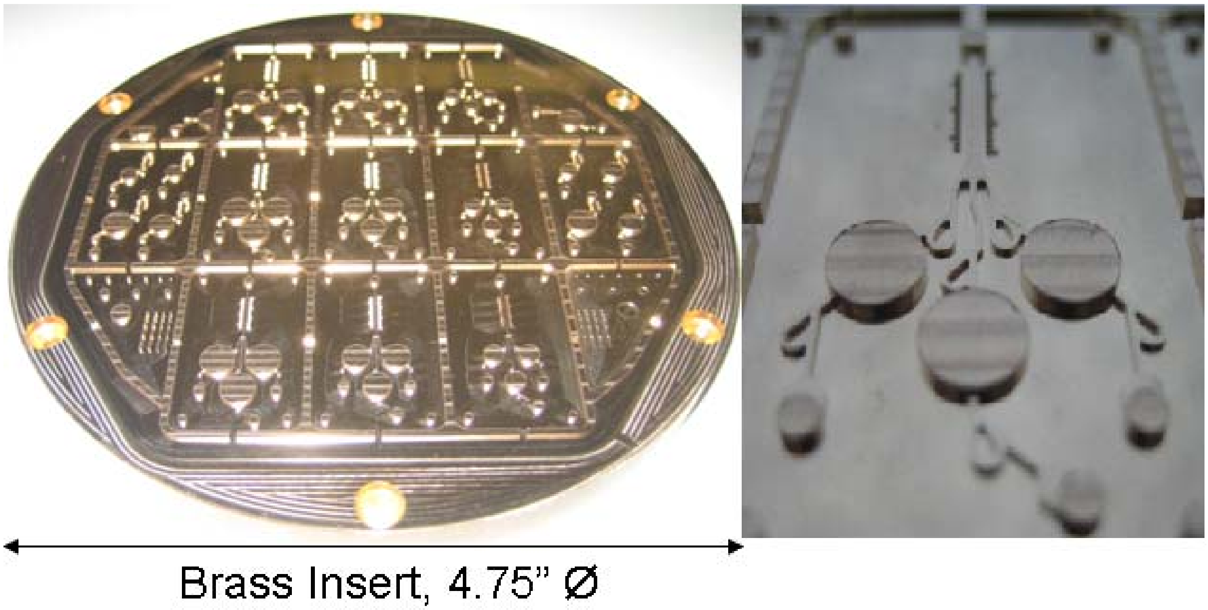


Fig. 13: MSM micropump brass mold after the mechanical micromilling.

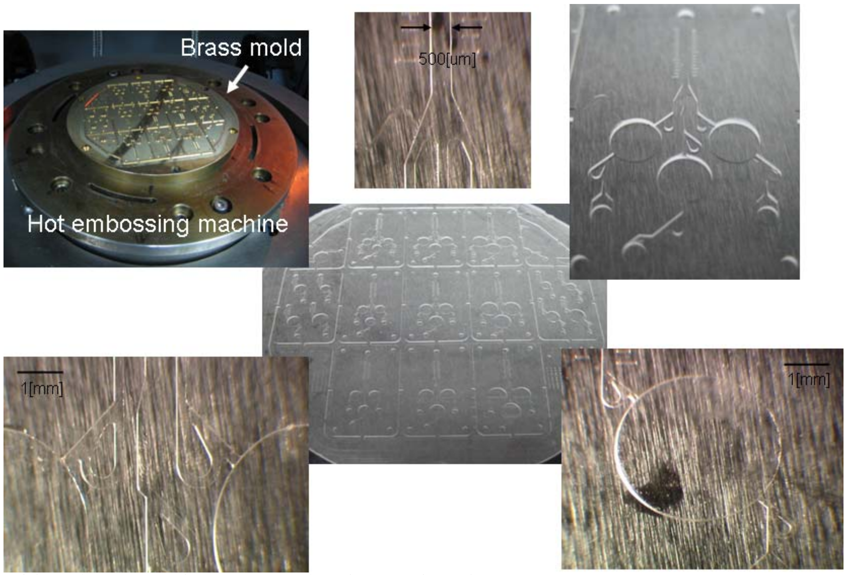


Fig. 14: PMMA chip of MSM-micropump after hot embossing process.

Publications:

N. Frische, P. Datta, J. Goettert, “Development of a biological detection platform utilizing a modular microfluidic stack”, Microsyst Technol online article March 2010, DOI 10.1007/s00542-010-1066-0.

P. Datta, G. George, S. Tiwari, J. Goettert; “Monolithic fabrication of electro-fluidic polymer microchips”, Microsyst Technol (**2009**) 15:463–469.

Conference Presentation

P. Datta, M.A. Witek, M. Hupert, S.A. Soper, J. Goettert: “Bacterial Species Detection in Whole Blood Using a Modular Microfluidic System”, Proc. HARMST 2009, Saskatoon, Canada (**2009**), 245-246.

N. Frische, P. Datta, Y. Jin, J. Goettert; “Development of a Biological Detection System Utilizing the Modular Microfluidic Stack”, Proc. HARMST 2009, Saskatoon, Canada (**2009**), 195-196.

P. Datta, J. Goettert; “Multi-level Modular Polymer Microfluidics with Optimized Form Factor”, Proc. HARMST 2009, Saskatoon, Canada (**2009**), 147-148.

O. Jinka, H. Wagemanns, J. Goettert, V. Singh; “Combinatorial Multi-level Mold Inserts Using X-ray Lithography”, Proc. HARMST 2009, Saskatoon, Canada (**2009**), 109-110.

Y. Jin, K.-N. Kang, P. Datta, J. Goettert, Z.-M. Zeng, W. Zhou; “Nanoimprinting Mold with Multi-level, High- Aspect-Ratio LIGA Microstructures“, Proc. HARMST 2009, Saskatoon, Canada (**2009**), 73-74.

Chldren's Hospital:
co-PI: Seth H. Pincus, M.D.

Project Name: Genetically engineered antibodies for nanosensors
1. Brief Narrative:

We are making genetically engineered antibodies (Abs) that will bind to nanomaterials better than the native antibodies. Working with two different antibodies we have introduced three different C-terminal domains onto them, and expressed them as full length Abs or Fab fragments. The bound antibody retains function and antigenic specificity. We have now tested the binding of these Abs to quantum dots (QDs) coated with polyethyleneglycol (QDots, Invitrogen), mercapto-undecanoic acid, and dendrons. We have attached Abs by chelation and by chemical coupling (EDC/NHS). We have now demonstrated that an engineered Ab with a 6X-His tail binds to QDs significantly better than does the parental Ab. Quantitative data suggests that another modification (oligo-lysine tail) may enhance coupling efficiency by EDC/NHS. Designing Abs specifically for binding to QDs will aid in the development of fluorescence-based biosensors.

2. Objectives:

We are making genetic modifications to antibodies to improve their utility in biosensors. These modifications allow for greater coupling efficiency and for orientation of the antibodies with their binding sites exposed. Two different antibodies are being modified: 1. RAC18, an antibody to ricin toxin, a molecule of biodefense interest, and 2. anti-HIV antibody HY, a neutralizing Ab directed to the virus envelope. For each antibody, we are attaching to the full length and Fab three different heavy chain carboxy-termini: 1. the metal binding 6X-His motif, 2. oligo-lysine (free amino groups), and 3. oligo-cysteine (sulfhydryl groups). We compare the function of these 12 constructs with native Ig. They will be studied free in solution and bound to nanowires and QDs. We have made all four 6XHis constructs, and the four full-length oligo-lysine and oligo-cysteine constructs. Antibodies for each have been made and purified. We are conducting tests of the coupling of these antibodies to QDs. Our studies of the binding of these molecules to nanowires have been delayed because the chemical modification of the nanowires has not been completed. We demonstrate promising results showing the function of 6X-his and 3X (Cys, Ala) modified antibodies when attached to QDs.

3. Research Progress:

Over the past year the following progress has been made.

Initial research progress was limited by difficulties in expressing the recombinant antibodies. Two problems contributed to this issue.

Problem 1: DNA quality. Because we are using transient expression protocols that require transfection of the DNA encoding the recombinant constructs, quantity of antibody produced is highly dependent upon transfection efficiency, which in turn is dependent upon the quality of the DNA. We now take measures to avoid contaminating our DNA with endotoxin, and to use specific kits to remove the endotoxin. We have found that Ab yields have approximately doubled as a result.

Problem 2: Plasmids with inserts reversed. Much to our chagrin we discovered that some plasmids that were making no antibody upon transfection had the insert, encoding the antibody, in the reverse orientation. This was found to be due to a methylated restriction site resulting in cutting within a shuttle plasmid and the resulting insert ligating into the opposite orientation . Once this was discovered, the mistake was corrected, and good yields of antibody are now being obtained. Having solved these problems, we have made 3-4 mg of each of the 6X-His ricin antibodies: native chRAC-18 IgG, 6X-His-RAC-18 IgG, and 6X-His-RAC-18 Fab.

Genetically engineered antibodies with 6X-His and 3x (Cys, Ala) tails have been compared to the parental antibodies for binding to QDs, and antibody function when bound to the QDs. Two different forms of QDs were first used: CdSe/ZnS nanocrystals surface functionalized with mercapto-undecanoic acid (termed nanocrystals, NC) or commercially available encapsulated QDs, with an amine-derivatized polyethylene glycol shell (termed QDots™) to which the antibodies are conjugated using free sulfhydryl groups using the hetero-bifunctional crosslinker SMCC. The function of these antibodies has then been studied by immunofluorescence on either HeLa cells (figures 1 and 2) by confocal microscopy, or on H9 cells, by flow cytometry (figures 3-6). The antibodies used bind to ricin, a toxin of biodefense importance. Cells were either pretreated with ricin, or as a negative control, not treated.

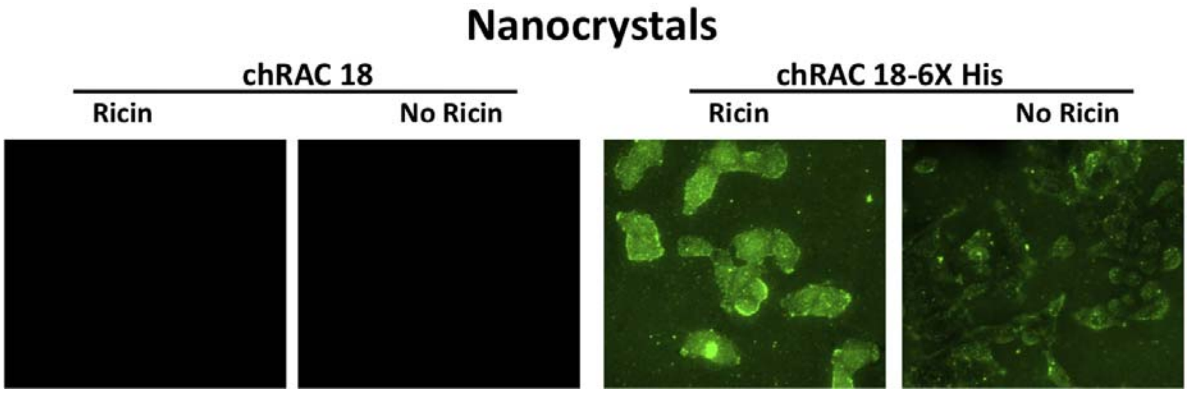


Figure 1. Binding of antibody-derivatized nanocrystals to HeLa cells. NCs were conjugated to parental or 6X-His antibodies in the presence of bovine serum albumin. Adherent HeLa cells were treated with ricin 10µg/ml for 1 hour, washed twice and incubated with the conjugated NCs at 10 µg/ml. There is background staining seen as ricin adhered to the slide, and a small amount of aggregates formed in the solution. But it is clear that the genetically modified antibody bound to the NCs, whereas the parental did not.

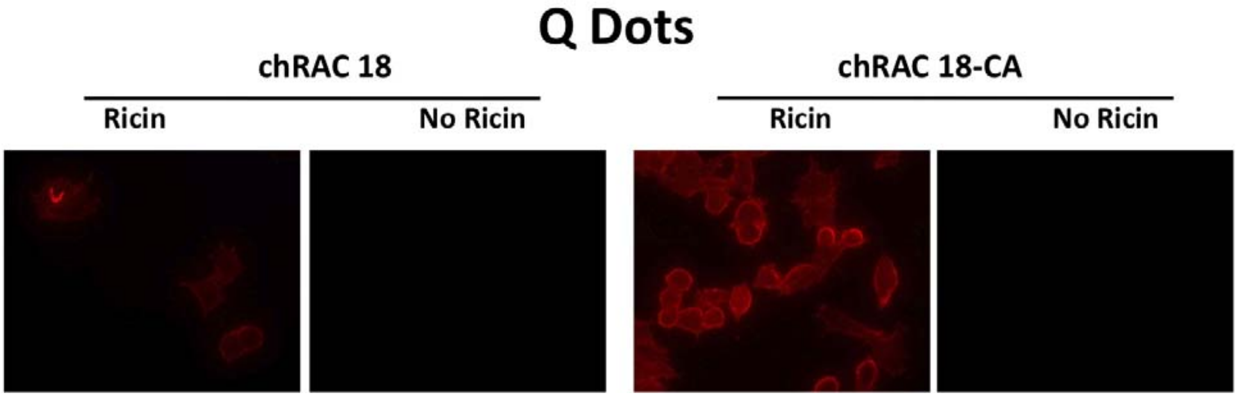


Figure 2. Binding of antibody-derivatized QDots to HeLA cells. Antibodies were conjugated to QDots using SMCC. Cells were treated with ricin and antibody as described in figure 1. Note that binding of the CA antibody appears to be greater than that of the parental antibody. Micrographs were taken at identical exposures.

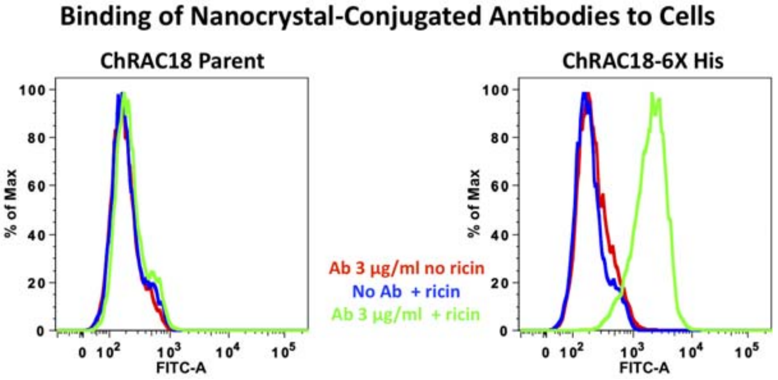


Figure 3. Binding of NC-conjugated antibodies to H9 cells. Nonadherent cells were treated with ricin, or not, as described above and then incubated with antibody-NC conjugates at the indicated concentration, and examined by flow cytometry. As compared to figure 1, note the lack of non-specific binding at a lower antibody concentration.

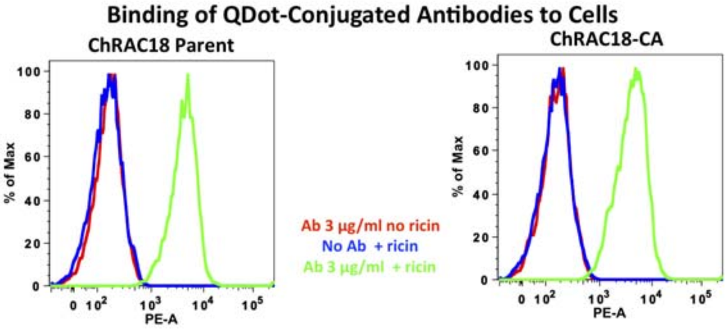


Figure 4. Binding of QDot-conjugated antibodies to H9 cells. The experiment was performed as in figure 3. Note that the data do not indicated greater binding by the engineered antibody, in contrast to figure 2.

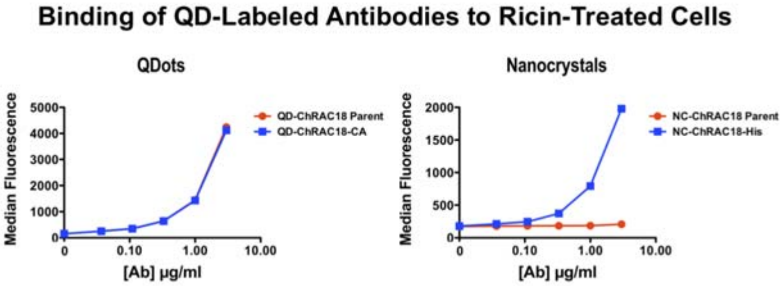


Figure 5. Comparative titration of QD conjugated antibodies to ricin coated cells. The experiment was performed as in figures 3 and 4, but with different concentrations of antibody-conjugated QDs. The results are median fluorescence. The curves confirm the results of figure 3 and 4.

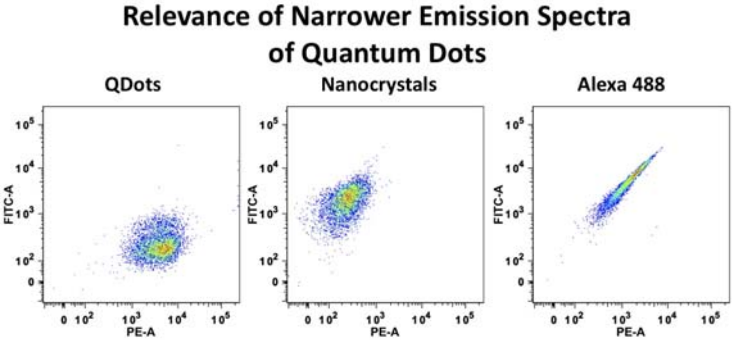


Figure 6. Bleed through of dyes from one fluorescent channel to another. Cells were stained as in figures 3-5 and analyzed by flow cytometry in 2 different fluorescent channels. Note that QDs fluoresce in only one channel, while the popular fluorescent dye Alexa-488 fluoresces in both.

We next focused on using our engineered anti-ricin antibodies to test a new generation of QDs, with greater stability in physiological salt solutions. The latest of these nanocrystals are coated with dendrons which have exposed COOH groups. We have compared different methods of attachment, including chelation and direct conjugation via NHS/EDC. Genetically engineered antibodies with 6X-His and 3x (Cys, Ala) tails have been compared to the parental antibodies. We have used flow cytometry to quantify the degree of binding. We have used two color confocal microscopy to track the ability of the nanocrystal labeled antibodies to remain attached as labeled-ricin moves through the cell. These studies demonstrate that dendron-coated nanocrystals have excellent binding capacity and are sufficiently small that they traffic through

Figure 7 shows flow cytometry results, where nanocrystal-antibody conjugates are incubated with cells following exposure (or not) of the cell to ricin. The results show that the LR nanocrystals give greater binding than the conventional nanocrystals (NC). The left hand panels compare the three mabs (parent, 6X-His, KA) conjugated to the dendrons using EDC/NHS; in the right hand panels the antibody is simply mixed with the NCs and binds by chelation. The results show that there is no binding in the absence of ricin. The LR nanocrystals give better results than the conventional nanocrystals. The 6XHis antibody functions best in all cases. The parental and KA antibody can also be conjugated to the LR nanocrystals, but only the 6XHis works when mixed (ie binds by chelation).

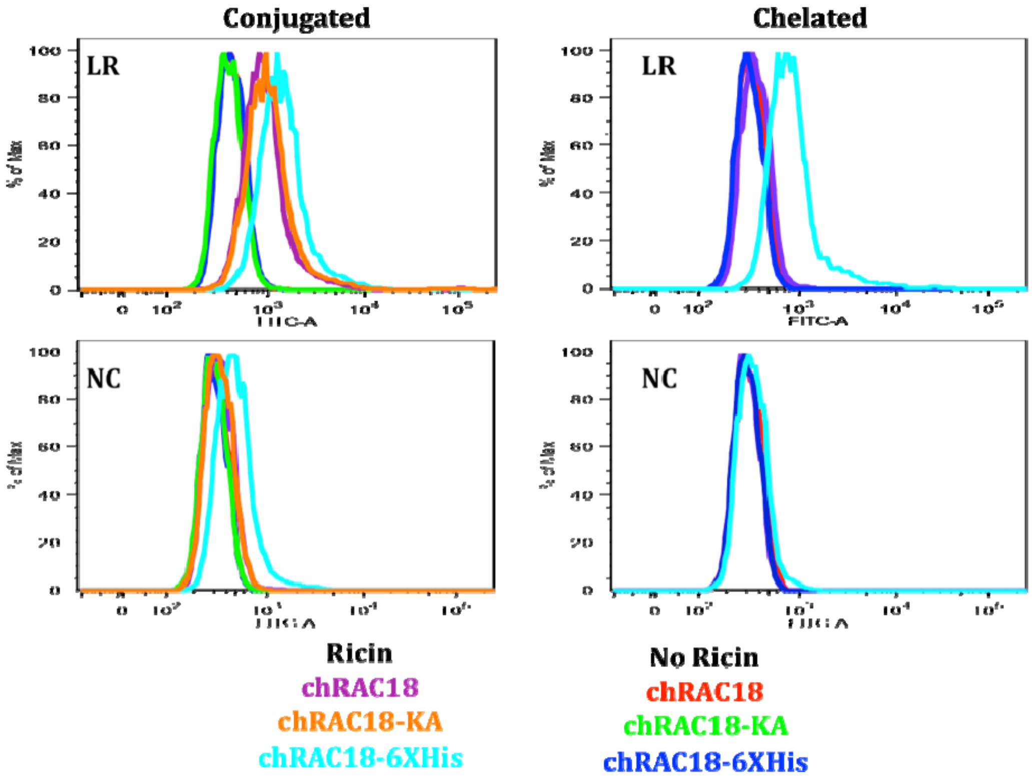


Figure 7. Binding of antibody-conjugated nanocrystals to cells coated with antigen (ricin) as measured by flow cytometry. Cells were incubated, or not, with ricin, washed, and then incubated with antibody-coupled nanocrystals. After a final wash, fluorescence was measured.

Figure 8 shows that antibodies can bind to cell-surface ricin on ricin treated cells. The cells are fixed prior to binding ricin or the antibody. Figure 9 demonstrate the trafficking of both ricin (labeled with Alexa-594) and anti-ricin antibody conjugated to LR nanocrystals, in live cells. The cells were incubated at 37 degrees with ricin and antibody for 120 minutes. Cells were fixed and then studied by confocal microscopy. Figure 9 shows 1μ z-sections through the cells, showing each channel (Ab, ricin, DIC) individually and merged. The data show that the LR-nanocrystals can enter the cells. Interestingly, the area of least antibody binding is found at the outer margins of the cell.

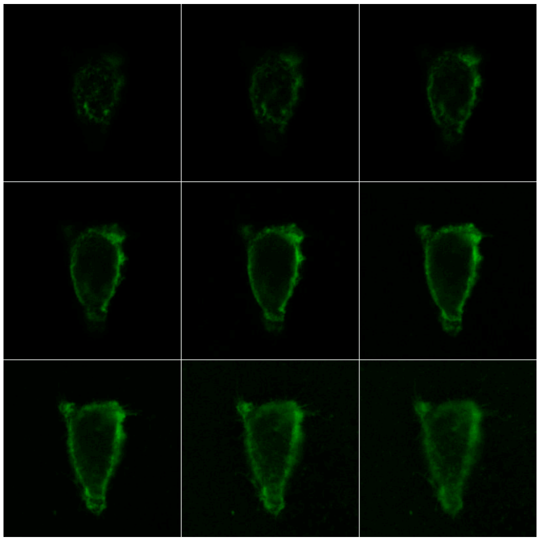


Figure 8. Confocal Z-stack of AB-conjugated LR nanorsytals binding to a ricin coated cell. Fluorescent images are collected at 0.5μ intervals.

Our studies have continued using flow cytometry and confocal microscopy to study binding of Abs to different QDs, each somewhat sophisticated than the last. The use of dendromer coatings has essentially solved the problem of QD stability in salt solution, while still retaining a much smaller size than PEG-coated QDots. Results of these experiments are provided in the appendix.

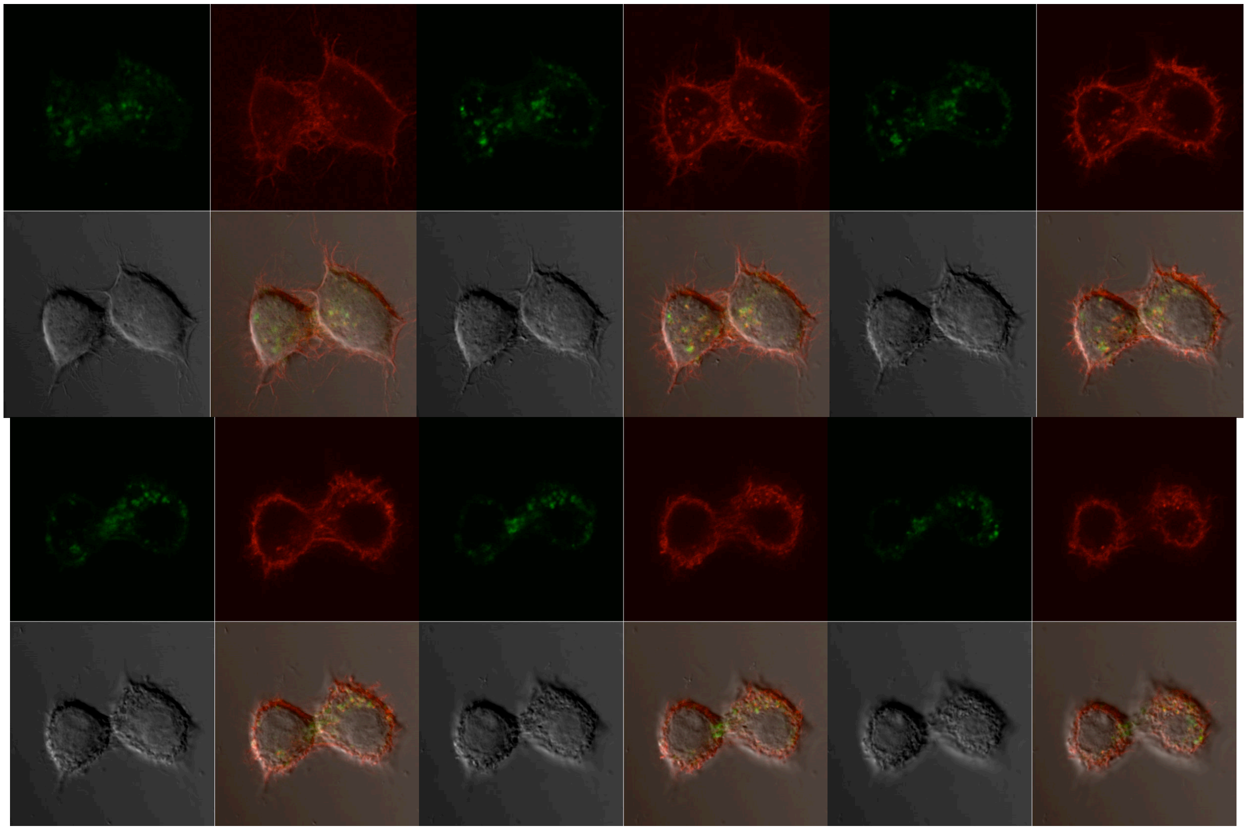


Figure 9. Z-Stack taken of cells incubated with ricin-Alexa-594 (red) and LR-nanocrystal-conjugated chRAC18-KA (green). Cells were incubated with ricin and Ab for 120 min. Z sections were taken in red, green, and DIC channels at 1 μ intervals. The slice at the top left are at the cell base. Slices move up as the photos go across and then down.

LA Tech:

Project 3: Dr. DeCoster. To develop highly sensitive nanowire based biochips for the fast detection of secreted phospholipase A_2 (sPLA$_2$) enzyme, including cell based sensors that will detect the release of stress-response molecules from living cells in situ.

1) We are using normal brain cells (astrocytes) and brain tumor cells (CRL 2199 and CRL 2020s) to evaluate the biocompatibility/toxicity of nanomaterials towards cells. Below in Figure 1 we show extensive evaluation of Silicon hollow shell/magnetic core nanoparticles provided by UNO (Zhou) compared to copper nanoparticles. Silica nanomaterials have little or no toxicity, while copper is very toxic. These results provide valuable foundation for comparing tailored materials for cell applications such as sensors and drug delivery.

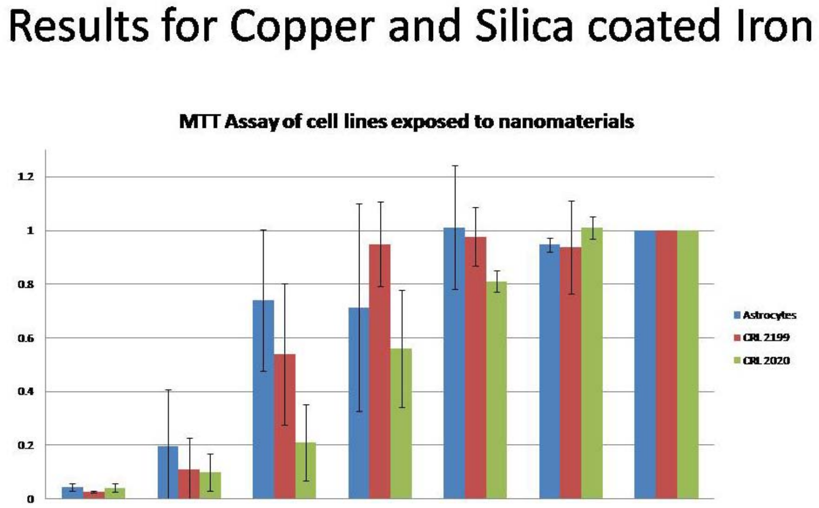


Figure 1: Comparison of toxicity of copper and hollow shell/magnetic core nanoparticles (Si) against normal brain cells (astrocytes) and brain tumor cells (CRL 2199 and CRL 2020).

For a given compound we need to calculate the half-maximal Lethal Dose (LD50). This indicates the concentration at which half of the cells are killed by the compound. By calculating the LD50 for a given compound, we can compare how toxicity of the compound varies for different cell types, in this case, normal brain cells (astrocytes and brain microvascular endothelial cells) vs. brain tumor cells. The results for this evaluation for copper nanoparticles is shown below in Figure 2.

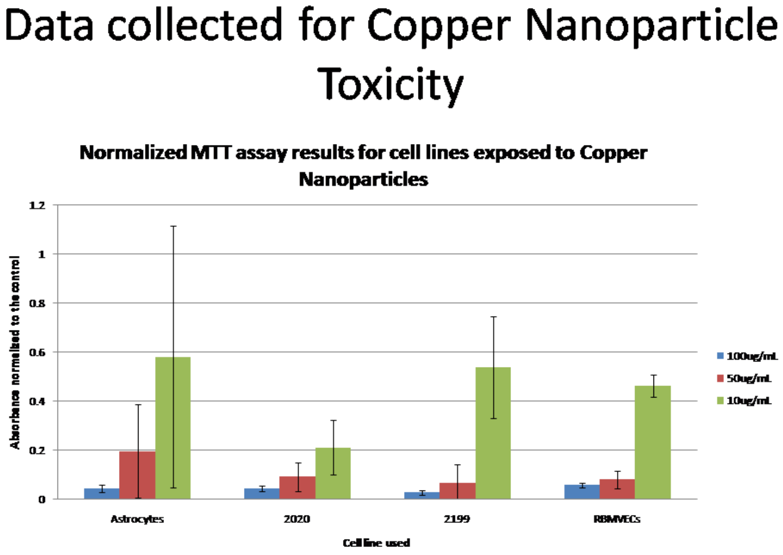
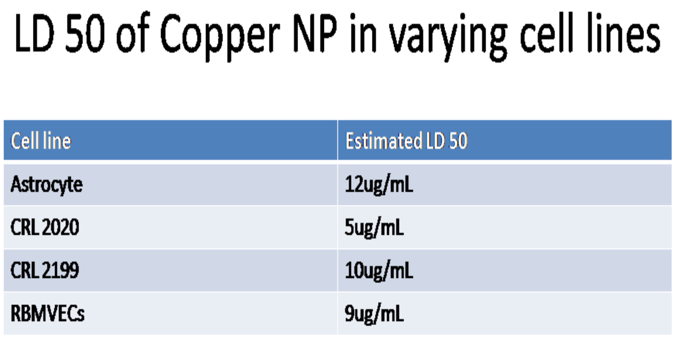


Figure 2: Comparison of copper nanoparticle toxicity across different concentrations for 4 different cell types. Astrocytes and rat brain microvascular endothelial cells (RBMVECs) are normal brain cells and 2020 and 2199 cells are brain tumor cells.

From the graphical data shown in Figure 2 above, we can calculate the LD50 values for these cells for copper nanoparticles. The results of this analysis are shown below in Table 1.



LD 50 of Copper NP in varying cell lines

Cell line	Estimated LD 50
Astrocyte	12ug/mL
CRL 2020	5ug/mL
CRL 2199	10ug/mL
RBMVECs	9ug/mL

Table 1: LD50 estimation of Copper Nanoparticle (NP) toxicity towards different normal brain cells (astrocytes and RBMVECs) and brain tumor cells (CRL 2020 and CRL 2199). Exposure to nanoparticles was for 21 hours before assay. RBMVECs= rat brain microvascular endothelial cells.

We have developed a protocol to determine the cytotoxicity of nanomaterials *in vitro*. This protocol is designed to be able to run quickly and be easily repeatable. The protocol is an MTT assay, which is used for the final measurement of cytotoxicity. This protocol is currently being used to assess a wide range on nanomaterials with a variety of cells lines. The majority of the present research deals with the central nervous system. Results from these experiments are helping establish trends between different types of nanomaterials and their current state. One set of nanomaterial that we are currently using was developed by the University of New Orleans. Others are available for purchase through chemical distributors. Nanomaterials range in composition as well as reactivity. Some of the materials being used include copper, oxidized copper, oxidized iron, an iron-copper hybrid, carbon coated cobalt, and oxidized cobalt. Different cell lines are also being used to test cytotoxicity for various cell lines found around the central nervous system. Some of these include cancer lines, while others are normal type. Some cell lines have shown to be more sensitive than others to certain nanoparticles.

Nanomaterials and cellular interaction with these materials has been the focus. We have used multiple neural cell lines in this research, and both cancerous and normal cells have been utilized. The lines used were ATCC supplied CRL 2020 - human glioma, CRL 2303- rat glioma, CRL 2199- rat glioma, CRL 2570 human T-lymphoma, and Lonza supplied astrocytes.

In coordination with Dr. Yuri Lvov's lab, we have tested the natural nanomaterial halloysite. Halloysite is a nanotubes material derived from clay that is composed of aluminum oxide and silica. Initial biocompatibility testing indicates normal cells are very tolerant, as shown here.

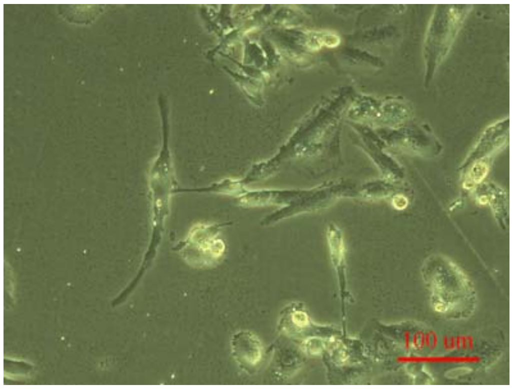


Figure 3: Normal brain glia (astrocytes) treated with 50µg/mL halloysite. Note cell clearance in immediate vicinity of membranes.

We are also looking at compatibility of Halloysite in tandem treatments with other nanomaterials. This could lead to drug delivery strategies nad cumulative treatment effects. We will begin to measure the inflammatory response of cells to halloysite, as we have already seen that it may decrease the toxicity of copper nanoparticles. These copper nanoparticles have been used as the standard of toxicity and incompatibility in previous work (H. Ma, et al. 11/2008), but pre-treatment with halloysite seems to blunt their effects.

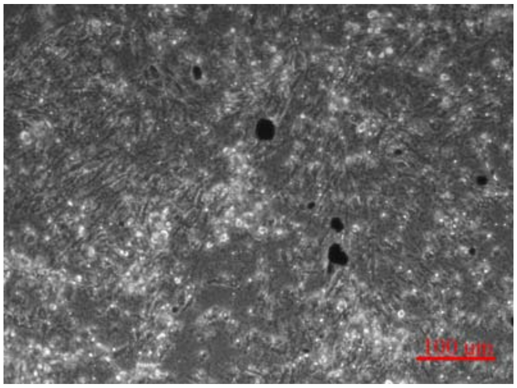


Figure 4: Astrocytes treated with 50µg/mL halloysite followed by 50µg/mL copper nps, shown here at 20 hour timepoint, cells are very obviously not dead as expected.

These findings suggest a basis for future work, along with investigations into sonication techniques that would ensure smallest particle size and fluorescent labeling of nanomaterials.

We have already received, through Dr. Lvov's lab, a sample of halloysite labeled with FITC, a fluorescent dye. We will be able to use this to show halloysite uptake into the cells with confocal microscopy. This will lead to longer term compatibility testing, with capacity for visualizing the substance of interest, as the cell continues along the lifecycle.

Currently a protocol is being developed that can be used to determine the cytotoxicity of nanomaterials *in vitro*. This protocol is designed to be able to run quickly and be easily repeatable. Currently, an MTT assay is used for the final measurement of cytotoxicity. This protocol is currently being used to asses a wide range on nanomaterials with a variety of cells lines. The majority of the present research deals with the central nervous system. Results from these experiments are helping establish trends between different types of nanomaterials and their current state.

2) Met with focused research group 1 (FRG 1) members Drs. Zhou and Pincus in New Orleans at the annual UNO-AMRI Mardi Gras review in February 2010. Provided Dr. Zhou with annual update information for his slide presentation. Provided Dr. Zhou and his Research Associate Baobao Cao with novel nanomaterials fabricated at Louisiana Tech for transmission electron microscopy (TEM) analysis. Samples were scanned and an example of scanned sample is shown in Figure 5 below:

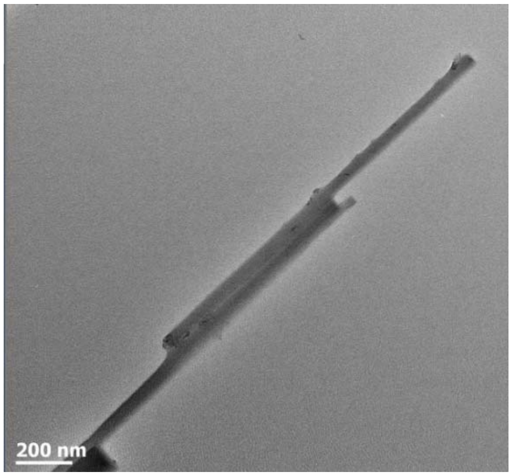


Figure 5: Transmission Electron Microscope (TEM) example image of synthesized nanostructure. Scale bar indicates 200 nanometers and demonstrates that diameter of final structures is 25 nm or less, with length in the micrometer range.

With Dr. Pincus' group discussed linking antibodies to novel linear nanostructures for development of bio-sensors. Two sets of materials were shipped to Louisiana Tech for this effort: 1) chRAC18 and chRAC18-His (6XHis) antibodies and 2) Transferrin-Alexa 594, Ricin-Alexa 594, and HY-His antibody (negative control for the chRAC-His antibodies). These reagents will be used to link antibodies to metals-based structures and then use the antibodies for biosensor detection purposes.

3) Submitted abstract to annual Society for Neuroscience (SFN) meeting describing effects of sPLA$_2$ on brain tumor cells (see below). Submitted white paper proposal to utilize novel nanomaterials for oil spill remediation. In collaboration with Dr. Lvov utilized nanoenabler instrumentation to print adhesive proteins and trap charged micro- and nano-capsules for developing better drug delivery and biochip development (Figure 6).

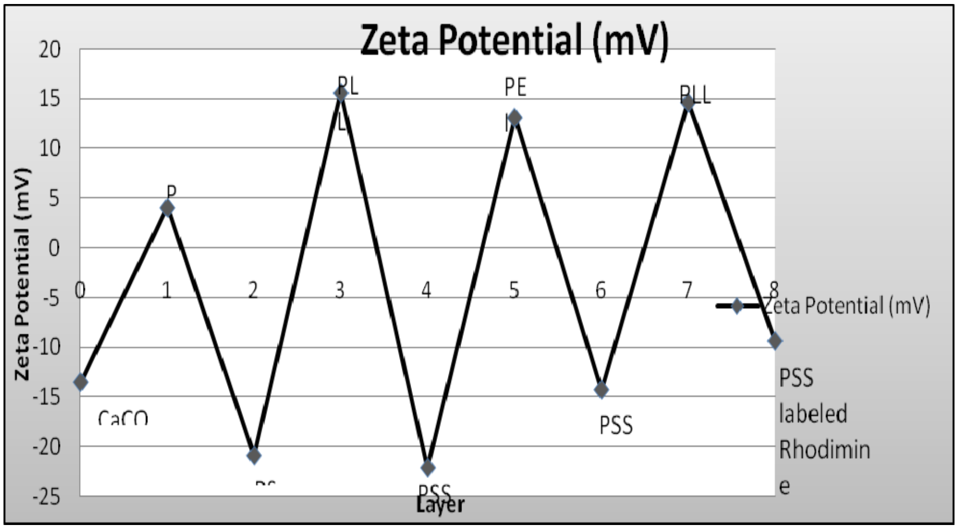


Figure 6: Zeta potential measurements were acquired by Zeta Potential Analyzer system to determine charge of capsule. As a final step capsules were labeled with rhodamine (red) for visualization.

Labelled microparticles were then trapped on a positively charged surface of PLL, labeled with Fitc (green) for visualization as shown in Figure 7.

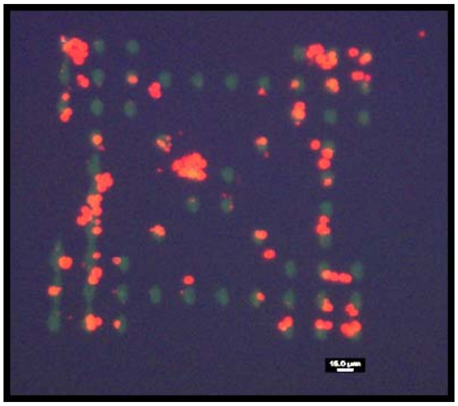


Figure 7 confocal merged image of coated microparticle attachment (red) to micropatterned nanoengineered surface (green) at 200x magnification. Scale bar= 15μms

.

Personnel: Drs. M. DeCoster, Y. Lvov D. Davis and 6 graduate students were involved (2 female) .

Nature and Scope of Partnership Activities; 1. Have provided Dr. W. Zhou with novel nanomaterials synthesized at Louisiana Tech for TEM scanning and have received digital images of these samples. 2. Have received antibodies, controls, and associated material from Pincus lab for linkage to metals-based nanomaterials for biosensor development. 3. Our clay nanotube samples loaded with silver were prepared for TEM study at AMRI, K. Stokes 4. Have discussed electron microscopy characterization of novel materials with Dr. W. Zhou. 5. Hollow silica shell magnetic-core nanomaterials provided by Dr. Zhou (UNO) continue to be evaluated for biocompatibility by DeCoster lab (LaTech).

Problems encountered during the last year of project activities. None

Contributions:

New proposals submitted / pending:

1. "Clay Tubule Nanocontainer for Responsive Corrosion Protection," NSF-nanomanufacturing, PI: Lvov, $270,000, Oct 2010- Sept 2013
2. "Halloysite Tubule Nanocontainers for Self-Healing Composites," DoD-STTR, PI: Y. Lvov (with Luna Innovation Corp), $90,000, July 2010-Jan 2011
3. "Substrates for Surface Enhanced Raman Scattering Sensing," DoD-STTR, PI: Y. Lvov (with Radiance), $90,000, July 2010-Jan 2011

New proposals funded:

1. "Layer-by-layer Nanocarriers for Highly Efficient Solubilization of Insoluble Drugs," PI-Lvov, 1-R01-CA-134951-01A2, $1,200,000 (with Northeastern University, my part $550,000); February 1, 2010 – December 31, 2014.
2. "Nanomaterials Safety Lab: Research Integrated with Service and Education (RISE)", DeCoster-PI, (Lvov, co-PI), Louisiana BOR enhancement proposal, $93,244 , July 2010- June 2011.
3. "Healing Polymer Composites Based on Clay Nanotubes," BoR NASA-LURA, $6,000, PIs: Lvov, July 2010-May 2011

Project Revision: Provide a listing of and explanation for any significant changes in the work plan for upcoming year, including any changes in the amount of investigators' time devoted to the project. – none

Work Products: List any tangible products (e.g., research publications and/or presentations, etc.). Please combine all products into one document.

National conference organizing:

Y. Lvov is appointed as an organizer and chair of International Symposium "Clay / Polymer Nanocomposites: from Nanoplates to Nanotubes" at 241st National Meeting of American Chemical Society, PMSE-Division, Anaheim, CA, March 27-30, 2011.

National funding agency review panel:

M. DeCoster, serving on NIH R03 cancer prevention study section (June 2010).

Peer reviewed papers / published:

1. R. Bellamkonda; T. John; B. Mathew; M. DeCoster; H. Hegab; J. Palmer; D. Davis, **Proceedings of SPIE- The International Society for Optical Engineering** V. 7318, 2009, Article number 73181H**, "**Microfabrication of nanowires-based GMR biosensor".
2. E. Abdullayev, R. Price, Y. Lvov, **ACS Applied Materials & Interfaces**, v.2, 1437-1442, 2009, "Halloysite Tubes as Smart Nanocontainers for Anticorrosion Agent Benzotriazole"
3. D. Fix, Y. Lvov, D. Shchukin, **Advanced Funct. Materials**, v.19, 1720-1727, 2009, "Application of Inhibitor Loaded Halloysite Nanotubes in Active Anticorrosive Coatings"
4. V. Vergaro, E. Abdullayev, R. Cingolani, Y. Lvov, S. Leporatti, **Biomacromolecules,** v.11, 820-828, 2010, "Cito/biocompatibility and Uptake for Clay Nanotubes,"

5. C. Yelleswarapu, E. Abdullayev, Y. Lvov, D. Rao, **Optics Commun.**, v.283, 438-441, 20
"Nonlinear Optics of Nontoxic Nanotubes"

6. Bellamkonda, R., John, T., Mathew, B., DeCoster, M.A., Hegab, H., Davis, D. "Fabrication and testing of a CoNiCu/ Cu CPP-GMR nanowire-based microfluidic biosensor." **J. Micromech. Microeng.** v.20, #025012, 2010

7. R. Mannam, M. Agarwal, A. Roy, V. Singh, K. Varahramyan, D. Davis, "Electrodeposition and Thermoelectric Characterization of Bismuth Telluride Nanowires" **J. Electrochemical Society**, v.156, B871-B875, 2009.

Presentations:

1. M. A. DeCoster, J. McNamara, K. Cotton, R. Masvekar, "Delay of staurosporine-induc apoptosis by glutamate in brain tumor glia and normal astrocytes" Society for Neuroscie Meeting, Chicago, October 20, 2009.
2. R. Masvekar, J.McNamara, X. Du, A. Kunjumon, D. Green, S. Dua, D. Davis, M. DeCost "Glial Cell Interfaces: Using Micro- and Nano-patterning for Brain Tumor Studies" Americ Soc. Cell Biology/ RIKEN joint meeting: "Building the Body Plan: How Cell Adhesi Signaling, and Cytoskeletal Regulation Shape Morphogenesis.", Kyoto Japan, September 2009.
3. M. DeCoster, "Neurotoxicity of Nanoparticles", South Central Society of Toxicology (SC SOT), Annual Fall Meeting October 8-9, 2009 Shreveport, LA.
4. Y. Lvov, R. Price, E. Abdullayev, "Halloysite- benzotriazole nanocomposites, low cost additi to metallic coatings for corrosion protection," 29th Biennial Western Coating Symposium, Vegas, NM, October 25-28, 2009

Report of Inventions:

1. DeCoster, M. and Wasserman, J.: "Biological production of ordered XXXX structures from nanoparticles". Filed with Louisiana Tech University, ROI #2009-17.
2. D. Mills, Y. Lvov, "Smart Bioactive Nanocoating with Sustained Drug Release Capability for Implants, Wound Repair rand Tissue Regeneration," April 23, ROI #2010-08
3. Y. Lvov, "Selective Hydrocarbon Grafting of Halloysite Lumen to Produce Inorganic Micel like Petroleum Sorbent Material," May 14, ROI #2010-12

PKSFI Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04

John Wiley
(PKSFI FRG-2, 2009-2010)

FRG-2 Nanomechanical Devices

1. Personnel:

This focused research group consists of researchers from the University of New Orleans (UNO) and Tulane University (TU). The principal investigators are John Wiley (UNO), Bruce Gibb (UNO), Leonard Spinu (UNO), Vijay John (TU), and Hank Ashbaugh (TU). A number of graduate students are also contributing to the work: Jianxia Zhang (UNO), Haiying Gan (UNO), Andrei Diaconu (UNO), Joy St. Dennis (TU), Bhanu Sunkara (TU), and Piyush Wanjari (TU). In one project, photoactive polymers are being synthesized and tested as possible light and/or solvent driven actuators in mechanical devices (Zhang in Wiley's group). In another project, sets of host-guest molecules are being synthesized and characterized as possible tethers for the directed self-assembly of nanocomponents (Gan in the Gibb's group). New magnetically guided tubular liposomes have also been produced for potential mechanical device components (Joy St. Dennis and Bhanukiran Sunkara in V. John's group; these researchers are working with Leonard Spinu in the characterization of these materials). The Ashbaugh group has studying solvent effects on solvent-mediated interactions between hydrophobic species.

2. Activities and Findings:

The activities and findings will be broken up into the various aspects of the program.

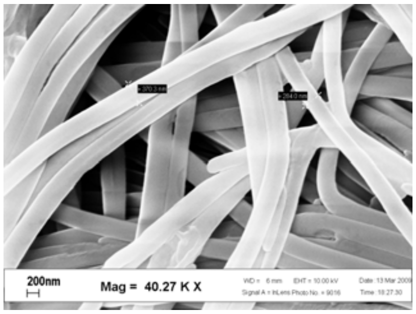


Figure 2-1. Diazobenzene wires. SEM of nanowires.

a. ***Photo- and/or solvent-active polymers.*** We are continuing our efforts to investigate the potential use of diazobenzene polymers for optically-active and solvent-active actuators. The polymers have been formed into nano- and micron-sized wires (Figure 2-1) and we are now studying the mobility of these object under various conditions. We can follow the movement of micron-sized wires with an optical microscope. Nanoscale wires are more of a challenge. We initially planned to carry out experiments to follow the movement with an STM, and while may still do so, we are now following a different strategy based on the insertion of quantum dots into the wires. In this case we can use a fluorescence microscope to follow the movement. In an additional part of this effort we are looking at asymmetric modification of wires prior to solvent treatment to direct the bending and spiraling of micron-sized wires. Figure 2-2 shows an example of a wire that was coated with metal on one side and then treated with solvent; the solvent caused swelling and bending of the wire component. In this case the wire curled into a spiral. We continue to examine both the effects of UV and solvent exposure on these various wires. We have a new scanning probe microscope on order that will allow us to monitor individual wires while they are exposed to UV light or different solvents.

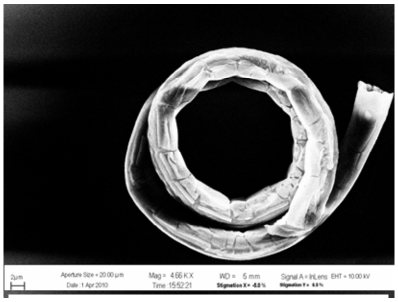


Figure 2-2. Spiral micron wire formed by swelling of asymmetrically coated surface.

b. ***Host-guest assembly.*** This program of research focuses on the controlled assembly of nano-objects into complex nano-systems. The general approach involves the development of hosts (H1, H2 and H3) that bind complementary guests (G1, G2 and G3). Each host-guest pair is orthogonal, i.e. H1-G1 strongly associates, but for example H1-G2 or H3-G1 do not. Hence, one surface of a nano-object coated with H1 will stick to another object coated with G1. Moreover, with three, orthogonal host-guest pairs, it is theoretically possible to assemble complex objects by selectively coating different objects (or different parts of objects) with different hosts and guests. Our strategy is to utilize thioether-functionalized deep-cavity cavitand hosts (DCC) and complementary guests that bind strongly to gold surfaces.

Currently the student involved in this project, Haiying Gan, is focusing on the binding behavior of a series of DCC. Various binding studies involving NMR and isothermal titration calorimetry. These solution studies serve as an important foundation for working with these hosts at surfaces and interfaces.

c. ***Modeling of Host-Guest systems.***

All our previous investigations provided a detailed knowledge about the hydrophobic interactions responsible for the recognition and binding of a variety of guests by the deep-cavitand hosts. We further moved towards understanding the interactions between these hydrophobic hosts, which forms capsular nanocomplexes in presence of suitable guest like adamantane. Recent experimental studies by Ramamurthy group at University of Miami indicated that neutral adamantane prefers both 2:1 and 2:2 host-guest capsuleplexes. By performing the umbrella sampling simulations combined with WHAM, we determined the potential mean forces (PMFs) for both the cases by following a similar procedure that we used for the evaluation of PMF between adamantane guest and cavitand. The PMFs shown for 2:1 and 2:2

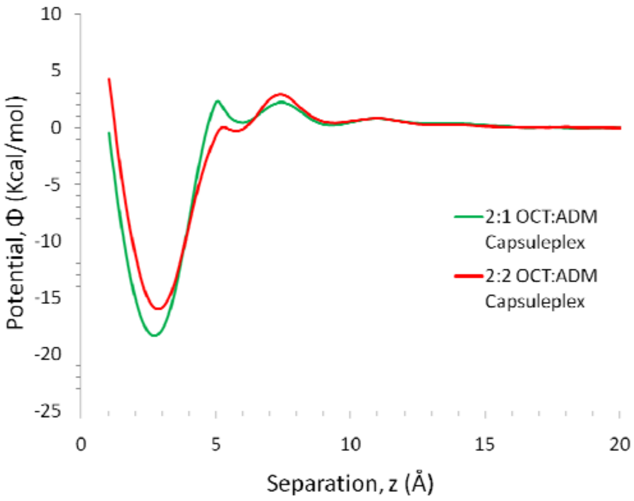


Figure 2-3. PMFs of capsule formation for 2:1 and 2:2 octacid-adamantane host- guest capsuleplexes

capsuleplex formation in figure 1 indicate the attractive interaction between the hosts with potential depth of −18.4 and -16.0 kcal/mol respectively.

Since our last reporting period, we have continued performing simulations to examine the interactions for capsule formation on the LONI supercomputer network. We have encountered issues concerning convergence of our simulation results, and are in process of simulating longer to overcome this difficulty. In addition we performed preliminary simulations to examine the free energy associated with the mutual rotation of the cavitands about their central axis. Unfortunately we found the constraints to maintain co-axial rotation were unstable and were unable to perform these calculations.

d. ***Biomimetic Nano Lubricants: Gels Based on Biomolecules and Nanoparticles with Ultralow Coefficients of Friction.***

Lubricants play an integral role in the operation of several technologies ranging from moving parts in machinery to the biolubrication of articular joints. The main purposes of a lubricant are to reduce friction and surface wear. We have found that an easily synthesized system of monodisperse hard carbon submicron spherical particles (HCS) has frictional coefficients that start approaching those of synovial fluids. When these observations are coupled with a novel discovery that a modified biopolymer (chitosan) is able to gel vesicles, we are able to realize a unique gel system containing the carbon microspheres serving as nodes in a network of this biopolymer. This forms the basis of our work to develop novel gel based lubricants containing monodisperse particles or cushioning vesicles. Our hypothesis is that these composite materials will be able to reduce friction and minimize surface wear synergistically through the boundary lubrication of biomolecules/biopolymers and the "rolling" mechanism (similar to ball bearings) employed by HCS particles. We are therefore developing biomimetic lubricants with ultralow coefficients of friction that are relatively easy to synthesize and are robust enough for applications either as potential substitutes for synovial fluid or in applications to microfluidics or microelectromechanical devices. Several formulations composed of phospholipid based liposomes, biopolymers and carbon microspheres will be explored systematically to determine the optimal molecular and particulate design that exhibits good lubrication properties including a low coefficient of friction and minimal surface wear.

3. Contributions:

Initially the focus was on building the research group, attracting students, initiating the research, and building the collaborations. This is now well established. All the students supported on this grant are getting extensive training in materials research.

Some team members (John and Ashbaugh) have recently been informed that their NSF proposal relating has been approved for funding. This will leverage the PKSFI efforts. The Principal Investigator on this grant is Dr. Noshir Pesika at Tulane and both Ashbaugh and John are co-PIs.

V. John is also using carbon microsphere technology for a project on the environmental remediation of chlorinated compounds. A startup company (NanoFex LLC) has been formed based on this technology.

Further members from this team along with members of the other FRG's are initiating efforts for a center of excellence grant to the NSF. Pre-proposal submissions are due in the fall.

4. Project Revision:

Scott Whittenburg is no longer on this grant. His funds have been shifted to two assistant professors to help further their careers.

5. Work Products:

Presentations

"Reverse Templating of Mesophase Ceramics to produce Highly Porous Structured Carbons from Sugars", Joy St. Dennis, Vijay T. John presented at the AIChE Annual Meeting, Nashville, November 2009.

"Multifunctional Hybrid Colloidal and Nanoscale Materials for Targeted Remediation of Chlorinated Hydrocarbons", B. Sunkara, V. John, presented at the AIChE Annual Meeting, Nashville, November 2009.

"Environmental Remediation of Chlorinated Hydrocarbons Using Multifunctional Nanoparticles with Optimal Reactive/Adsorptive/Transport Characteristics", Vijay T. John, Jingjing Zhan and Bhanukiran Sunkara, ACS Colloid and Interface Science Symposium, Akron, June 2010.

"Hard Carbon Spheres as Micro-Bearings for Water-Based Lubrication", Noshir Pesika, Vijay John, Joy St Dennis and Kejia Jin, ACS Colloid and Interface Science Symposium, Akron, June 2010.

"Reactions Inside and Outside Water-Soluble Nano-Capsules," Bruce C. Gibb, University of Georgia, April **2010**.

"Reactions Inside and Outside Water-Soluble Nano-Capsules," Bruce C. Gibb, Symposium on Self-Assembled Molecular Containers, American Chemical Society 239th National Meeting, March, **2010**.

"Magnetization Dynamics for NonVolatile Memory Technologies," Leonard Spinu, Invited talk at the 10th International Conference on Development and Applications Systems - DAS 2010, Suceava, Romania 2010.

Publications:

J. E. St.Dennis , Pradeep Venkataraman , Jibao He, Vijay T. John, Stephen J. Obrey, Robert P. Currier , Marisabel Lebrón-Colón , Francisco J. Sola, Michael A. Meador. "Rod-like carbon nanostructures produced by the direct pyrolysis of α-cyclodextrin", submitted to *Carbon*.

Bhanukiran Sunkara, Jingjing Zhan, Jibao He, Gary L. McPherson, Gerhard Piringer, and Vijay T. John, "Nanoscale Zero-Valent Iron supported on Uniform Carbon Microspheres for the *In situ* Remediation of Chlorinated Hydrocarbons," submitted to *ACS Applied Materials and Interfaces.*

Zhan, J.; Sunkara, B.; Zheng, T.; McPherson, G.; Piringer, G.; Lu, Y.; Kolesnishenko, V; John, V. "Nanostructured Multifunctional Materials for Environmental Remediation of Chlorinated Hydrocarbons", in *Environmental Application of Nanoscale and Microscale Reactive Particles*, ACS Symposium Series, K. Carvalho-Knighton, C. Geiger, Eds., 2009, *1027*, 163.

"Bending Behavior of Polymer Films in Strongly Interacting Solvents," Jianxia Zhang and John B. Wiley, *Mater. Res. Soc. Symp. Proc.* **2009**, *1129*, 1129-V04-05.

"Kinetic Resolution of Constitutional Isomers via Protection by a Supramolecular Nanocapsule," Simin Liu, Haiying Gan, Andrew T. Hermann, Steven W. Rick and Bruce C. Gibb. *Nature Chemistry*, in press.

"ITC Analysis of Guest Binding to a Deep-Cavity Cavitand," Haiying Gan, Bruce C. Gibb, *J. Supramolecular Chem.*, submitted.

PKSFI Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04

Kevin L. Stokes
(PKSFI FRG-3, 2009-2010)

FRG-3: Nanomaterials for Energy Conversion and Storage

1. Personnel:

LATech/IfM

Silky Abbott, Graduate Research Assistant, Thermoelectrics
Abdullayev, Elshad. Graduate Research Assistant, Hydrogen storage materials
Davis, Despina. Co-PI, Thermoelectrics
Lvov, Yuri. Co-PI, Hydrogen storage materials
Mannam, Raja. Graduate Research Assistant, Thermoelectrics
Wei, Wenbo. Graduate Research Assistant, Hydrogen storage materials

LSU

Haldolaarachchige, Neel. Graduate Research Assistant, Thermoelectrics
Karki, Amar. Staff Scientist, Thermoelectrics
Young, David P. Co-PI, Thermoelectrics

UNO/AMRI

Gabrisch, Heike. Co-PI, Battery materials
Malkinski, Leszek. Co-PI, Ferroic composites
Mohanty, Debasish. Graduate Research Assistant, Battery materials
Nolting, Westly, Undergraduate Research Assistant, Thermoelectrics
Stokes, Kevin L. Co-PI, Thermoelectrics
Ward, Tom. Graduate Research Assistant, Ferroic composites

Dr. Kevin Stokes reviews quarterly progress reports from LSU and La Tech to ensure that these contributions meet the project's requirements.

2. Activities and Findings

Major Research and Educational Activities Undertaken

This focused research group (FRG) is applying the science and engineering of nanometer-scale materials to several areas of energy conversion and storage. Stokes, Davis and Young are investigating various aspects of nanocomposites thermoelectric materials and microdevices, Gabrisch is investigating novel electrode materials for electrochemical storage applications (rechargeable batteries); Malkinski is researching novel magnetic to electrical power conversion composites for micropower applications and Lvov is developing techniques for the nanoassembly of nanoparticles and tubule nanocontainers for possible hydrogen storage applications. There are six principle investigators, one senior researcher, seven graduate students (total) and two undergraduate students from the University of New Orleans, Louisiana State University and Louisiana Tech. The results for June 2009 to June 2010 are summarized below.

Major Findings and Results

a. Giant Magnetosresistive (GMR) Sensors (Davis)

GMR-based microfluidic biosensors are used in applications involving the detection, analysis, enumeration and characterization of magnetic nano-particles attached to biological mediums such as antibodies and DNA. Here, we introduce a novel multilayered CoNiCu/Cu nanowire GMR based microfluidic biosensor. Figure 3.1 shows the major steps in the micro-device sensor fabrication. Figure 3.1 (a) exemplifies the GMR nanowire array (magnetic sensing element material) placement on the “master” silicon wafer. The CoNiCu/Cu GMR multilayered nanowire based material has been electrodeposited in-house from a single electrolyte using a pulsed potential technique. The GMR nanowire array with electrical contacts was placed on a UV-lithographically patterned (300 μm width, 60 μm height and 4 cm length) silicon wafer (1μm oxide layer). Figure 3.1 (b) illustrates how the GMR nanowire array gets embedded in the PDMS laid to mold after the patterned silicon wafer.

PDMS is poured onto the silicon master wafer with the GMR membrane placed above of the protruding pattered mounts. The GMR electrical contacts were brought out of the PDMS and the polymer was allowed to solidify for 24 hours. Figure 3.1 (c) shows the embedded GMR nanowire array PDMS being peeled-off the master wafer and the resulting microchannels replica. Figure 3.1(d) illustrates how the micro-channel in the PDMS containing GMR was sealed using Oxygen- Reactive Ion-Exchanger (RIE) onto glass. The operating conditions used for bonding of PDMS and glass were: pressure = 700 mT, power = 20 W and time = 30 s. Figure 3.1 (e) reveals a schematic of the final device ready for testing. Tygon tubing was secured by epoxy into the previously drilled glass holes. Figure 3.2 shows a schematic of the sensor testing mechanism.

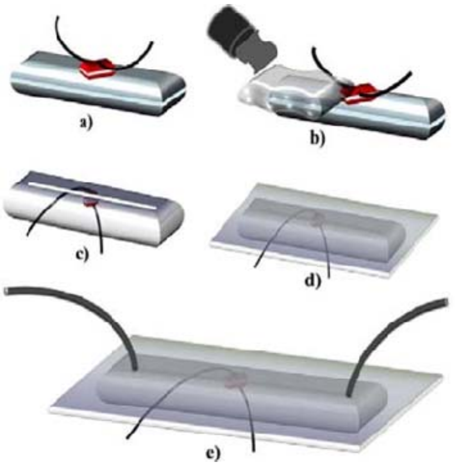


Figure 3- 1. Sensor Microfabrication Schematic a) GMR nanowire array with electrical contacts, b) PDMS coverage of the nanowire array (sensing element) on positively patterned silicon wafer, c) Peeled off PDMS mold with open channel, d) Glass sealed GMR-PDMS channel mold, e) Final GMR microfluidic device with attached tygon tubing.

The CoNiCu/Cu multilayered nanowire GMR based microfluidic sensor was tested potentiostatically using a computer controlled function generator (Solatron, SI 1287). A syringe pump was used to control the flow of various magnetic and non-magnetic fluids through the microchannel.

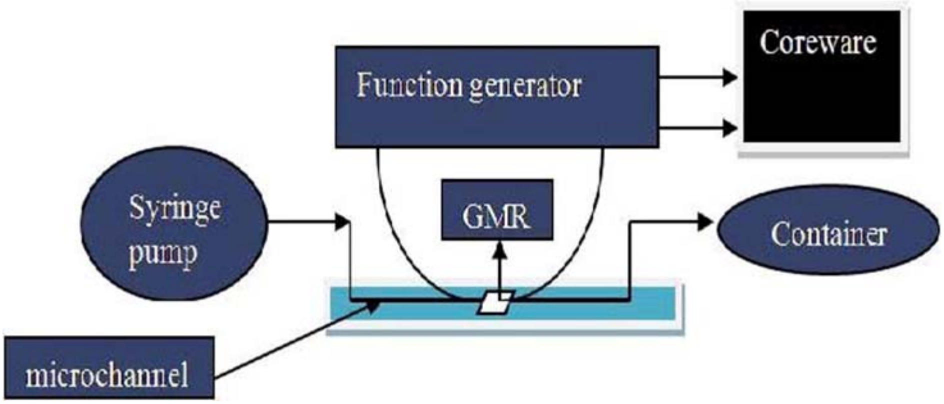


Figure 3.2. Sensor testing schematic.

b. Electrodeposition of bismuth telluride (Davis)

Nanostructured bismuth-telluride (Bi_2Te_3) materials are the focus of intensive research since this thermoelectric material combines a high power factor and a low thermal conductivity. Thermoelectric (TE) materials can generate electricity from heat and can act as cooling devices when a voltage drop is applied. The thermo-electric phenomena provides a way to locally control temperature. Bismuth telluride (Bi_xTe_y) nanowires were electrodeposited from aqueous acidic solutions containing different $Bi^{3+}/HTeO^{2+}$ (20/20 mM, 20/10 mM) concentration ratios. The polarization plots predicted that combined solutions exhibit more noble reduction potentials than individual solutions. Optimized deposition potentials were obtained from the combined electrolyte polarization plots. An anomalous codeposition behavior caused increase in Te concentration for depositions in the kinetic region of bismuth telluride; otherwise decreasing Te concentrations with increased deposition potentials was observed from composition analysis. X-ray diffraction showed a dominant (110) orientation for nanowires at low deposition potentials. N-type nanowires were obtained from both electrolytes, while p-type nanowires were only obtained from the 20/10 electrolyte for low Te (< 30%) concentrations. An intrinsic to extrinsic transition was observed for nanowires deposited from 20/10 electrolyte. The highest measured Seebeck coefficient was -318.7 μV/K and 117 μV/K for n-type and p-type nanowires, respectively.

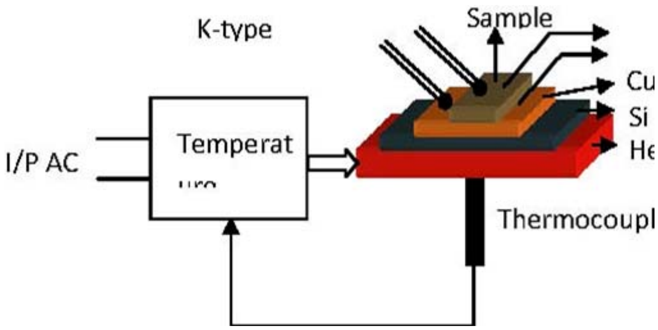


Figure 3.3. Thermoelectric measurement device.

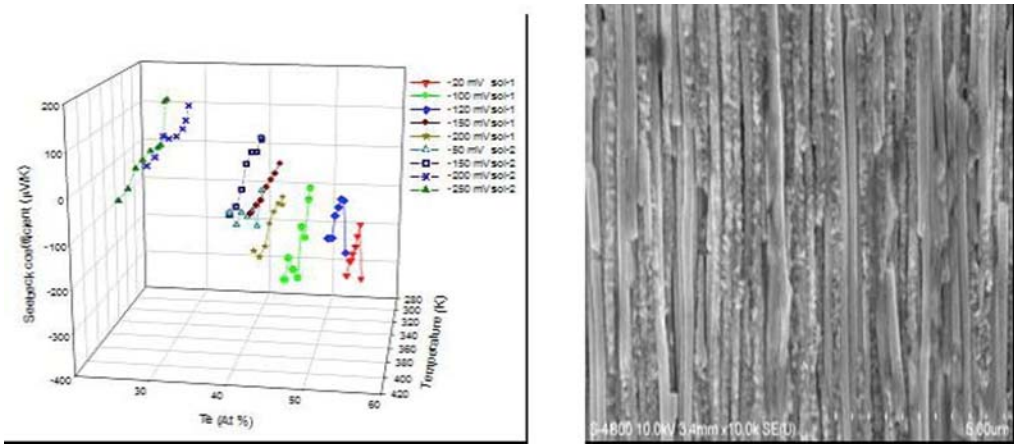


Figure 3.4. Seebeck coefficient with respect to tellurium concentration and temperature.

Bismuth antimony telluride (BiSbTe) nanowires were electrodeposited at constant potentials into polycarbonate templates from a tartaric-nitric acid baths having different electrolyte compositions. Composition analysis showed that Sb deposits at higher potentials compared to BiTe. Maximum seebeck coefficients of 337.7 µV/K and 227.2 µV/K n-type and p-type, were obtained for nanowires samples $Bi_{4.6}Te_{5.4}$ and $Bi_{4.3}Sb_5$ respectively. Nonmonotonic resistance behavior was observed for all the nanowires. Figure 3.5 shows the representative SEM image of the nanowires in the background of dissolved polycarbonate template, deposited at -150 mV. Even though the template pore diameter is 50 nm, the SEM analysis shows that the nanowires have larger average diameter of (110 nm ±5 nm standard deviation), which indicates the bulging of the nanowires in the pores during the electrodeposition process. Thermoelectric properties of fully grown nanowires having different alloy compositions Bi_xTe_z, Bi_xSb_y, $Bi_xSb_yTe_z$, deposited at -250 mV from sol-A and -20 mV, -100 mV, -150 mV, -200 mV, and -250 mV from sol-B were determined.

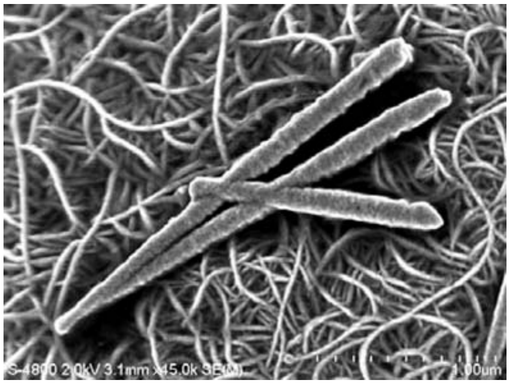
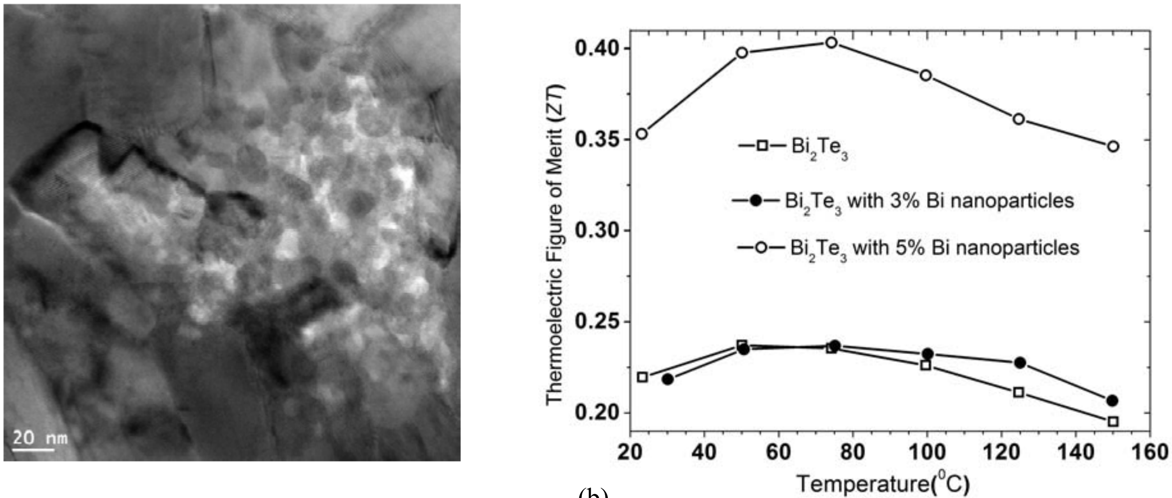


Figure 5. SEM image of the nanowires deposited in polycarbonate membranes -150 mV.

In conclusion, BiSbTe nanowires were successfully electrodeposited into polycarbonate template from different electrolytes. A mutually induced co-deposition mechanism was observed with the addition of Te in the electrolyte. Maximum Seebeck coefficients of -337.7 μV/K and 227.2 μV/K n-type and p-type, were obtained for nanowires samples $Bi_{4.6}Te_{5.4}$ and $Bi_{4.3}Sb_5$ respectively. High Sb concentration negatively affected the Seebeck coefficients. More experiments are underway to study the effect of Sb and Te doping in BiSbTe nanowires.

c. Nanoparticle Composites (Stokes, Nolting)

We have synthesized and measured the thermoelectric properties of several $Bi_{2-x}Sb_xTe_3$ (x=0 and 0.5) compounds as well as $Bi_{2-x}Sb_xTe_3$/nanoparticle composites. The nanocomposites consist of metal nanoinclusions (Bi) inside a nanostructured bulk $Bi_{2-x}Sb_xTe_3$ matrix. Structural properties characterization has been performed by x-ray diffraction and electron microscopy. A study of the thermal and electrical properties has been completed (electrical conductivity, thermal conductivity, Seebeck coefficient and Hall effect measurements). The effect of different volume fractions of Bi nanoinclusions (3% and 5%) on the properties of the composite has been demonstrated. Figure 3.6 shows a nanocomposite which is a combination of ball-milled Bi_2Te_3 with chemically-synthesized Bi nanoparticles. A transmission electron microscope cross section is shown in Fig. 3.6 (a). Thermoelectric figure of merit is shown in Fig. 3.6 (b) for three materials: the unmodified Bi_2Te_3 along with Bi_2Te_3/Bi nanoparticle composites with 3% and 5% Bi nanoparticles. We found that the figure of merit of the nanocomposite ($ZT=0.4$) was twice the figure of merit of Bi_2Te_3 alone($ZT=0.2$). Interestingly, we found that the electrical conductivity increased due to an increase in carrier concentration but that the Seebeck coefficient did not decrease, as would be expected in a bulk semiconductor material.



(a)

(b)

Figure 3.6. (a) Transmission electron microscope image of Bi_2Te_3 with Bi nanoparticle inclusions. (b) Thermoelectric figure of merit for three nanocomposites. Note the almost factor of 2 increase in the figure of merit for the nanocomposite with 5% (vol) Bi nanoparticle inclusions.

d. Thermoelectric Transport in Wires (Champagne, Karki, Walker andYoung)

This research project has focused on the synthesis and characterization of novel intermetallic systems in reduced dimensions. By measuring the magnetotransport and thermal behavior of these materials in reduced dimensions, we gain insight into the physics driving the transport properties between these low-dimensional structures and the bulk. As mentioned previously, we have been successful at coating carbon microfibers with different intermetallic systems, such as $MgCNi_3$, Mo_3Sb_7, MoN, and $ZnNNi_3$. We have recently published the work on the $ZnNNi_3$.

Part of this project has focused on the synthesis of nanowires and nanotubes of Bi_2Te_3 and Sb_2Te_3 by electrodeposition (Fig. 3.7). We have previously investigated the Bi_2Te_3 system, and just recently submitted an article for publication on the Sb_2Te_3 wires and tubes. Scanning electron microscopy was employed to characterize the morphology and size of the fabricated Sb_2Te_3 nanowires and nanotubes. Wavelength dispersive spectroscopy analysis confirmed the composition of the fabricated nanowires and nanotubes. The composition of the nanowires fabricated at a cathodic current density of 10 mA/cm^2 and nanotubes fabricated at a cathodic current density of 5.5 mA/cm^2 was found to be ~39% Sb and ~61% Te (2:3 ratio between Sb and Te). The fabricated Sb_2Te_3 nanowire and nanotube arrays were found to be polycrystalline with no preferred orientation. The average lamellar thickness of the nanowires and nanotube crystallites were determined using the Scherrer equation and found to be ~36 nm and ~43 nm respectively. The Seebeck coefficient measurements at room temperature obtained for the Sb_2Te_3 nanowires and nanotubes were +359 μV/K and +332 μV/K respectively, confirming that the Sb_2Te_3 nanowires and nanotubes are *p*-type (Fig. 3.8). The high values of the Seebeck coefficients exceed that of bulk Sb_2Te_3 crystals by almost a factor of 4, making these structures attractive for further study. Electrical resistance measurements indicated that resistance of the Sb_2Te_3 nanowires and nanotubes decreased with increasing temperature, suggesting that these nanostructures are indeed narrow- band gap semiconductors.

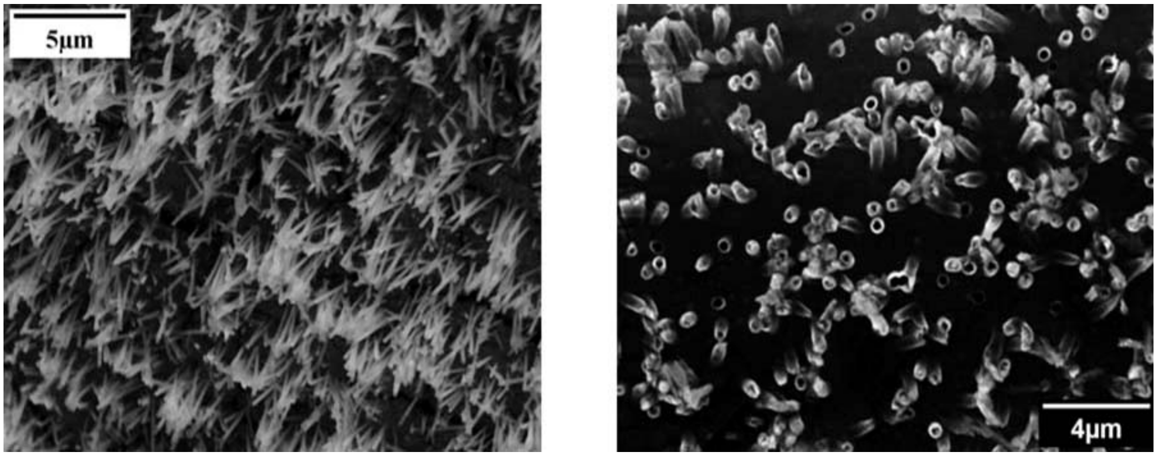


Figure 3.7. SEM images of arrays of electrodepositied nanowires (left) and nanotubes (right) of Sb_2Te_3.

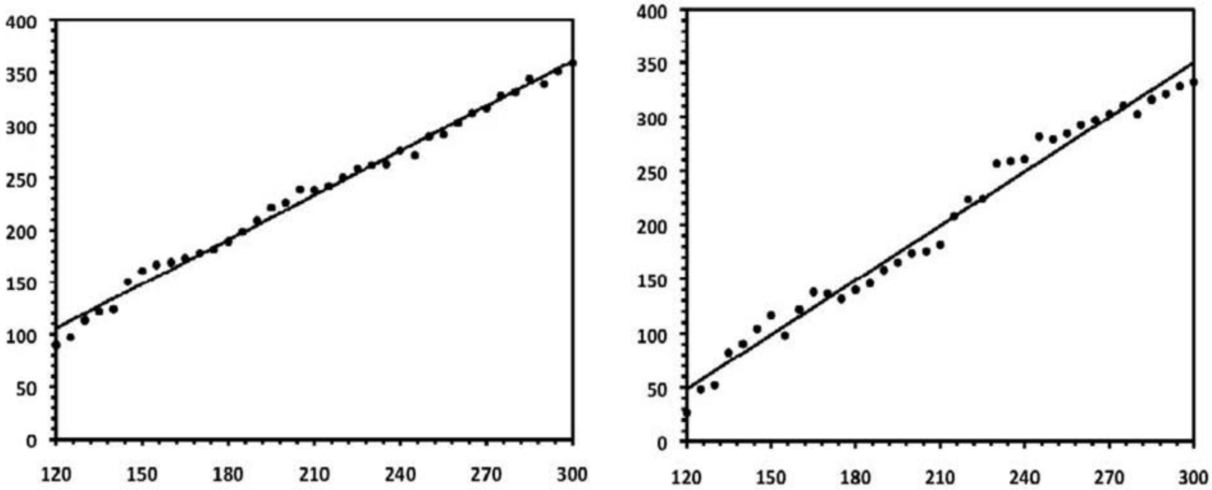


Figure 3.8. Temperature dependence of the Seebeck coefficients for nanowires (left) and nanotubes (right) of Sb_2Te_3.

In addition, we have begun an extensive study into the thermoelectric, transport, and magnetic properties of a series of isostructural compounds, *TM*3, where *T* is a transition metal (Fe, C, Ru, Rh, Os, or Ir) and *M* is the main group elements Ga or In. For trivalent transition metals, such as Fe^{3+} or Os^{3+}, the compounds are semiconducting. However, replacing the trivalent element with a divalent one, such as Co^{2+} or Rh^{2+} results in metallic behavior. Undoped $FeGa_3$ has a very large and negative thermoelectric power (~-450 µV/K), and doping with small concentrations of cobalt reduces this value, but overall produces an enhancement in the power factor (S^2/ρ). This work on Co-doped $FeGa_3$ will soon be submitted for publication. Our current research project in this area is focusing on $Ru_{1-x}Rh_xIn_3$, where a metal-insulator (MI) transition exists as a function x.

This ongoing research program offers postdocs the opportunity to work on novel systems, provides graduate students with an avenue to perform dissertation directed research, and trains undergraduates in a variety of synthesis and characterization techniques. Overall, materials synthesis provides a natural bridge between teaching and research, especially for undergraduates. They are able to make real contributions in a relatively short amount of time. Chris Champagne, an undergraduate physics major, worked last summer on the project involving Ag_8TeGe_6. He is currently a graduate student at Louisiana Tech.

e. Ferroic Materials (Malkinski)

This project deals with nonconventional methods of mutual conversion of electric to magnetic fields. One way of converting electric to magnetic field is developing multiferroic materials consisting of ferroelectric and ferromagnetic materials. More specifically, the ferroelectrics with superior electrostrictive properties can transfer over 90% of electric energy through elastic coupling to ferromagnetic materials with excellent magnetostrictive properties. The materials in the form of powders of ferroelectric PZT and PMN materials and ginat magnetostrictive Terfenol powder have been purchased to make composite materials. Multiferroic composites have been fabricated consisting of a highly magnetostrictive alloy Galfenol (Ga19%Fe81%) in the form of a powder, with grain size of 20 micrometers combined with PMN-15 relaxor type electrostrictive powder. The magneto-electronic properties of this material is being investigated. The student supported through this PKFSI grant is currently developing a new method to measure properties of bulk multiferroic composites by modifying our existing vibrating sample magnetometer. A new collaboration has been initiated between UNO (Malkinski and Stokes) and Dr. Urban, Director of NSF Institute for Polymers at the University of Southern Mississippi. The purpose of this collaborative research is to synthesize new magnetoelectric composites where the piezoelectric material will be replaced by piezoelectric polymer such as polyvinylidene difluoride -PVDF or PVDF-Tr).

f. Nanoassembly of nanoparticles and tubule nanocontainers (Lvov)

Halloysite aluminosilicate nanotubes with a 15 nm lumen, 50 nm external diameter, and length of 800 ± 400 nm have been developed as an entrapment system for loading, storage, and controlled release of anticorrosion agents and biocides. Halloysite ($Al_2Si_2O_5(OH)_4 \bullet nH_2O$) is a two-layered tubule aluminosilicate with multilayer walls. The neighboring alumina and silica layers and their water of hydration create a packing disorder causing them to curve and roll up forming multilayer tubes. We use halloysite nanotubes with a diameter of 50 nm, lumen of 15 nm and length ca 1000 nm. The specific surface area of this halloysite is 105 m^2/g; pore volume is 1.30 mL/g; refractive index is 1.54; specific gravity is 2.53 g/cm^3; and chemical composition is Al_2O_3 - 36.9 %, SiO2 -48.0 %, Fe_2O_3 – 0.4 %, CaO - 0.20 %, TiO_2 - 0.04 %. The outermost surface of halloysite is relevant to silica, and the inner lumen surface may be compared with alumina. Halloysite tubes have ξ-potential of -42 ± 2 mV in water. Strong surface charge makes halloysite easily dispersible in polar media. Fundamental research to enable the control of release rates from hours to months is being undertaken. By variation of internal fluidic properties, the formation of nanoshells over the nanotubes and by creation of smart caps at the tube ends it is possible to develop further means of controlling the rate of release. Anticorrosive halloysite coatings are in development and a self-healing approach has been tested for repair mechanisms through response activation to external impacts. Applications of halloysite as nanometer-scale containers are also discussed including the use of halloysite clay tubes for sustained corrosion inhibitors release, for bone implant composites, and for chemical separations. Halloysite nanotubes are available in thousands of tons, and remain sophisticated and novel nanomaterials which can be used as smart nano-containers. Halloysite is also a "green" material and due to the fact that it is a natural product will not add risk to the environment.

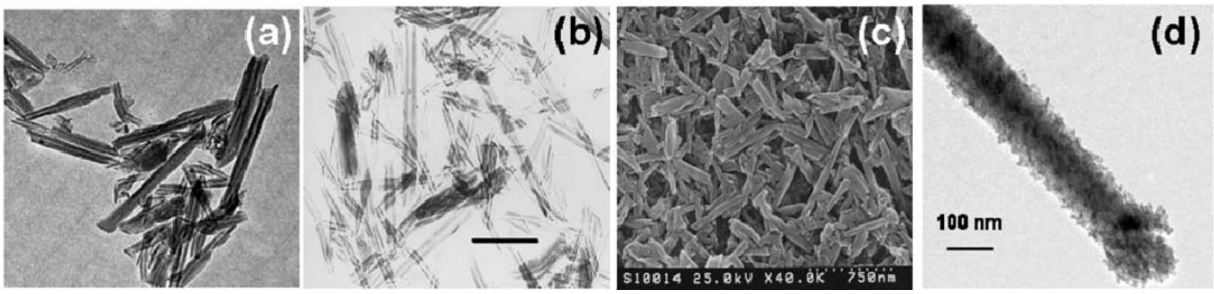
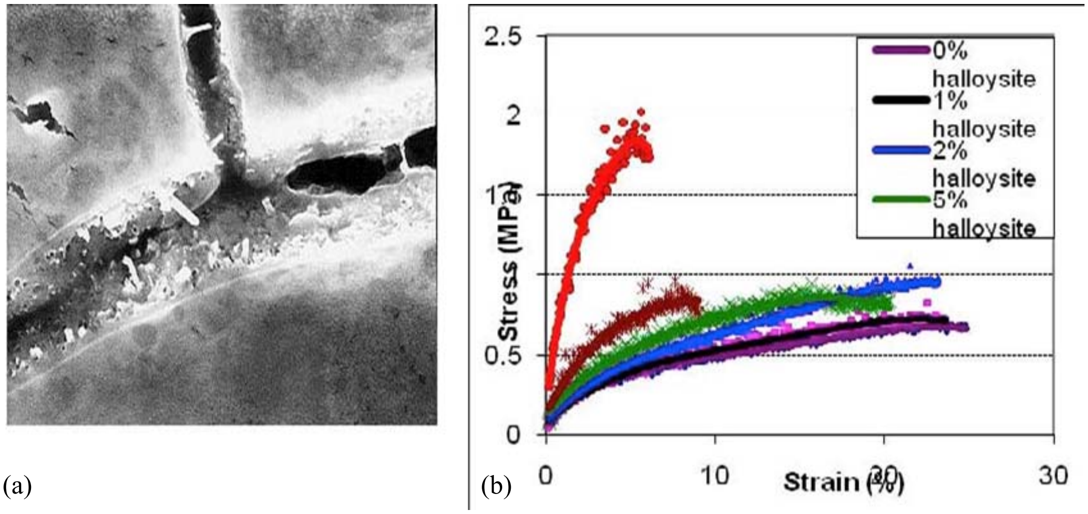


Figure 3.9. Transmission electron microscope images of halloysite nanotubes dispersed in water (a-b), SEM image of layer-by-layer nanocoating with halloysite multilayer (c), and halloysite nanotube coated with polyelectrolyte + 7 nm diameter silica

Halloysite nanotubes loaded with corrosion inhibitor benzotriazole can be admixed into paint to improve its anticorrosion performances as well as the coating tensile strength. Corrosion protection of such coating was evaluated by direct exposure of the coated metal (copper) substrates to highly corrosive media. Loading and release characteristics of benzotriazole from these nanotubes were studied. Benzotriazole release kinetics corresponds to the time needed for formation of metal protective layer through copper complexation. For formation of the tube end stoppers, benzotriazole loaded halloysite was exposed to the solution of Cu(II) ions, and kinetics of the stopper complex formation was analyzed. Tunable release of benzotriazole was achieved by controlling the strength of the stopper complexes, and it may be varied from ten to hundreds hours. A possibility for the tube on/off release switch was demonstrated.

New self-healing technologies for composite materials will reduce the downtime and repair costs of high performance systems as well as potentially reduce system weight by reducing overdesign. For composites used in missile systems, where the graphite composite motor cases are fabricated using a case-on-propellant manufacturing technique, any self-healing strategy must employ a non-catalytic self-healing solution, as the composite may come in contact with flammable material used in the solid rocket motor. This program will develop a self-healing composite for use in filament wound missile applications based on halloysite clay nanotubes filled with a solvent/epoxy blend for healing. We have prepared a proposal for the DoD on this topic based on our preliminary results.



(a)

(b)

Figure 3-10. (a) Scanning electron microscope image of cracks in dry layer of the composite with inclusion of 5 wt % halloysite nanotubes (b) Stress-strain relationship of halloysite / epoxy composite.

New project in response to Louisiana Gulf oil spill: Selective Hydrocarbon Grafting of Halloysite Lumen to Produce Inorganic Micelle-like Petroleum Sorbent Material

The composition difference between external (SiO_2) and internal (Al_2O_3) halloysite wall surfaces allows selective chemical modification of the tube interior to make it hydrophobic. With this we will create inorganic nanomaterial having properties of micelle which will selectively adsorb hydrophobic impurities from water. This selective lumen treatment will be performed with phosphoric fatty acids, such as $CH_3H_2PO_4(CH2)_{3-17}CH_3$ or with polyphosphates. After halloysite cavity which is ca 30-40 % of the total volume is filled with oil, it may be recycled by washing out oil with gasoline or kerosene. One tone of halloysite may adsorb ca 100 kg of oil. Halloysite nanotubes are natural clay material which is mined in USA in the amount of ca 50,000 ton per year, and its' price is ca 5-10 per kg depending on purity and costs of the chemical modification. Halloysite is a "green" material and due to the fact that it is a natural product will not add risk to the sea environment. Figure 3.10 shows a TEM image of the halloysite and a schematic illustration showing the grafting of phosphoric fatty acids into lumen of halloysite and adsorption and controlled release hydrophobic impurities (e.g. petroleum pollutants). This work will be developed in the following year as response to environmental disaster. A detailed proposal on this will be developed and first experiments will begin in July-August.

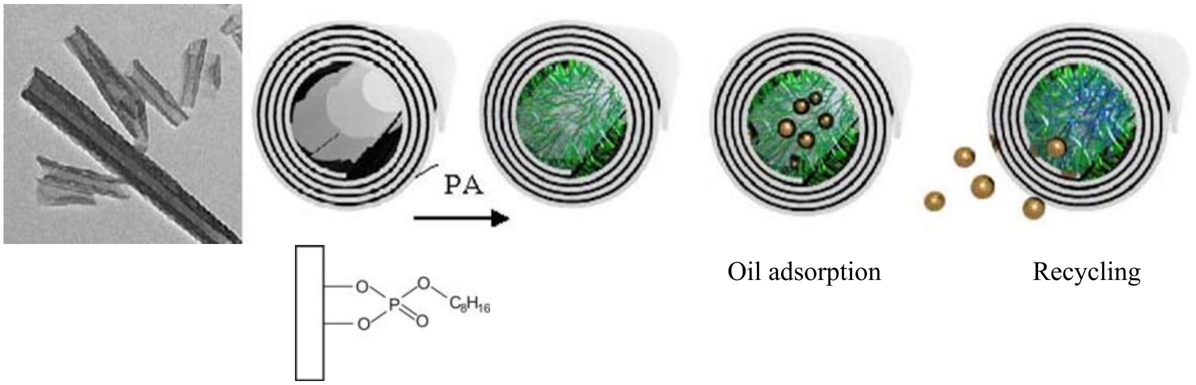


Figure 3.11. Oil sequestering and recycling scheme based on environmentally-friendly halloysite nanotubes.

Partnership Activities

- Stokes (UNO) continues to work with Nanohmics, Inc. (Austin, TX) and United Technologies Research Center on a project concerning flexible thermoelectric devices.
- Dr. Lvov –AMRI annual conference in February 2010, and discussed results with AMRI researchers. Two joint reports were presented at AMRI Mardi Gras symposium. Our clay nanotube samples loaded with silver were prepared for TEM study at AMRI in collaboration with K.L. Stokes.
- A new collaboration has been initiated between UNO (Malkinski and Stokes) and Dr. Urban, Director of NSF Institute for Polymers at the University of Southern Mississippi. A joint proposal to the NSF was submitted in Feb. 2010, titled "Collaborative Research: Negative Index of Refraction Metamaterials with Chiral Nanostructures," $265,000 (UNO).

3. Contributions

- Papers published: 15 papers published in scientific journals covering areas of nanoscience and nanotechnology, functional materials, materials science, physics and electrochemistry.

- Conference presentations: 30 presentations at national and international scientific conferences. Some selected notable presentations are listed below.
  - E. Abdullayev (Lvov, IfM)- Award for the Best Student Poster at 29th Biennial Western Coating Symposium, Las Vegas, NM, October 28, 2009.
  - Debasish Mohanty (Gabrisch, UNO) - First Place Poster Competition at the 215th Electrochemical Society meeting in San Francisco, CA, May 24-May 29, 2009.
  - S. Sumithra (Stokes, UNO) Poster – Nominated for Best Poster award, 2009 Materials Research Society Fall Meeting, November 30-December 4, 2009, Boston, MA.

- Grants and Contracts/Economic Development: Several grants and contracts which have used data and/or ideas generated from the PKSFI research have been received including:
  - Biofuel: Nanoreactors or ethanol production, Y. Lvov, co-PI, Department of Energy, $300,000; Nov 1, 2008 – July 31, 2010

- SBIR Phase II: Compact night vision focal plane array cooling using FlexTEC high-ZTape, K. Stokes, co-PI, Army Research Office/Nanohmics, Inc., Austin TX. $750,000 Jan 2009 to Mar 2011.
- Women in Engineering, D. Davis, co-PI. NSF $750,000, Sept 2009-Aug 2012
- Pending Proposals: 9 Individual and/or multi-PI Federal proposals which use data generated from this PKSFI-FRG. Agencies include NSF (including NSF-EPSCoR RII), NASA, Dept. of Energy and NIH.

- Student Outcomes: Six graduate students and two undergraduates directly supported (Physics, Chemistry, Nanosystems Engineering). There were two PhD graduates (Engineering, LATech). In addition, four summer students supported on other grants (REU) worked on PKSFI-related projects.

- Constructed a high-temperature probe for measuring the Seebeck coefficient. The probe is used in conjunction with a Lindberg/Blue M small tube furnace. Data are collected with nanovoltmeters, and the program is controlled by LabView software.

4. Project Revision

Dr. Heike Gabrisch left the University of New Orleans in March 2010. After consultation with the lead-PI (O'Connor) and other Focused Research Group leaders, it was decided that Dr. Ferdinand Poudeu will now be part of FRG #3. His research will be in the area of thermoelectric nanocomposites and compliments the on-going research of Stokes, Davis and Young.

5. Work Products

Papers:

[1] E. Abdullayev, R. Price, and Y. Lvov, "Halloysite Tubes as Smart Nanocontainers for Anticorrosion Agent Benzotriazole," *ACS Applied Materials and Interfaces,* vol. 2, pp. 1437-1442, 2009.

[2] R. Bellamkonda, T. John, B. Mathew, M. DeCoster, H. Hegab, J. Palmer, and D. Davis, "Microfabrication of nanowires-based GMR biosensor," in *Proceedings of SPIE, Micro- and Nanotechnology Sensors, Systems, and Applications* vol. 7318 Bellingham, WA: SPIE, 2009, p. 73181H.

[3] R. Bellamkonda, T. John, B. Mathew, M. A. DeCoster, H. Hegab, and D. Davis, "Fabrication and testing of a CoNiCu/ Cu CPP-GMR nanowire-based microfluidic biosensor," *Journal of Micromechanical Microengineering,* vol. 20, p. 025012, 2010.

[4] D. Fix, Y. Lvov, and D. Shchukin, "Application of Inhibitor Loaded Halloysite Nanotubes in Active Anticorrosive Coatings," *Advanced Functional Materials,* vol. 19, pp. 1720-1727, 2009.

[5] P. Garrity and K. L. Stokes, "Thermal Noise as a Spectroscopic Tool to Determine Transport Properties," *Philosophical Magazine,* vol. 89, pp. 2129-2147, 2009.

[6] P. L. Garrity and K. L. Stokes, "Direct Measurement of the Absolute Seebeck Coefficient for Pb and Cu at 300 K to 450 K," in *Thermoelectric Materials—Growth, Properties, Novel Characterization Methods, and Applications, Mater. Res. Soc. Symp. Proc.* vol. 1267, J. D. Baniecki, Ed. Warrendale, PA: MRS, 2010, pp. 1267-DD11-0.

[7] N. Haldolaarachchige, W. A. Phelan, J. Y. Chan, and D. P. Young, "Chemical Doping

Effect on Thermoelectric Properties of Intermetallic Narrow Band Semiconductors ($TMGa_3$: TM = Fe, Ru & Os)," *Journal of Applied Physics,* **to be submitted**, 2010.

[8] A. B. Karki, Y. M. Xiong, D. P. Young, and P. W. Adams, "Superconducting and magnetotransport properties of $ZnNNi_3$ microfibers and films," *Physical Review B,* vol. 79, p. 212508, 2009.

[9] D. Pinisetty, M. Gupta, A. B. Karki, D. P. Young, and R. V. Devireddy, "Fabrication and Characterization of Electrodeposited Antimony Telluride Nanowires and Nanotubes," *Chemistry of Materials,* **submitted**, 2010.

[10] S. Sumithra, D. K. Misra, C. Wei, H. Gabrisch, P. F. P. Poudeu, and K. L. Stokes, "Solvothermal synthesis and particle size distribution analysis of Bi, Sb and $Bi_{0.88}Sb_{0.12}$ nanoparticles," *Journal of Nanoparticle Research,* **submitted**, 2010.

[11] S. Sumithra, N. J. Takas, N. L. Henderson, W. M. Nolting, D. M. Misra, P. F. P. Poudeu, and K. L. Stokes, "Metal Nanoinclusions (Bi and Ag) in Bi_2Te_3 for Enhanced Thermoelectric Applications," in *Thermoelectric Materials—Growth, Properties, Novel Characterization Methods, and Applications, Mater. Res. Soc. Symp. Proc.* vol. 1267, J. D. Baniecki, Ed. Warrendale, PA: MRS, 2010, pp. 1267-DD07-11.

[12] S. Sumithra, N. J. Takas, D. M. Misra, P. F. P. Poudeu, and K. L. Stokes, "Nanocomposites of Bi_2Te_3 with Metal Nanoinclusions for Advanced Thermoelectric Applications," in *Energy Harvesting - From Fundamentals to Devices, Mater. Res. Soc. Proc.* vol. 1218E, H. Radouski, J. D. Holbery, L. H. Lewis, and F. Schmidt, Eds. Warrendale, PA: MRS, 2009.

[13] V. Vergaro, E. Abdullayev, R. Cingolani, Y. Lvov, and S. Leporatti, "Cito/biocompatibility and Uptake for Clay Nanotubes," *Biomacromolecules,* vol. 11, pp. 820-828, 2010.

[14] C. Yelleswarapu, E. Abdullayev, Y. Lvov, and D. Rao, "Nonlinear Optics of Nontoxic Nanotubes," *Optics Communications,* vol. 283, pp. 428-441, 2010.

Presentations:

[1] Y. Lvov, R. Price, and E. Abdullayev, "Halloysite- benzotriazole nanocomposites, low cost additives to metallic coatings for corrosion protection," in *29th Biennial Western Coating Symposium*, Las Vegas, NV, October 25-28, 2009

[2] S. Sumithra, N. J. Takas, N. L.Henderson, W.M.Nolting, D. K.Misra, P.F.P.Poudeu, and K.L.Stokes, "Effect of Metal Nanoinclusions in bulk $Bi_{2-x}Te_{3+x}$ and $Bi_{0.5}Sb_{1.5}Te_3$ system," in *Materials Research Society Symposium*, San Fransisco, CA, April 4-9, 2010.

[3] K. L. Stokes, "Progress in PKSFI Focused Research Group 3: Energy Conversion and Storage Materials," in *12th Annual DARPA-AMRI Symposium and Review*, New Orleans, LA, Feb. 11-12, 2010.

Report of Inventions:

[1] D. Mills and Y. Lvov, “Smart Bioactive Nanocoating with Sustained Drug Release Capability for Implants, Wound Repair rand Tissue Regeneration,” April 23, 2010. ROI #2010-08

[2] Y. Lvov, “Selective Hydrocarbon Grafting of Halloysite Lumen to Produce Inorganic Micelle-like Petroleum Sorbent Material,” May 14, 2010. ROI #2010-12

PKSFI Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04

Matthew A. Tarr
(PKSFI Broader Impacts, 2009-2010)

Broader Impacts (Educational and Commercial Outreach)

1. **Personnel:** List all key personnel and other staff who provided *significant* contributions to the project. Provide information about the types of contributions made by each listed participant and controls in place to ensure that these contributions are adequate to the project's requirements.

Matthew Tarr, Professor, Dept. of Chemistry, University of New Orleans – planned and coordinated academic year outreach activities (Science*REACH* program) with subcontractor, Communities In Schools of New Orleans (CISNO); reviewed CISNO quarterly reports; presented program updates at quarterly meetings; conducted site visit to CISNO to evaluate subcontractor progress; coordinated planning and recruiting for summer outreach program; supervised by project PI, Dr. Charles O'Connor.

Sara Massey, Director, Communities In Schools of New Orleans – directed all activities carried out by CISNO including academic year outreach programs in New Orleans public or charter schools; responsible for hiring and supervising Science*REACH* program coordinator; evaluated via quarterly reports submitted to Dr. Tarr and by site visits conducted by Dr. Tarr.

Deidra Schauer, Science*REACH* Coordinator, Communities In Schools of New Orleans – implemented academic year outreach activities; directly supervised and evaluated by Sara Massey.

2. **Activities and Findings:**
   - Describe major research and educational activities undertaken in this reporting period

This portion of the project included two components: 1) a summer research program for high school students and 2) an academic year support program (Science*REACH*) for high school students.

The summer research program hosted 12 high school student participants during the summer of 2009 and 10 high school student participants during the summer of 2010. Each participant conducted research on an independent project in chemistry, physics, materials science, biology, or psychology. In addition, weekly seminar programs allow for discussion of current scientific issues, general research concepts, and scientific ethics.

During this project year, the Science*REACH* program worked in five schools; McMain Secondary School, Sarah T. Reed High School, George W. Carver High School, Walter L. Cohen High School and John McDonough High School. The programs implemented included: Rocketry Program, Forensics Program, in-class presentations, field trips, in-class assistance, college assistance and tutoring as well as mentoring, which combined reached a total of 263 students across 82 sessions vs. 204 students last year, representing a 30% increase.

- Describe and provide data supporting the major findings resulting from these activities

The summer research component of this project hosted 12 high school student participants in the summer of 2009. A summary of representative student research projects is given below.

Kewe Ukpolo, Synthesis of TiO_2 nanowires by hydrothermal method
Titania (TiO_2) is getting more attention in recent years as it can exhibit a wealth of important photovoltaic, semiconductor photo-catalyst, catalytic support and gas-sensing properties especially when prepared as nanomaterials. Nanowires are essentially shrunken down versions of modern day wires and are made of various metals. We believe by creating nanowires out of titania we can UV protection more efficient, can also reduce the cost of making solar cells, and also make Photocatalysis (photocatalytic activity of titania results in the material exhibiting self cleaning and disinfecting properties under exposure to UV radiation.) In this research we investigate the effect of the parameters (reagent, duration, concentration etc.) on the morphologies of TiO_2 nanowires. We also achieved thin TiO_2 nanowires by hydrothermal process. The synthesis and characterization of these novel analogs will be presented.

Corinne Bachaud, Differences in Magnetic Signatures of Various Types of Music on Cassette Tape
This experiment was conducted to observe differences in the magnetic signature of different types of music recorded on the magnetic tape in an audio cassette. The types of music tested include heavy metal, techno, acoustic, classical, and hip-hop, as well as a control with no music at all. The samples were tested on the Vibrating Sample Magnetometer to find any differences in the starting points of the magnetic graphs. These starting points varied quite a bit from each sample. The sample was them measured with the Magnetic Force Microscope to observe any differences in the magnetic domain images, of which there were very few, most likely due to a magnetic component of the machine.

Arianna E. Rivera, Synthesis and Characterization of the Quaternary Selenides $FeSn_3Bi_4Se_{10}$ and $NiPb_3M_4Se_{10}$ (M = Sb, Bi)
Three new quaternary mixed metal selenides with compositions $FeSn_3Bi_4Se_{10}$, $NiPb_3Bi_4Se_{10}$ and $NiPb_3Sb_4Se_{10}$ were synthesized via solid-state reactions involving elemental Fe, Ni, Sn, Pb, Sb, and Se at 500°C. Powder X-ray diffraction (PXRD) and Differential Scanning Calorimetry (DSC) suggested that all the reaction products were single phase. The compounds melt incongruently with onset temperatures at 629 °C, 685 °C and 574 °C for $FeSn_3Bi_4Se_{10}$, $NiPb_3Bi_4Se_{10}$ and $NiPb_3Sb_4Se_{10}$ respectively. Electronic charge transports measurements on $FeSn_3Bi_4Se_{10}$ and $NiPb_3Bi_4Se_{10}$ indicated that both phases are n-type semiconductors with room temperature electrical conductivity and thermopower values of 0.254 S/cm and $-62.5\mu V/K$ for $FeSn_3Bi_4Se_{10}$; and 709 S/cm and $-52\mu V/K$ for $NiPb_3Bi_4Se_{10}$.

The Science*REACH* component of this project reached a total of 204 students across 225 different sessions.

(1) Rocketry After School Program: This program continued from last year, and was conducted at McMain Secondary School. In the Spring of 2010, David Koscielniak, a mentor from the National Association of Rocketry, is assisting students in designing and building their competition rockets. Students also designed and built bottle rockets and model rockets and launched them. The program served a total of 40 students, and was held for 10 mentoring sessions this quarter and will continue in the spring.

(2) Forensics After School Program: The Forensics Program has also continued from last year. The program met seven times between August 2009 and November 2009; there were 35 students involved in 5 sessions. The students worked in different areas of Forensics, such as: DNA Analysis, Forensics labs, which included pH Testing and Fingerprint analysis, Forensic Math, Forensic Anthropology, Handwriting Analysis, Computer Forensics, and Blood Typing. Detective Tanisha Santemore, a Forensic Scientist/Criminologist II, taught students how to investigate a crime scene, collect evidence, and analyze evidence in a lab. In addition, the students participated in various experiments about data collection.

(3) In-Class Presentations: Between September 2009 and November 2009 there were 3 In-Class Presentations. 1 Loyola Service Learner, 5 Xavier Service Learners, and 3 Tulane Service Learners gave students a presentation about college life. The college students and the high school students met in small groups so that the high school students could ask questions about scholarships, the admissions process, and college life. They presented to 80 students during 7 sessions in Mr. Brown's Physical Science class, Mr. Peace's Biology class, and Mr. Crooks Math GEE class. The presenters talked to the students about college, careers in health sciences, and spoke specifically about their chosen majors.

(4) Field Trips: In addition to exposing students to a variety of STEM fields, Science*REACH* has expanded the field trip component in order to increase students' hands on experiences in areas of interest to them. As part of this there were four field trips between September 2009 and November 2009. Students from Sarah T. Reed and Walter L. Cohen visited the science departments at Xavier University of Louisiana. Dr. Anderson Sunda-Meya , a physics professor at Xavier did four presentations to 195 students on Nanotechnology. Visiting students also participated in 8 demonstrations conducted by the Xavier's physics majors. Students ended the visit with a campus tour and eat lunch and ask questions about majors in the STEM fields.

(5) Tutoring/ Mentoring: Gabriel Fette, the Science*REACH* AmeriCorps member, Catherine Cresson, and service learners from Delgado Community College, Tulane University, Loyola University, and Xavier University have tutored at George W. Carver High School, Eleanor McMain High School, John McDonough High School, and Sarah T. Reed High School this quarter. The services were as follows:

- Reed - 28 students for a total of 24 hours on 12 days
- Cohen - 60 students for a total of 129 hours on 31 days,
- McMain - 6 students for a total of 30 hours on 15 days
- John Mac - 32 students for a total of 12 hours on 6 days.
- Carver- 26 students for a total of 36 hours on 18 days

In addition to individual tutoring and mentoring, Gabriel Fette, Catherine Cresson, and the service learners have provided in-class assistance by being additional support for the students as well as helping teachers with labs and experiments. In addition to using the service learners at Delgado, Loyola, Tulane, and Xavier, Science*REACH* is planning to incorporate service learners from Dillard University and the UNO STARS from University of New Orleans into the tutoring and mentoring curriculum.

(6) College Assistance: The Science*REACH* Coordinator worked individually with students helping them pick colleges that had a science curriculum best suited to their needs, and helped them map out their college classes and requirements. This fall Science*REACH* introduced the scholarship component of the college assistance curriculum. Sara Massey and Deidra Schauer attended the National Scholarship Providers Association Convention in New Orleans, LA. Science*REACH* is now equipped to customize scholarships to fit the students' needs as well as utilize a database that will expose students to scholarships on a local, regional, and national level. The scholarship information and assistance has been shared with juniors and seniors at Sarah T. Reed High School, Eleanor McMain High School, and Walter L. Cohen High School.

Science*REACH* is adding one new component to the curriculum. The Science of Sport, which was developed by Gabriel Fette, will encourage outdoor activity while reinforcing grade level expectations. This program will expose the students to careers in the health sciences. In this program we aim to serve more than 150 students at Carver High, Cohen High and John McDonogh High.

- Describe the opportunities for faculty recruitment, retention and development, as well as post-doc, graduate and undergraduate student training provided by your project

There have been multiple interactions with UNO Personnel. The Science*REACH* Coordinator continues to cultivate the relationship with the UNO STARS Program. The Coordinator continues to work with the UNO Admissions Office in order to plan for a UNO Admissions counselor to be present at the college day.
Science*REACH* also continues to work with UNO's Upward Bound Program to provide the STEM enrichment portion of the Upward Bound Summer Program.

- Describe the nature and scope of partnership activities

  CISNO served as the primary agency for design, coordination, and implementation of all academic year outreach activities as described above.

- Describe any problems encountered during the last year of project activities.

  No problems were encountered.

3. **Contributions:** Summarize efforts made to build research and education capacity, secure external federal and private-sector funding, build infrastructure, contribute to economic development, and ensure project sustainability over the long term.

Summer research programs substantially impact the education and career paths of high school participants. Many of our participants go on to study science or engineering in college. This influx of students helps to provide future employees in STEM fields.

Academic year outreach programs were designed to attract high school students into college study in science and engineering fields. All schools targeted in this study have student bodies that are majority African-American. Furthermore, these schools have a high percentage of students receiving reduced or free lunch. Developing these human resources will provide a stronger base for science and technology development within the state of Louisiana.

4. **Project Revision:** Provide a listing of and explanation for any significant changes in the work plan for upcoming year, including any changes in the amount of investigators' time devoted to the project. If you made significant changes to the project design as outline in the proposal during the past year, please list and explain the changes, the purposes for the changes, and the results.

Several programs developed by CISNO will continue to be implemented in project year four. Refining of these programs will be undertaken in order to make them more efficient, but no major changes are foreseen. Efforts will be made to increase the number of undergraduate students involved in the project.

5. **Work Products:** List any tangible products (e.g., research publications and/or presentations, patents, licensing agreements etc.). Please combine all products into one document.

"Synthesis and Characterization of the Quaternary Selenides of $FeSN_3Bi_4Se_{10}$ and $NiPb_3M_4Se_{10}$ (M=Sb,Bi)," Arianna E. Rivera, Ronald J. Coats Jr., Nathan J.Takas, Clarence J. Anglin, P. Ferdinand P. Poudeu, Student Research Poster Session, American Chemical Society Louisiana Local Section, September 30, 2009, University Center Ballroom, Xavier University of Louisiana, New Orleans, LA.

PKSFI Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04
Leszek M. Malkinski
(PKSFI-ESIP Clean Room, 2009-2010)

Title: Nanodevice Processing Laboratory

1. Personnel:

Leszek Malkinski, Associate Professor of Physics and Materials Science. Dr. Malkinski is in charge of design and management of this part of the project.

2. Activities:

The aim of this project is to provide research support for AMRI and collaborating institutions with the cleanroom facilities and technology to do competitive research in the field of nanofabrication. The evaluation of the purity of the air is based on number of dust particles in a unit volume. “Class 1000” cleanroom is the minimum requirement for the research activities on nanotechnology. This requirement was exceeded by designing a higher class purity cleanroom with re-circulating air. Due to this design the number of particles present in the unit volume dropped to below 100, which elevates the rank of the cleanroom to “class 100”.

The Installation of the laboratory was completed in December 2008 and after testing by the independent professional contractor (ENV Services) a certificate of Compliance was issued, stating that our Nanodevice Processing Laboratory meets the ISO standards of “class 100” cleanroom.

In January, February and March 2009 the technological and measurement equipment installed and the laboratory:
- mask aligner and UV exposure station for photolithography,
- spin coater and hot plate for photoresist coating,
- ion milling system for dry etching of the patterns for devices,
- wire bonder for making electric connections with micron thick wire.
- atomic force microscope for characterizing the structure of the devices.

Also, in the same time period the laboratory was fully furnished with chairs, desks, tables and cabinets which meet class 100 cleanroom specifications.

The equipment was tested within next 3 months and in the summer 2009 first group of users of the Nanodevice Processing Laboratory has been trained in using the instruments and equipment and obeying the cleanroom rules. The remaining funds in the Nanodevice Processing Laboratory were used for the purchase of coveralls, boots and hoods for the users of the laboratory.

Currently about 20 users from AMRI received cleanroom training and are qualified for unrestricted use of the Laboratory. In addition two users from the Tulane University, from the collaborating group of Prof. Z. Mao got access to our laboratory.

The laboratory has been extensively and successfully used for realization of the PKFSI and other research projects by the faculty, postdoctoral researchers and student from UNO and collaborating institutions.

Annual Report for Year 2 (ending 6/30/2009)

A Center for Advanced Materials and Nanotechnology in AMRI
at the University of New Orleans

Louisiana Board of Regents Contract
LEQSF(2007-12)-ENH-PKSFI-PRS-04

Annual Progress Report - 2009

June 30, 2009

SUMMARY

The purpose of this report is to provide an annual progress report for the LA Board of Regents funded project entitled: "A Center for Advanced Materials and Nanotechnology in AMRI at the University of New Orleans" through LA Board of Regents Contract LEQSF(2007-12)-ENH-PKSFI-PRS-04 during the second year of the project from July 1, 2008, through June 30, 2009. Included are progress reports from the three Focus Research Groups (FRGs) and the Broader Impacts group which comprise the organization of the overall project, plus a progress report on the Clean Room Project for which received ESIP funds for development of a Nanodevice Processing Laboratory to support ongoing research projects in nanotechnology at UNO.

The second year of this project was very productive and has been successfully completed. A research consortium organization for this project continues in place and includes as participants the University of New Orleans and the following five partner institutions: Louisiana State University, Tulane University, Louisiana Tech University, Children's Hospital, and Communities in Schools of New Orleans, Inc. The subcontracts from the University of New Orleans to the five collaborating partner institutions continue in place and the work at these institutions is progressing well. The overall effort of the project is organized into three FRGs based on technical areas and one Broader Impacts group, which provides community outreach support for the project. These groups are: FRG-1: Nanomaterials for Biological Sensing and Imaging; FRG-2: Nanoscale Mechanical Devices; FRG-3: Nanomaterials for Energy Conversion and Storage; and the Broader Impacts (Educational and Commercial Outreach) group. All research activities within each group are progressing well.

Report for LEQSF(2009-06)-ENH-PKSFI-PRS-04

Weilie Zhou

(PKSFI FRG 1, 2008-2009)

1. Personnel: List all key personnel and other staff who provided *significant* contributions to the project. Provide information about the types of contributions made by each listed participant and controls in place to ensure that these contributions are adequate to the project's requirements.

A. AMRI personnel involves with this project

- **Weilie Zhou**- co-Leader of FRG 1. He is mainly responsible for overall management for biosensor part and coordination of AMRI tasks with other partners
- **Zhongming Zeng**-Postdoctoral Research Associate; Zhongming is in charge of nanowire assemble, e-beam nanolithography, and detection of antigen fabricated from Children Hospital of LSUHSC.
- **Hui Ma**-Ph.D student: She is fabricating magnetic nanocarriers for drug delivery and meanwhile she is in charge of modifying the nanowire surface for bio-detection.
- **Charles J O'Connor**-Principal investigator, investigating the whole project and looking for the new grant for whole teams. He is also directing magnetic nanoparticle synthesis.
- **Daniela Caruntu**-Postdoctoral Research Associate; She is in charge of magnetic nanoparticle synthesis for biomedical application.
- **Zeev Rosenzweig**-Professor in Chemistry, His group is fabricating quantum dots for biomedical imaging.

B. CAMD personnel involved with this project

- **Jost Goettert** – main responsibility is overall project management for CAMD part and coordination of CAMD tasks with partner efforts;
- **Yoonyoung Jin** – Research Associate (RA); Jin is leading senior researcher at CAMD with expertise in lithography, thin films, system integration, and measurements; he was carrying out RIE process and was in charge of the rapid prototyping solutions for microfluidic;
- **Kyung-Nam Kang** – PhD student; he is supporting Jin with lithography and thin film deposition/etching related processing;
- **Proyag Datta** – Research Associate (RA) 5; he joined the team in the last 2 months providing expertise in molded microfluidic structures and fluidic system control and integration; he is currently molding hard plastic fluidic chips and works on chip integration with Si sensors.

C. LSUHSC Children Hospital involved with this project

- **Seth Pincus**-co-leader of this project. He is responsible for antigen engineering.
- **Chad Gustafson** (50%) **–** Bachelor's level Technician, working on the engineering
- **Grace Maresh** –Technician, working on quantum imaging.

D. Louisian Tech personnel involved with this project

- **Mark DeCoster**-Professor in biochemistry; he is in charge of biocompatible testing and alive cell detection
- **James McNamara**-Ph.D student; he is in charge of alive cell culture and testing
- **Ruturaj Masvekar**- M.S student; he is responsible for toxicity test for magnetic carriers and nanowires

2. **Activities and Findings:**

I. Metal Oxide Nanowire for biosensor application

A. Field effect transistor fabrication based on In_2O_3 nanowires

In the second year, we have improved the In_2O_3 nanowire field-effect transistors (FET) by bottom-up method. The In_2O_3 nanowire devices were fabricated into FETs by e-beam lithography, metal evaporation and lift-off process. The basic electrical transport properties and biological response of In_2O_3 nanowire device were also characterized.

Figure 1a shows the *I-V* curves of a typical In_2O_3 device with applying different gate-voltages. It was found that the device is significantly sensitive to electrostatic gating and the nanowire is working as n-type channel. This can be clearly observed in the I_{ds}-V_g curve shown in Figure 1b, where a change up to three orders in device conductance was observed when V_g was swept from -25 to +25V. Meanwhile, the *I-V* curves are found to be linear at low bias, which indicates the good ohmic contact formed between nanowire and metal electrodes. This is good to investigate the biological detection.

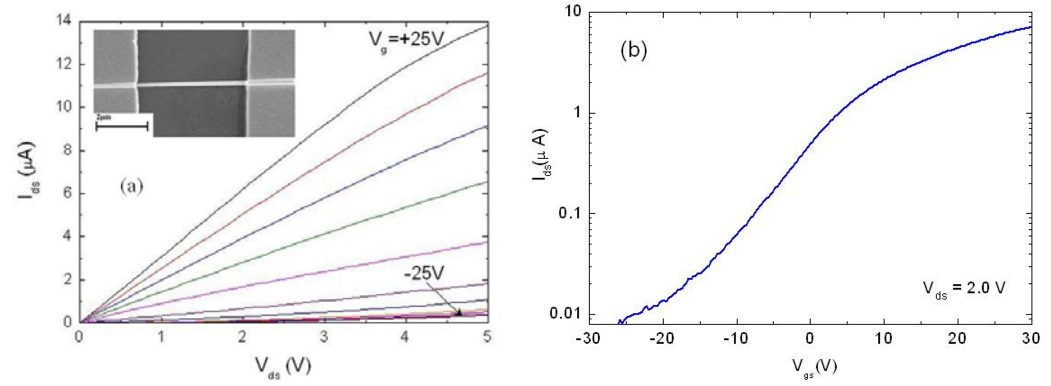


Fig. 1: (a) I-V curves of a typical In_2O_3 device with respect to back-gate voltage (V_g = from +25 to -25V with a step of 5V). The inset is the corresponding SEM image. (b) The corresponding I_{sd}-V_g curve at V_{sd} of 2.0V.

B. Microfluidic channel integration

The In_2O_3 FET devices were used to work as biological sensors. Firstly, PMMA was used to passivate the devices. The stability of the devices was investigated by measuring the conductance as a function of time (shown in Fig. 2). It can be seen that the conductivity of the nanowire is very sensitive to the environment, e. t., a peak in conductance appears once the noise is introduced. Therefore, the noise is a big obstacle for the stable and reliable measurement.

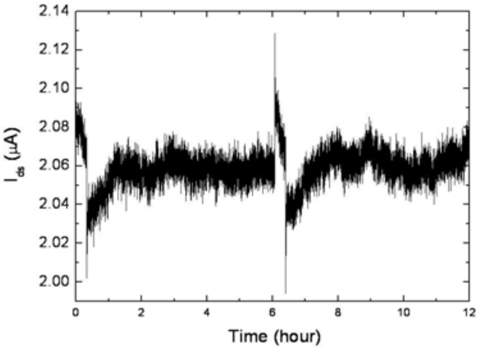


Fig. 2: Current-time dependence of a typical In_2O_3 device in dry air.

In order to resolve this noise issue, the microfluidic system is necessary to introduce into our measurement. Figure 3(left) shows a device integrated with microfluidic system. The two pipes and PDMS microchannel form a microfluidic system. After combined with microfluid channel, we investigated the basic electrical properties. Two devices show the FET properties, and others were broken during the integrated process. Figure 3 (right) shows the *I-V* curves of one device with applying different gate-voltages, indicating the nanowire is working as n-type channel.

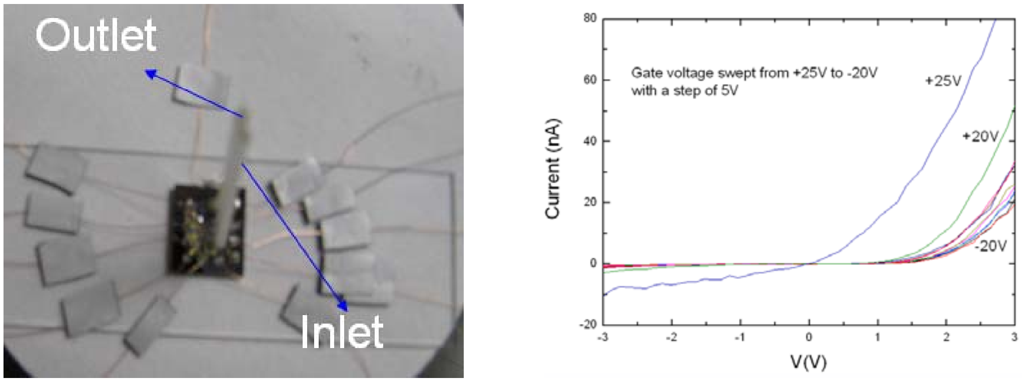


Fig. 3: (Left) SEM image of one chip device integrated with microfluid channel. (Right) I-V curves of one typical FET device with respect to back-gate voltage (V_g = from +25 to -20V with a step of 5V).

C. Biological detection study based on In_2O_3 nanowires

Initial biological tests of In_2O_3 FET devices were done by introducing biological solution through pipe. In order to repeatable test the reaction of the nanowire to surface bonded molecules, it is necessary to flow fluids across the nanowire surface in a precisely controlled manner. This step is also an important step for further development towards packaged, user-friendly sensors with integrated microfluidics.

We injected PBS buffer at 0.1M, and Ricin antibody and antigen (0.03mg/ml) into the microfluidic channel in sequence. Figure 4 shows the current-time curve when exposure to different solutions. It can be clearly found that PBS increased the conductivity of the nanowire. At first we hoped to inject PBS buffer into the channel to establish baseline conductivity. However, the conductance is unstable as shown in Figure 4. Although we observed the response of ricin antibody and antigen, it is not sure that the conductance change is really from the ricin at present.

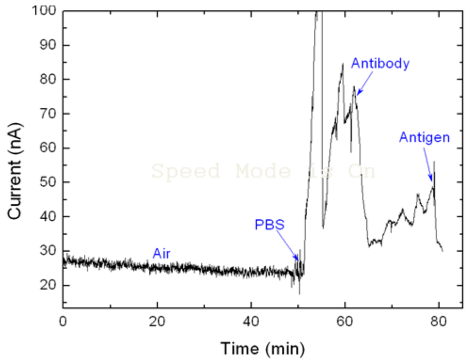


Fig. 4: PBS buffer, and biological response of an In_2O_3 device.

The reason for unstable conductance may be attributed to the poor passivation. In our experiment, we used PMMA to passivate the device, but PMMA layer may worsen when exposure to solution, and further affects the electrical properties. In the future, we'll employ metal insulator (for example, Si_3N_4) to passivate the device and do dynamic biological detection.

Ⅱ. Silicon Nanowire for biosensor application

The mechanism of nanowire sensors is based on carrier density changes when targeting molecules attach on the nanowires surface. Applying a gate voltage on the nanowire will simulate the carrier change process in the nanowire channels. So, the effect of gate voltage on the conductivity change of nanowire is an efficient benchmark on the sensitivity of nanowire based sensors. Up to now, most of nanowire based biosensors were fabricated through bottom-up method. However, this method suffers from certain limitations such as incompatibility with modern semiconductor manufacturing techniques and its large scale integration.

One solution is to utilize semiconductor processing techniques (top-down) to fabricate Si nanowire devices. The main advantage of this method is that the location of the nano-wires is now pre-determined by the lithography process and doesn't require 'manual' wire alignment.

Figure 5 illustrates the process of top-down approach, summarized as follows: i) Starting with silicon-on-insulator (SOI) wafer that consists of a 380nm buried oxide layer and a 100~280 nm silicon layer on insulator; ii) Cr mask fabrication by e-beam patterning, Cr metal deposition and liftoff process; iii) Silicon etching by a reactive ion etching system and Cr mask remove by Cr etching solution; iv) After that Ti/Au electrodes deposition by e-beam pattern, metal deposition and liftoff; v) Finally, depositing Si_3N_4 insulator layer to passivate the electrodes and exposing the Si nanowires.

In the process the e-beam lithography and the reactive ion etch are the key steps to obtain the Si nanowires with high quality. The former defines the nanowire size and the latter dominates the performance of this method. If the etching time is not enough, the Si layer would etch incompletely. In contrast the insulator layer (SiO_2) may remove partially, worsening the dielectric properties of nanowire devices. Initial etching conditions were using an ICP power of 600 W, an Rf power of 15W, and a pressure of 20mtorr with CF_4 as etch gas. The results are shown in Figs.6 clearly stating that more process optimization is required to achieve smooth sidewalls of the channel/wire structures.

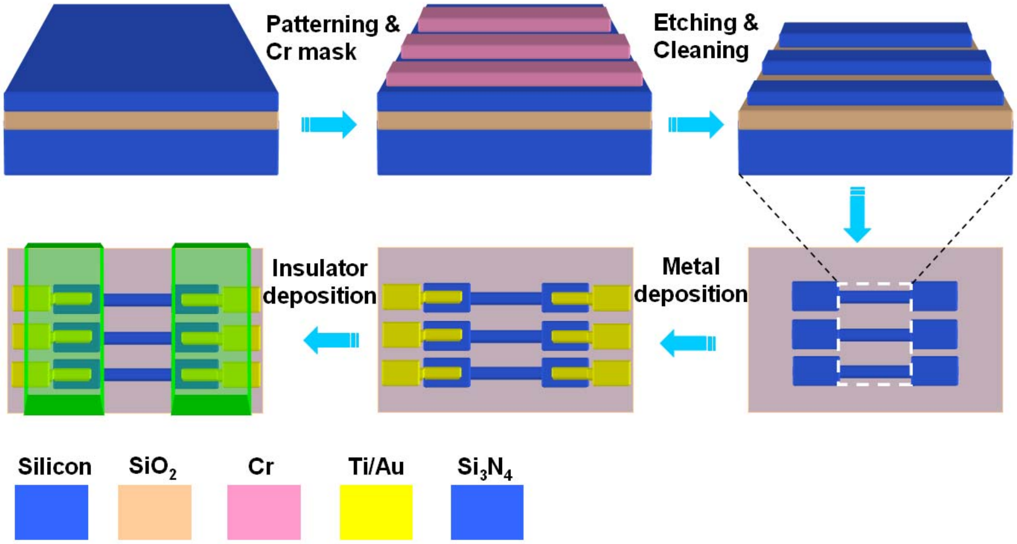


Fig. 5: Schematic diagram showing the Si nanowire device fabrication process through top-down method

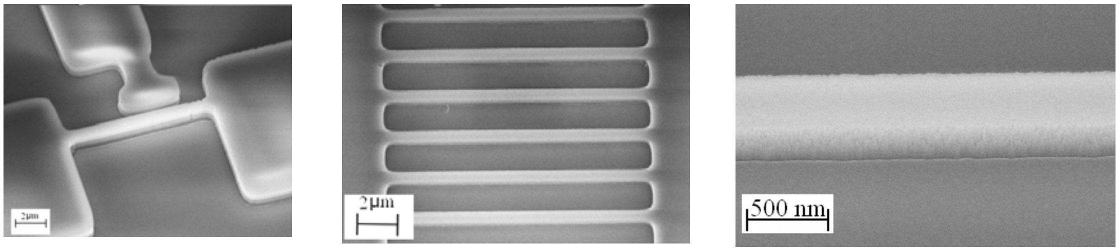


Fig. 6: Examples of etched nanowires and channels, the Cr layer was nearly etched away allowing the gas to attack the covered silicon layer and also partly the SiO_2 layer.

In order to enhance etch contrast between Au and Si/SiO_2 another Cr layer was added as well as leaving the e-beam resist on top of the metal layer for further protecting it from the etch gas. While using of Cr for a high-selectivity etch-mask layer, the etching conditions of ICP power and bias voltage could be enhanced to control the etch-rate and uniformity. Figure 7 (a) and (b) show the SEM image of single and double Si nanowire device with optimized process, the width and height of the Si nanowire is about 300nm and 280nm, respectively. Meanwhile, it can be seen that the Si nanowire has good shape. The basic electrical properties were investigated by measuring current (I)-voltage (V) curves as shown in Figure7 (c) and (d). I-V curves shows the Si nanodevices have good conductivity, indicating the Si nanodevices are suitable for biological detection.

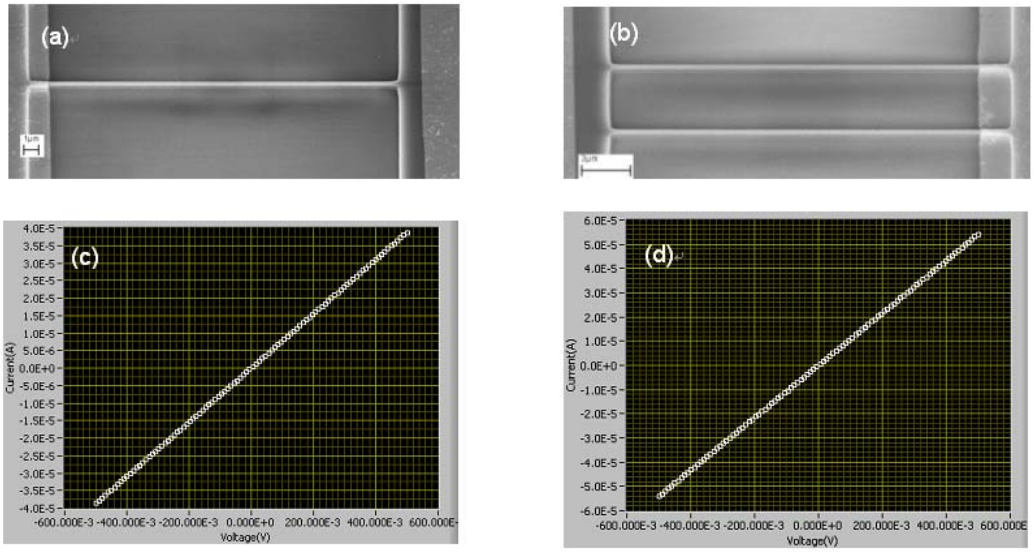
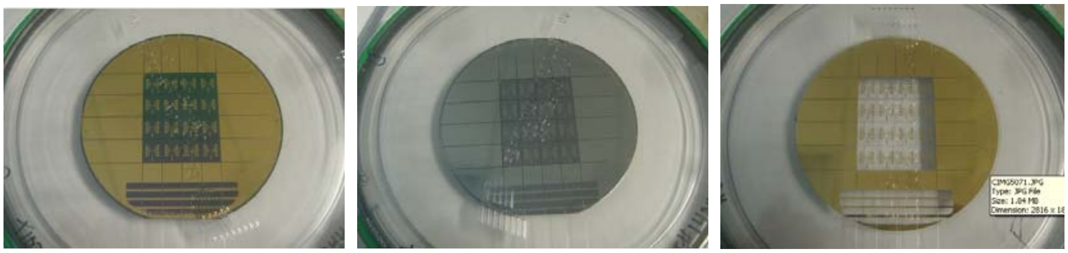


Fig.7: SEM image of single (a) and double (b) Si nanowire device, (c) and (d) are the corresponding current- voltage curves.

In preparation of using dies from different materials as sensor chip embedded into the fluidic stack different substrates have been shipped out for dicing and received back recently (Fig. 8). The initial metrology indicates that the tolerances of diced chips are tightly controlled and that integration of these chips with fluidic PMMA modules should yield similar results as achieved with glass dies so far.

Figs.



(a) (b) (c)

Fig. 8: Diced sensor chips from (a) SiO_2/Si wafer (b) SOI wafer (c) glass wafer.

Ⅲ. Microfluidic Engineering Research

A. Status last report and novel approach

Figure 9 illustrates the principle arrangement of the biosensor device. A Si-based nanowire electrode chip is sealed with a polymer fluidic cap which allows for introduction of sample fluid into the cavity. Through selective binding to molecules (Antigens) attached to the nanowires a change in electrical signal from the nanowire will be induced and allows registration of the presence of specific molecules in the sample.

The electrode pattern is covered with an insulating resist layer leaving only defined areas (mainly nanowire) of the electrode pattern accessible to fluids carrying biological samples across the electrode area. Figure 10 illustrates a basic experimental setup using PDMS caps with electrode test structures reported last year.

A number of limitations associated with the handling and interconnecting of silicon dies and polymer microfluidics resulted in a novel approach utilizing the microfluidic stack concept developed at CAMD. The overall concept is outlined in Fig. 10 and explained briefly in the text.

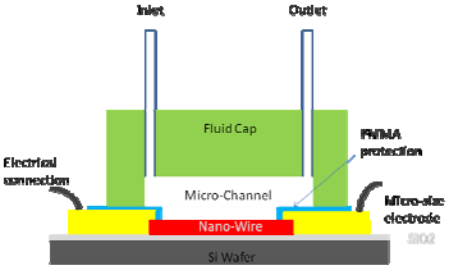


Fig. 9: Schematic of the sensor dye – polymer fluid cap assembly.

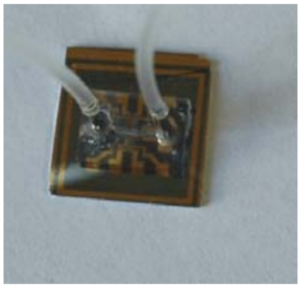


Fig. 10: Completely assembled die with fluidic cap and tube interconnects.

Ⅲ. Microfluidic Engineering Research

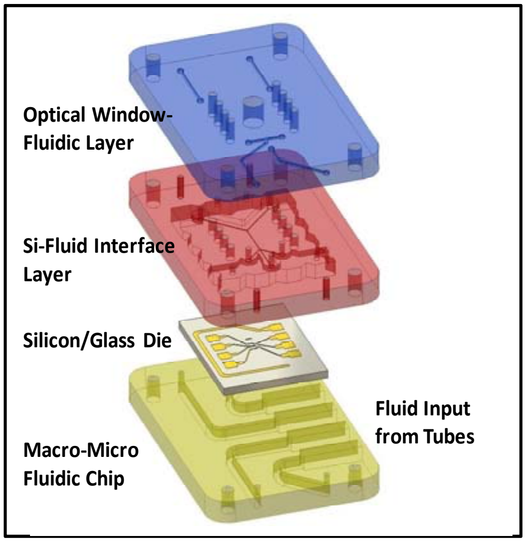


Fig. 11: exploded inventor model of impedance spectroscopy module, consisting of 3 PMMA modules containing fluidic structures and glass die with microelectrodes.

The sensor device is built from different polymer modules (outer dimensions are roughly 25mm x 15mm x 5mm) each performing specific functions or providing standardized interface feature. In particular the device is made from three PMMA modules is illustrated. Starting from the bottom chip (yellow module) fluids (up to 4 different solutions) can be injected into the stack using syringe pumps connected to flexible tubes. Four channels provide a well-defined position for steel-tubes that are glued into the chip and can be connected to external fluid media as needed. Within the yellow chip fluids are directed to different locations from where they flow up to the next level (red chip). The red chip is patterned on its bottom with a recess to accommodate the silicon or glass dies which contain microelectrodes (or electrodes with nanowires) as well as open microfluidic channel. There are an additional 6 holes to fill in conductive glue connecting to the bond pads of the Si dice. The fluidic microstructure is a simple, straight channel connected to one inlet and one outlet passing fluid across the electrode area. The stack is completed with the blue chip that has openings for the electrical connections (same as in the red module), an optical window (= hole to minimize the cap thickness for microscope inspection) and two fluidic channels connecting to the inlet/outlet of the red chip and also to the fluid outlets of the yellow chip. A number of designs with different channel sizes were fabricated and also additional features like hydrodynamic focusing are implemented to enable controlled movement of the sample stream to the electrode pattern.

B. Microfabrication and Assembly Efforts

The modules containing the microfluidic channel structures were fabricated in biocompatible Polymethylmethacrylate (PMMA) sheets by polymer hot embossing on a Jenoptik® Mikrotechnik HEX02 machine. The master mold (see Fig. 12) was fabricated in brass from an AutoCAD® design by direct milling with a KERN® precision micromill. For embossing, the substrate was first was heated to 160°C, and then a pressure of 1.77MPa was applied to press the mold into the softened PMMA substrate. After cooling, the mold and substrate were separated leaving a channel pattern transferred into the PMMA. The chips were fly cut by a Precitech Optimum130 to a thickness of 1.5mm opening up fluidic vias and also removing material between adjacent chips, allowing easy separation of individual modules (Fig. 13).

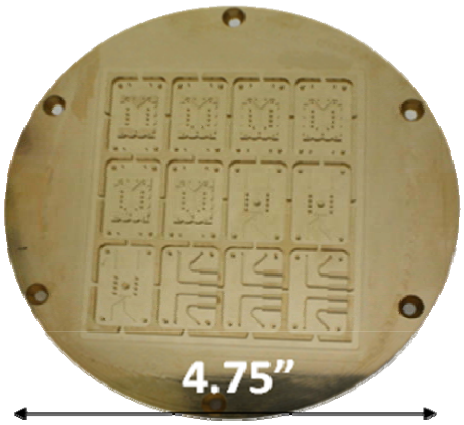


Fig. 12: Micro-machined brass mold inserts containing 12 different chip designs.

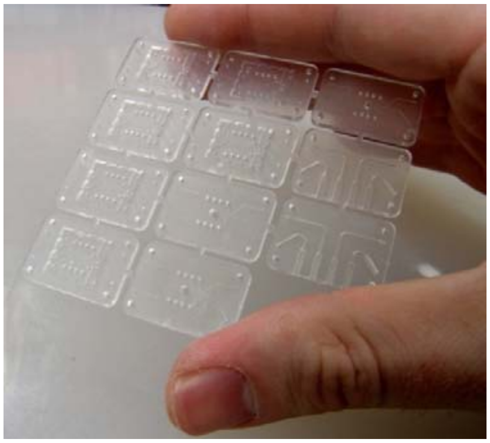


Fig. 13: Molded and fly-cut chips ready for assembly.

An optical UV-mask containing the original electrode array design was used to pattern microelectrodes onto a gold-coated silicon dioxide substrate using UV-lithography and wet-etching. The microelectrode patterns are patterned onto a 4” silicon wafer which is subsequently precision-diced to the format of the fluid module with an accuracy of ±25µm. (see also Fig. 14).

Prior to thermal bonding all three modules into a fully sealed stack additional assembly steps are performed. For example, steel tubes are cut to length (~2cm) and glued into the Macro/Micro interface module using UV-glue and flood exposure with UV-light (Oriel UV-lithography station). Another critical step is the exposure of the glass die and fluidic interface module to RF oxygen plasma at 100mW for 1 minute before fitting the die tightly into the cavity to enable leak-free sealing (see Fig. 15). To further enhance the bonding quality, a sheet from low molecular weight PMMA was cut to the size of the cavity/glass die and placed between the macro/micro - fluid interface chip and the glass chip. After completing assembly of all modules a thermal bonding process at a pressure of 0.5MPa for 2h at 104˚C, which is slightly below the glass transition point (Tg=105°C) of the PMMA modules was performed that resulted in a tightly sealed stack. Initially, surgical rubber tubes were bonded to the steel tubes in an effort to strengthen the fluidic interconnects. However, this method didn't provide the necessary firmness. To overcome this issue, a septum was created by injecting silicone into the fluidic interconnections replacing the steel tubes. This way, small syringe needles can be used to leak-free inject the sample and buffer fluids into the stack. Figure 16 shows a fully packaged stack where Cu wires were glued into openings using a conductive glue that also established the electrical connection with the microelectrodes.

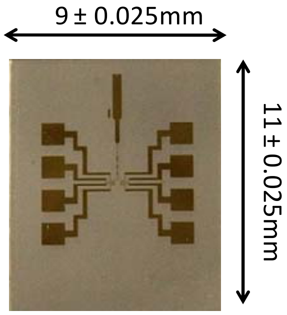


Fig. 14: Precision diced Au/Cr electrodes patterned on glass substrate.

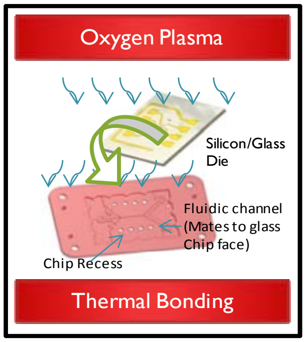


Fig. 15: Surface modification and assembly of die into the molded fluidic module.

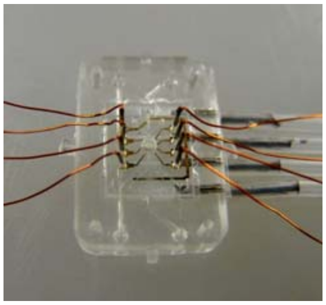
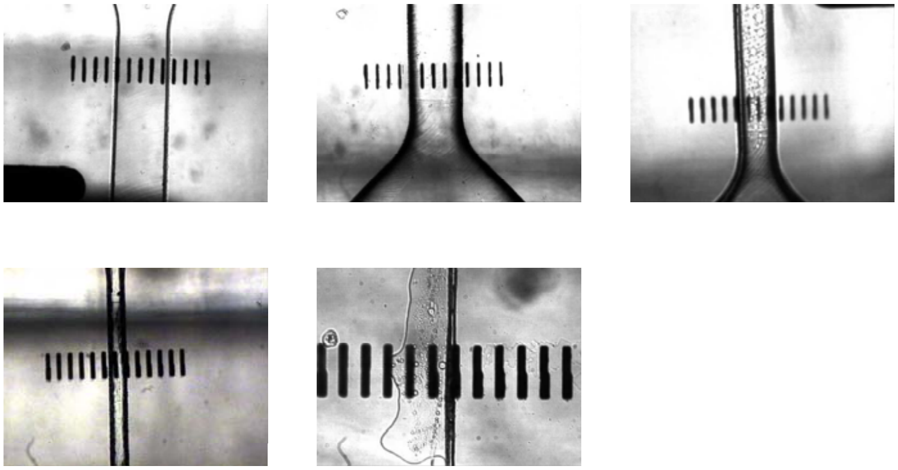


Fig. 16: assembled stack with glass die, fluidic and electrical interconnect structures to the outside world.

Taking advantage of the high precision microfabrication process employed to patterning the custom-designed PMMA module, Si or glass dies can be passively inserted into the recesses with minimal assembly efforts (passively aligned). On-chip alignment markers with dimensions of 20µm with 20µm gaps were patterned onto the glass chip, too to enable visual inspection after the assembly process was completed. Since the microfluidic channels were fabricated symmetrically to the z-axis comparing the position of the channel to position of alignment markers provides information about the alignment accuracy during the assembly process. Evaluating the information from the markers shown in Figs.17 illustrates that alignment accuracy of better than 15µm was routinely achieved.



Figs. 17: Markers (~20 µm) from gold on glass die aligned to different channel sizes; from up left to down right: 200µm, 150µm, 100µm, 60µm, 20µm. Passive alignment yielded an accuracy of better then 15µm.

After optimizing process parameters excellent bond strength was achieved that allowed fluid testing using a dyed water fluid. Figures 18 show fluid flow through channels of different width past a microelectrode assembly. A study done by Han *et al.* [Han A et al (2003) “Multi-layer plastic/glass microfluidic systems containing electrical and mechanical functionality”, Lab Chip 3:150–157] ascertained a maximal bond strength of 20kPa at a PMMA/Glass interface

Our bonding process yielded leak free channels up to fluid pressures of 83 kPa indicating an even better bond and superior performance of our fluidic package. In addition to simple fluidic structures an arrangement of microelectrodes was patterned that was used to optimize the electrical interconnection within the assembled stack.

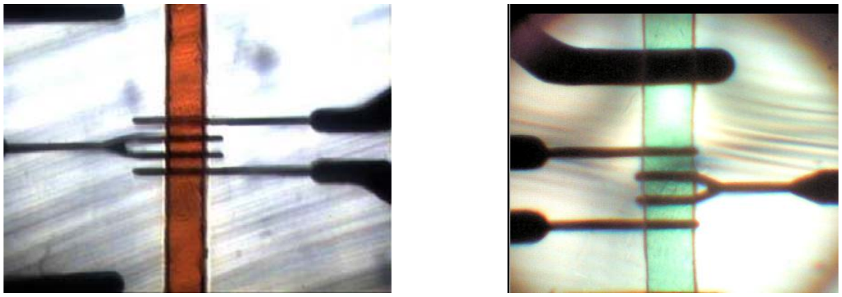


Fig. 18: Demonstration of leak-free PMMA/Glass interface with (a) red dyed water in a w=60µm, and (b) green dyed water in a w=200µm wide channel. The ensemble of four microelectrodes (~10um wide) interfaces the fluid and allows observation of fluid flow (see next chapter).

C. Initial Electrode Measurements

Using the configuration of four microelectrodes in a Wheatstone bridge configuration a potential difference between two sub-circuits can be measured allowing to analysis and evaluate the electrical interconnection. Two resistors (1MΩ each in order to reduce the settling time) were connected in series between excitation signal and measurement electrodes. Since this potential change is typcially very small and noisy, an amplification circuitry was designed and fabricated (PCB technology). As shown in the schematic (Fig. 19) the microfluidic sensor was connected to an off-chip fast settling instrumentation amplifier, which uses a differential amplifier to multiple the differences between the two sub-circuits with a high frequency bandwith. The instrumentation amplifier consists of three AD854JN with an adjustable gain configuration, giving an overall gain of 201 at 10MHz bandwidth. Since microfluidic channels interfacing with electrodes provide a high noise environment and the recorded/excitation-signal-ratio is approximately 1/1000 the signal had to be demodulated in order to eliminate noise by using an extreme band-pass filter. The amplified representation signal feeds a self-made lock-in amplifier circuitry which is connected to the function generator due to a unity gain buffer operational amplifier (LT1037).

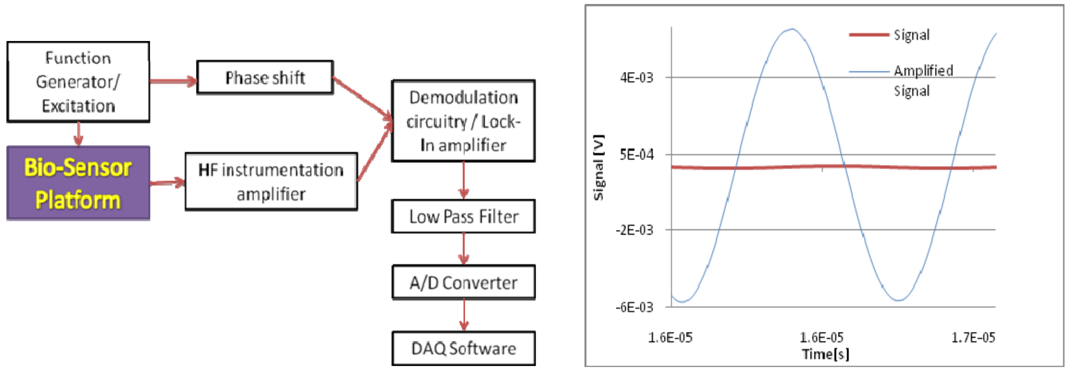


Fig. 19: (a) Block diagram of electronic circuitry (b)Magnitude of normal and amplified signal due to cell passing detector at 1MHz for 5μm cell in PBS (Multisim simulation).

Heart of the circuitry is a phase trim configuration in series with a comparator connected to the function generator and a LTC1043 capacitor switch configuration to demodulate the signal and sense small impedance changes (usually μV) in high-noise environments. INA114 based low-pass filters were added to minimize the noise and regulate the bandwidth.

Signals were acquired by an AD/Converter and MCC-DAQ-Software. First electrical measurements using air bubbles within a continuous flow of water to detect signal changes illustrate that the assembly was completed successfully and the detection scheme works (Fig. 20). These initial tests were performed by interfacing the assembly to NE-OEM application syringe pumps with 1ml BD plastic syringes to inject a dyed buffer fluid to perform visual leakage tests and connection the soldered copper wires and signal-processing electronics to a data acquisition program.

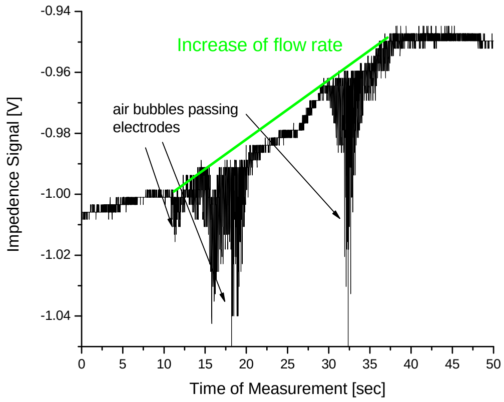


Fig. 20: Impedance measurement proving successful connection of electrodes within the stack.

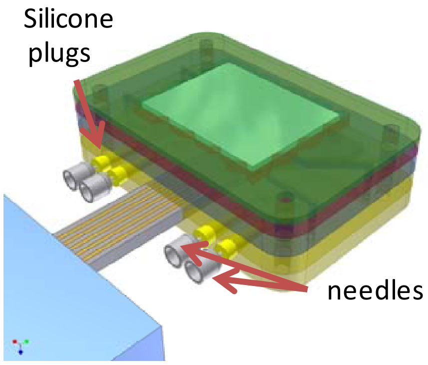


Fig. 21: Schematic of an advanced stack package using a customized PCB solution embedded into the stack and connected to an external circuit (blue box); fluid interconnects will be realized using a silicone septum and syringe needles for leak-free, simple interconnection of fluids.

D. Summary and Outlook

In the past year our efforts have been focused on designing and optimizing a stack based integration concept for silicon/glass die based sensing devices. Design, fabrication, and assembly have been successfully tested using microelectrode configurations interfacing with fluid transported through microchannels. The initial electrical tests indicate that more advanced electronic circuit design is needed in order to improve signal-to-noise ratio and enable reliable detection of electrical changes indicating a selective binding events of target molecules with engineered nanowires.

While our recent efforts are promising a number of details still need to be addressed and optimized, including:

- interface issues within the stack, in particular electrical interconnects and optimized electrical circuits; these efforts will focus on a customized printed circuit board (PCB) and methods to integrated them as additional module into the stack in order to minimize the length of the electrical interconnect (see Fig. 21);
- design of additional fluidic modules to support sample flow manipulation, esp. ensuring that the sample will be passed across the embedded nanowires;
- further explore the lithography based patterning of Si nanowires as an alternative approach to the manually attached nanowires; pursuing an all lithography based fabrication process will ensure wafer-scale fabrication and ultimately cost-effective fabrication of sensor devices.

Ⅳ. Genetically engineered antibodies for nanosensors

A. Brief Narrative

We are making genetically engineered antibodies that will bind to nanomaterials better than the native antibodies. Working with two different antibodies we have introduced three different Cterminal domains onto them, and expressed them as full length antibodies or Fab fragments. We have now demonstrated that an engineered antibody binds to unencapsulated quantum dots, whereas the wild type antibody does not. The bound antibody retains function and antigenic specificity. We have also devised methods to maintain these QDs in solution in the presence of physiologic salt solutions.

B. Objectives

We are making genetic modifications to antibodies to improve their utility in biosensors. These modifications should allow for greater coupling efficiency and for orientation of the antibodies with their binding sites exposed. Two different antibodies are being modified: 1. RAC18, an antibody to ricin toxin, a molecule of biodefense interest, and 2. anti-HIV antibody HY, directed to the virus envelope. For each antibody, we are attaching to the full length and Fab three different heavy chain carboxy-termini: 1. the metal binding 6X-His motif, 2. oligo-lysine (free amino groups), and 3. oligo-cysteine (sulfhydryl groups). We will compare the function of these 12 constructs with native Ig. They will be studied free in solution and bound to nanowires or quantum dots. We have made all four 6XHis constructs, and the four full-length oligo-lysine and oligo-cysteine constructs. Antibodies for each have been made and purified. We are conducting tests of the coupling of these antibodies to quantum dots and to proteins. Our studies of the binding of these molecules to nanowires have been delayed because the chemical modification of the nanowires has not been completed. We demonstrate promising results showing the function of 6X-his modified antibodies when attached to quantum dots.

C. Research Progress

We have continued to work with QD-bound antibodies and demonstrated that they have functioned effectively for periods of up to one month post conjugation.

The majority of our efforts have been directed towards producing large quantities of theantibodies that we desire to study further. We currently are able to express 1-2 mg antibody/liter of tissue culture using transient transfection. We have been unable to identify stable transfectants producing meaningful quantities of antibody. To achieve higher expression levels we are using an expression system in which the expression is driven by transactivation via the Epstein-Barr Virus Nuclear Antigen and then by the SV40 T antigen. The antibody genes have been transferred to a plasmid containing the EBV Ori-P and transactivation domain. These will be transfected into 293 cells expression EBNA. This will maintain the plasmid as an episomal element. The cells can then be transduced with a retrovirus vector expressing SV40-T. This will drive plasmid replication (the plasmids encoding the antibodies also contain SV40-Ori) and should result in a massive increase in antibody production. We are currently selecting the cells containing the transfected plasmids.

V. Project 3 (Mark DeCoster - LA Tech). Patterning and characterization of nanowires integrated into a biochip detection device; Modification with linkers and tails for secreted phospholipase A_2 detection using LBL technology and biocompatibility assessment

1. Personnel

co-PI: Dr. M. Decoster; Undergraduates: Michelle Sibille, Enkhjin Bayarsaikhan, and Chris Chain; Master's level graduate students: Raj Masvekar, Jessica Wasserman, and Dustin Green; Ph.D. student: Jim McNamara provided significant research and training for the lab for this project.

2. Activities and Findings

Results- Testing of Nanomaterials toxicity to brain cells.

All cultures were exposed to nanomaterials for approximately 21 hours. MTT assay was then run to test culture activity. Results for MTT assays were read using spectroscopy set at 570nm. Figure 1 gives an indication that specific concentrations of Si nanoparticles may increase cell activity in astrocytes, without causing toxicity observed with copper nanoparticles. A similar curve is seen in figure 3 at the same concentrations. Aged nanomaterials tested in figure 2 suggest that allowing opper to oxidize may make it less reactive to the cells.

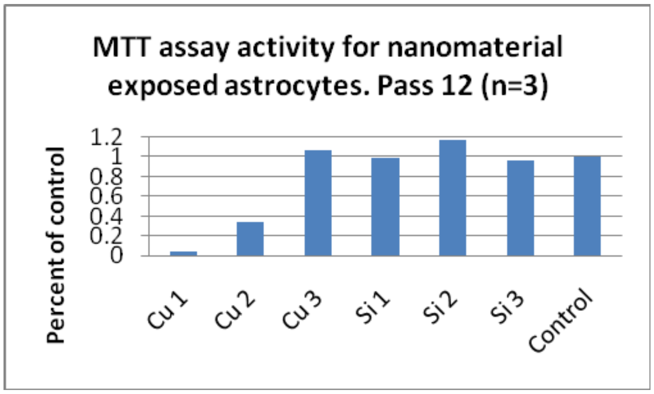


Figure 1. Pass 12 astrocytes exposed to nanomaterials. Astrocytes were taken from culture of rat brain astrocytes.

Cu 1= copper nanoparticles, 100µg/mL; Cu 2= 50µg/mL; Cu 3= 10µg/mL; Si 1= silica nanoparticles (UNO), 100µg/mL; Si 2= 50µg/mL; Si 3= 10µg/mL. Control = Locke's solution

- Describe the opportunities for faculty recruitment, retention and development, as well as post-doc, graduate and undergraduate student training provided by your project;

Undergraduates who were trained in the project: Michelle Sibille, Enkhjin Bayarsaikhan, and Chris Chain. Michelle Sibille has been accepted to medical school for fall 2009. Master's level graduate students: Raj Masvekar, Jessica Wasserman, and Dustin Green. Raj Masvekar and Dustin Green have been accepted into Ph.D. programs away from Tech for fall 2009 and Jessica Wasserman has been accepted into the Ph.D. program in Biomedical Engineering at Tech for Fall 2009. Post doc Dr. Mangilal Agarwal worked for the project for one year.

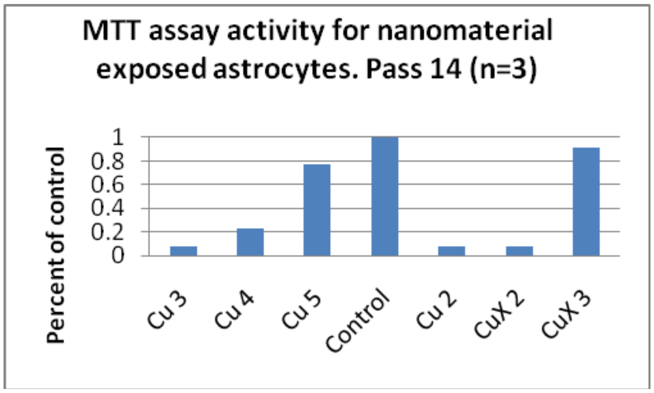


Figure 2. Pass 14 astrocytes exposed to fresh nanomaterials and some nanomaterials that had been aged for approximately one month in Locke's solution.

Cu 3= copper, 100µg/mL; Cu 4= 50µg/mL; Cu 5= 10µg/mL; CuX 2= 50µg/mL aged in Locke's solution for one month; CuX 3= 10µg/mL aged in Locke's solution for one month

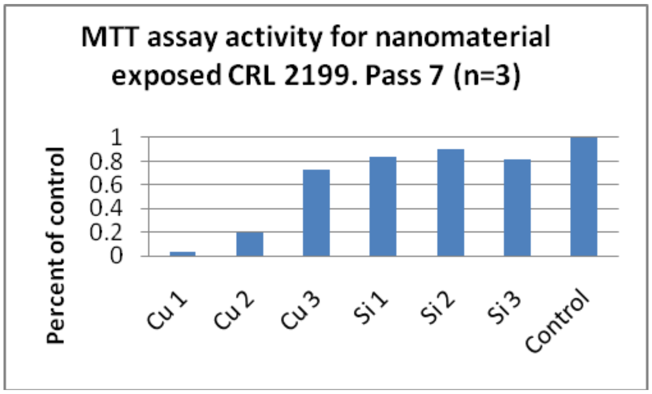


Figure 3. Pass 7 CRL 2199 type cancer cells exposed to nanomaterials.
Cu 1= copper, 100µg/mL; Cu 2= 50µg/mL; Cu 3= 10µg/mL; Si 1= silica nanoparticles (UNO), 100µg/mL; Si 2= 50µg/mL; Si 3= 10µg/mL. Control = Locke's solution.

- Describe the opportunities for faculty recruitment, retention and development, as well as post-doc, graduate and undergraduate student training provided by your project;

Undergraduates who were trained in the project: Michelle Sibille, Enkhjin Bayarsaikhan, and Chris Chain. Michelle Sibille has been accepted to medical school for fall 2009. Master's level graduate students: Raj Masvekar, Jessica Wasserman, and Dustin Green. Raj Masvekar and Dustin Green have been accepted into Ph.D. programs away from Tech for fall 2009 and Jessica Wasserman has been accepted into the Ph.D. program in Biomedical Engineering at Tech for Fall 2009. Post doc Dr. Mangilal Agarwal worked for the project for one year.

- Describe the nature and scope of partnership activities;

Drs. Lvov and Decoster –AMRI annual conference in February 2009, and discussed results with AMRI researchers. 2 joint reports were presented at AMRI Mardi Gra symposium. With Prof. Kevin Stokes, we are working on preparation of the project on clay nanotube smart nanocontainer for anticorrosion coating.
Describe any problems encountered during the last year of project activities. Second year funding was delayed for six months and money received in December 2008, therefore, again we will need extension till December 31, 2009.

3. Contributions: Summarize efforts made to build research and education capacity, secure external federal and private-sector funding, and ensure project sustainability over the long term.

1. "Clay Nanotubes for Controlled Release of Corrosion Inhibitors," NASA-EPSCOR LA BoR, pre-proposal, PI, $200,000, Jan 2010-Dec 2011.
2. "Clay Tubule Nanocontainer for Responsive Corrosion Protection," NSF-nanomanufacturing, PI, $270,000, Sept- 09- Aug 20012
3. 'Microfluidic Device for Directed Assembly of Nanoparticles and Polyelectrolytes on in situ Generated Templates," NSF-nanomanufacturing, PI, $280,000, Sept- 09- Aug 20012
4. "Materials Synthesis in Clay Nanotubes," PI, NSF, $340,000, Sept 2009- Aug 2012

5. “Clay Tubule Nanocontainer for Responsive Corrosion Protection,” NSF-nanomanufacturing, PI, $270,000, Sept 09- Aug 2012
6. ‘Collaborative Research: Microfluidic Device for Directed Assembly of Nanoparticles and Polyelectrolytes on in situ Generated Templates,” NSF-nanomanufacturing (with Virginia Tech), PI, $280,000, Sept- 09- Aug 20012
7. pre-proposal: “IGERT Multi-Scale Integration of Biomimetic Systems,” NSF, PI: M. Decoster, NSF, $2, Sept 2010- Aug 2015

4. Project Revision: Provide a listing of and explanation for any significant changes in the work plan for upcoming year, including any changes in the amount of investigators' time devoted to the project. – Dr. Despina Davis replaced as co-PI Kody Varahramyan with responsibility for the first project

Publications

“Detection of H_2S at room temperature by using individual indium oxide nanowire transistor”, Zhongming Zeng, Kai Wang, Zengxing Zhang, Jiajun Chen, and Weilie Zhou, Nanotechnology **19**, 225303 (2008).

“Synthesis of Magnetic Porous Hollow Silica Nanotubes for Drug Delivery,” H. Ma; J. Tarr, M. A. DeCoster; J. McNamara; D. Caruntu; J.F. Chen; C. J. O’Connor; W. Zhou, J. Applied Physics, v.105, 981, 2009.

Presentations

AMRI DARPA review presentation “Field effect transistor for Antigen detection” Weilie Zhou and Seth Pincus (2009).

Q. Xing, S.Chen, M. DeCoster Y. Lvov, “Porous 3D Cellulose Fiber Based Microscaffold for Cell Culture,” TERMIS-NA 2008 (Annual Conference of Tissue Engineering & Regenerative Medicine International Society), San Diego, Dec 10, 2008.

J. McNamara, M. Decoster, Society for Biomaterials conference in San Antonio, Texas April 25, 2009. “Characterization of Micro-Patterned Templates for Promoting Spatially Defined Attachment and Growth of Neuronal Cells”.

M. Decoster American Society for Cell Biology, annual meeting in San Francisco, California, December 5, 2008. “Selective Adhesion and Growth of Astrocytes and Gliomas on Microscale Patterns Using Novel Molecular Printing Techniques”.

M. Sibille, J. McNamara, M. Decoster, Biomedical Engineering Society Meeting, St. Louis, Missouri, October 22, 2008. “CNS Glial Injury and Inflammatory Response in Normal and Cancer Cells”.

J. McNamara, M. Decoster, Conference on Magnetism and Magnetic Materials, Austin, Texas, November 12, 2008. “Synthesis of Magnetic Porous Hollow Silica Nanotubes for Drug Delivery”.

PKSFI Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04

John Wiley
(PKSFI FRG-2, 2008-2009)

FRG-2 Nanomechanical Devices

1. Personnel:

This focused research group consists of researchers from the University of New Orleans (UNO) and Tulane University (TU). The principal investigators are John Wiley (UNO), Bruce Gibb (UNO), Scott Whittenburg (UNO), Leonard Spinu (UNO), Vijay John (TU), and Hank Ashbaugh (TU). A number of graduate students are also contributing to the work: Jianxia Zhang (UNO), Haiying Gan (UNO), Ovidiu C. Trusca (UNO), Joy St. Dennis (TU), Bhanukiran Sunkara (TU), Piyush Wanjari (TU), and Ashish Sangwai (TU). In one project, photoactive polymers are being synthesized and tested as possible light driven actuators in mechanical devices (Zhang in Wiley's group). In another project, sets of host-guest molecules are being synthesized and characterized as possible tethers for the directed self-assembly of nanocomponents (Gan in the Gibb's group). New magnetically guided tubular liposomes have also been produced for potential mechanical device components (Joy St. Dennis and Bhanukiran Sunkara in V. John's group; these researchers are working with Leonard Spinu in the characterization of these materials). Both the Ashbaugh and Whittenburg groups have been modeling various properties of host-guest systems. Ashbaugh's group (Piyush Wanjari and Ashish Sangwai) is studying mixed solvent effects on solvent-mediated interactions between hydrophobic species and Whittenburg is studying Brownian dynamics simulations of host-guest interactions as well as micromagnetic simulation of the nanoparticles. The latter project involves joint project between Whittenburg, Spinu and Trusca.

2. Activities and Findings:

The activities and findings will be broken up into the various aspects of the program.

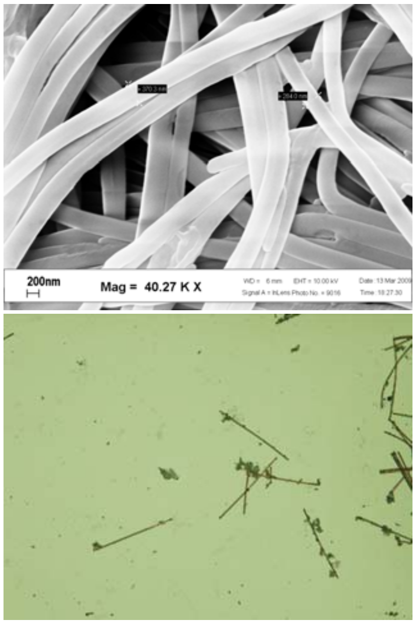
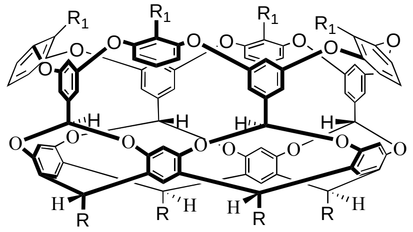


Figure 2-1. Diazobenzene wires. Top – SEM of nanowires. Bottom – optical micrograph of micron-sized wires

a. *Photoactive polymers.* We are continuing our efforts to investigate the potential use of diazobenzene polymers for optically-active and solvent-active actuators. The polymers that we made last year have now been formed into nano- and micron-sized wires (Figure 2-1). We are currently examining both the effects of UV and solvent exposure on these wires. Individual micron wires have been dispersed and their optical response examined; while there are some bending in the wires, it is not as dramatic as what is seen in polymer films. We are currently looking to prepare asymmetric micron wires to see if we can influence the bending properties of these systems. We have also worked to disperse individual nanowires. We have a new scanning probe microscope on order that will allow us to monitor individual wires while they are exposed to UV light or different solvents. We hope to begin these experiments by mid-summer.

b. *Host-guest assembly.* This program of research focuses on the controlled assembly of nano-objects into complex nano-systems. The general approach involves the development of hosts (H1, H2 and H3) that bind complementary guests (G1, G2 and G3). Each host-guest pair is orthogonal, i.e. H1-G1 strongly associates, but for example H1-G2 or H3-G1 do not. Hence, one surface of a nano-object coated with H1 will stick to another object coated with G1. Moreover, with three, orthogonal host-guest pairs, it is theoretically possible to assemble complex objects by selectively coating different objects (or different parts of objects) with different hosts and guests. Our strategy is to utilize thioether-functionalized deep-cavity cavitand hosts (DCC) and complementary guests that bind strongly to gold surfaces.

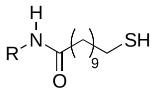
The design of the hosts **1** and **2** (below) was based on work reported by Reinhoudt for a smaller host.[1] Of importance is the choice of thioether feet for the DCC over long chain thiols. Reinhoudt has reported that better surface coverage is obtained using the thioether feet since they are able to fold back under the resorcinarene head group upon binding of the sulphur atom to the gold surface to more effectively pack the space under the receptor. This results in a densely packed, more organized monolayer that passivates the gold surface better.[2] Hosts **1** and **2** have been synthesized following Reinhoudt's procedure.



1: R = $(CH_2)_{10}S(CH_2)_9CH_3$, R_1 = H

2: R = $(CH_2)_{10}S(CH_2)_9CH_3$, R_1 = CH_3

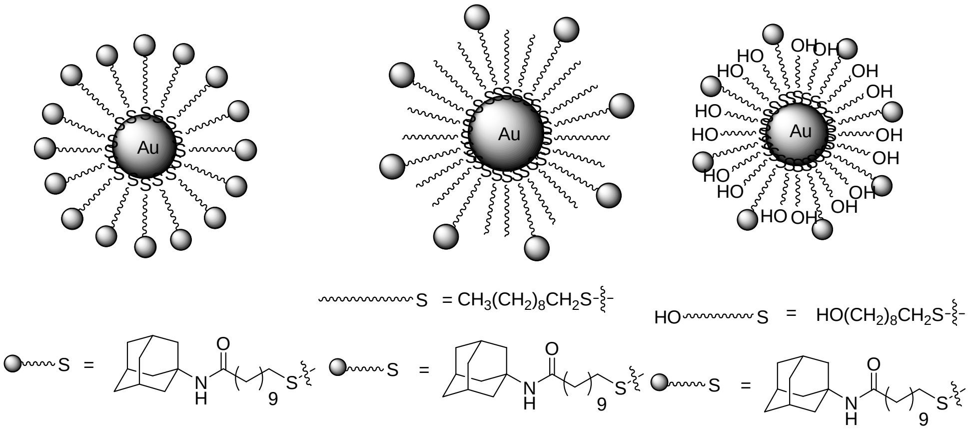
The corresponding hosts for **1** and **3** (**3** and **4** respectively), have also been synthesized.



3: R = 1-adamantane

4: R = cyclopentyl

Since the last annual report, we have been focusing on synthesis of guest **3** coated gold nanoparticles.[3] We have synthesized three generations of this type of gold nanoparticles (**5**-**7**). NMR titration studies have been carried out using a (easily synthesized) model host with an identical cavity volume as **1**. No binding could be observed by this approach. To possibilities as to why this is the case are: 1) Insufficient solubility of the gold nanoparticles in DMSO (the best solvent for this type of study). 2) A very dense coating of guest molecule on the gold surface, which inhibited host complexation. In order to solve those problems, we designed **6** and **7**. In both of these entities, long carbon chain thiol that function as spacers were incorporated into the particle to increase the accessibility of the binding (guest) groups. In 7, these spacer groups were terminated with hydroxy groups to make the particles more soluble in polar solvents such as DMSO. We have not completed the binding studies with these particles. These will include NMR studies, as well as TEM experiments.



5 **6** **7**

c. *Modeling of Host-Guest systems.* Over the past reporting period, research in the Ashbaugh lab has focused on calculating forces between cavitand hosts and adamantane guests in solvents of varying polarity. The molecular dynamics packages GROMACS was used in these calculations and simulations were performed on the LONI network. Umbrella sampling with weighted histogram analysis was used to evaluate the potential of mean force between the guest and host along the symmetry axis of the cavitand. Figure 2-2 shows a snapshot of adamantane adsorbed in the cavitand's hydrophobic pocket in water (water's not shown for clarity). Also shown is the potential of mean force evaluated in pure water and a 20 mol% mixture of ethanol in water. This plot shows that as the polarity of the solvent is decreased the attractive well depth decreases, indicating a reduced affinity for of adamantane for the cavitand. Ongoing research is examining a series of seven solvent mixtures studied experimentally by the Gibb group (UNO) to explain the observed binding affinity trends.

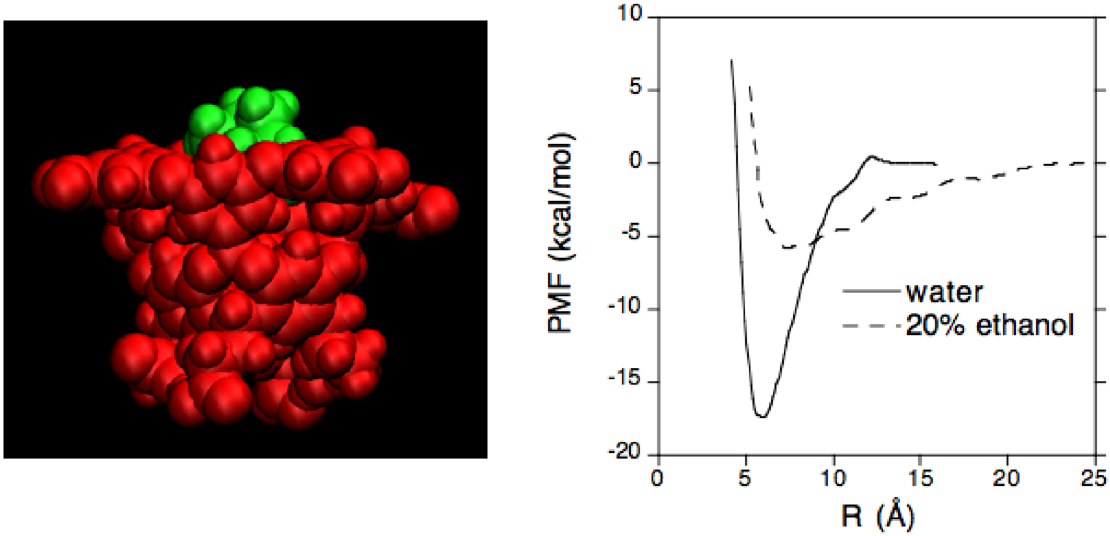
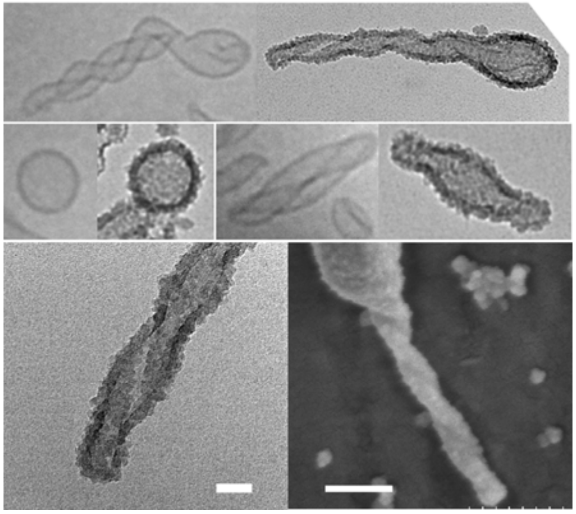


Figure 2-2. Snapshot of adamantane (green) tucked away into a cavitand (red) in water (left-hand figure). Potential of mean force for adsorbing adamantane into a cavitand in water and a 20 mol% ethanol – water mixture (right-hand figure).

In Prof. Whittenburg's efforts in the study of the Brownian Dynamics (BD) of the host-guest systems, he has worked to move his BD computer code to the LONI supercomputers. He has successfully compiled the code and has used it to conduct simulations on the binding of hydrogen bromide (as simple test case) to deep-cavity cavitands. The experimental work on this binding studies is done in collaboration with co-PI Gibb. Whittenburg has also written programs to enable visualization of the resulting BD trajectories. The next step involves adding the magnetic force field from his micromagnetics code to allow simulation of the three-dimensional controlled ordering of nanometer-sized structures. The magnetic phase of this work is being done in collaboration with Spinu.

d. *Magnetically guided tubular liposomes.* A dual-lipid liposome system consisting of a phospholipid and a skin ceramide extruded though a 100 nm membrane yields novel tubular and helical liposomes. These liposomes were used as templates to generate highly aspherical silica nanocapsules with length to diameter aspect ratios exceeding 10. Many of these nanocapsules have the morphology of a bulbous end attached to a long tip, mimicking microneedles attached to a reservoir. The fidelity of helical liposomes is transcribed to the silicas and the long tips indicate helically entwined left-handed silica structures. The silica coating is expected to protect and stabilize the internal contents of the liposomes, as well as enable surface functionalization for applications in drug or targeted delivery.



This work is a variation from the general liposome literature that is usually focused on spherical liposomes. Since recent literature highlights the importance of particle shape influencing clearance of particles from the body, we are interested in forming aspherical liposomes and extending the work to templation of such liposomes. We believe the liposomes especially those with high aspect ratio is interesting as the different shapes may give rise to non-conventional dissolution profiles. In the study, we show that liposomes composed of L-α-phosphatidylcholine and ceramide VI can be transcribed to form highly aspherical silica nanoshells with thin walls of 10 nm, while preserving the unique undulating feature of the liposomes. It is potentially possible to extend the technique to effect controlled release of the encapsulated liposome contents by an external stimulus e.g. infrared radiation or pH. In continuing research we are entrapping magnetic nanoparticles into these ceramized liposomes to form magnetically guided liposomal systems.

All of these projects offer extensive opportunities for the training of students and postdocs. Further, all the faculty involved in the project have greater opportunities for collaboration, beyond that outlined above, and this will lead to greater efforts in faculty retention as well as opportunities for successfully securing of joint funding. The success demonstrated by this faculty will serve to attract other highly motivated scientists and engineers to the New Orleans area.

The nature and scope of these projects are outlined above.

There have been no problems encountered over the last year.

3. Contributions:

Initially the focus was on building the research group, attracting students, initiating the research, and building the collaborations. This is now well established. Further efforts have gone to the purchase of a new scanning probe microscope from funding secured through the LA BOR Enhancement program by some of the PI's (Wiley, Gibb, Spinu); this instrument will serve several aspects of this program. In other cases (V. John), aspects of this project have been promoted to NASA, Sandia Laboratories and Los Alamos Laboratories where agencies are examining application potential.

4. Project Revision:

None

5. Work Products:

Presentations

"Fabrication of photosensitive polymer nanowires," Jianxia Zhang, Jin-Hee Lim and John B. Wiley, 235th American Chemical Society National Meeting, New Orleans, LA, April 6-10, 2008.

"Carbons from sugars: Morphology, microstructure and applications to gas storage," J. E. St.Dennis, Pradeep Venkataraman, Vijay T. John, Gary McPherson, Jibao He, Camille Y. Jones, Stephen J. Obrey, and Robert P. Currier, 235th American Chemical Society National Meeting, New Orleans, LA, April 6-10, 2008.

Effects of magnetic interactions in Ni nanowire arrangements Ovidiu Trusca, Dorin Cimpoesu, Jin-Hee Lim, John B. Wiley, and Leonard Spinu, APS March meeting, New Orleans, March 10-14, 2008.

"Interaction effects in Ni nanowire arrays," Leonard Spinu, Intermag Conference, Madrid, Spain, May 4-8, 2008

"Solvomechanical Response of Diazobenzene Polymer Films in Organic Solvents," Jianxia Zhang and John B. Wiley, Materials Research Society Meeting, Boston, MA, December 1 - 4, 2008.

Publications:

"Interaction effects in Ni nanowire arrays," Ovidiu C. Trusca, Dorin Cimpoesu, Jin-Hee Lim, Xiequn Zhang, John B. Wiley, Andrei Diaconu, Ioan Dumitru, A. Stancu, and L. Spinu, *IEEE Transactions on Magnetics* **2008**, *11*, 2730.

“Shear Induced Formation of Patterned Porous Titania with Applications to Photocatalysis”, Li, X.; John, V.T.; He, G.; Zhan, J.; Tan, G.; McPherson, G.; He, J.; Bose, A.; Sarkar, J. *Langmuir*, in press.

“Undulating tubular liposomes through incorporation of a ceramide into phospholipid bilayers”, Xu, P.; Tan, G.; Zhou, J.; He, J.; Lawson, L.; McPherson, G.; John, V. *Langmuir*, in press.

“Bending Behavior of Polymer Films in Strongly Interacting Solvents,” Jianxia Zhang and John B. Wiley, *Mater. Res. Soc. Symp. Proc.* **2009**, *1129*, 1129-V04-05.

PKSFI Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04

Kevin L. Stokes
(PKSFI FRG-3, 2008-2009)

FRG-3: Nanomaterials for Energy Conversion and Storage

1. Personnel:

LATech/IfM
Abdullayev, Elshad. Graduate Research Assistant, Hydrogen storage materials
Agarwal, Mangilal. Laboratory Coordinator, Thermoelectrics
Carbo, Daniel. Undergraduate Research Assistant, Hydrogen storage materials
Davis, Despina. Co-PI, Thermoelectrics
Lvov, Yuri. Co-PI, Hydrogen storage materials
Mannam, Raja. Graduate Research Assistant, Thermoelectrics
Roy, Amitava. Graduate Research Assistant, Thermoelectrics
Singh, Varshni. Graduate Research Assistant, Thermoelectrics

LSU
Champagne, Chris. Undergraduate Research Assistant, Thermoelectrics
Karki, Amar. Graduate Research Assistant, Thermoelectrics
Walker, Nick, Undergraduate Research Assistant, Thermoelectrics
Young, David P. Co-PI, Thermoelectrics

UNO/AMRI
Gabrisch, Heike. Co-PI, Battery materials
Malkinski, Leszek. Co-PI, Ferroic composites
Mohanty, Debasish. Graduate Research Assistant, Battery materials
Nolting, Westly, Undergraduate Research Assistant, Thermoelectrics
Stokes, Kevin L. Co-PI, UThermoelectrics
Swart, Donald. Graduate Research Assistant, Thermoelectrics

Dr. Kevin Stokes reviews quarterly progress reports from LSU and La Tech to ensure that these contributions are adequate to the project's requirements.

2. Activities and Findings

A. Major Research and Educational Activities Undertaken

This focused research group (FRG) is applying the science and engineering of nanometer-scale materials to several areas of energy conversion and storage. Stokes, Davis and Young are investigating various aspects of nanocomposites thermoelectric materials and microdevices, Gabrisch is investigating novel electrode materials for electrochemical storage applications (rechargeable batteries); Malkinski is researching novel magnetic to electrical power conversion composites for micropower applications and Lvov is developing techniques for the nanoassembly of nanoparticles and tubule nanocontainers for possible hydrogen storage applications. There are six principle investigators, one senior researcher, seven graduate students (total) and four undergraduate students from the University of New Orleans, Louisiana State University and Louisiana Tech. The results for June 2008 to June 2009 are summarized below.

B. Major Findings and Results

a. Electrodeposition of bismuth telluride (Davis)

This project aims to fabricate high quality TE nanomaterials (bismuth telluride nanotubes and nanowires) and to improve the Seebeck coefficient (power factor) by nanofabrication. The plan is to use complex pulsed electrodeposition techniques to make multilayered metallic and semiconductor nanotubes and nanowires. This unique (magnetic-thermoelectric) nano-architecture is not trivial to control, therefore complex, multipulse/pulse-reverse electrodeposition techniques will be explored and implemented. Using electrodeposition, a cost efficient and highly controllable method to fabricate Bi_2Te_3 nanotube and nanowires, it is possible to tailor the main carrier type in the alloy and to obtain either n-type or p-type semiconductors.

In this project different size nanotubes and nanowires of thermoelectric material Bi_2Te_3 will be synthesized inside the nanoporous polycarbonate (PC) and AAO membranes using electrodeposition. The plan is to study the effect of electrolyte composition and concentration on the resulting nanotubes Seebeck coefficients (thermo power). The plan is to evaluate the membrane pore diameters (resulting tube/wire sizes) effect of Seebeck coefficient values. Finally, a thermoelectric cooling device will be electrodeposited on a single membrane supporting the bismuth rich (p-type) and tellurium rich (n-type) nanostructures. Seebeck coefficient is one the key parameters that could be improved in large aspect ration nanotube/nanowire geometry and could lead to a higher thermoelectric power. Nanowires of bismuth-telluride Bi_2Te_3 are ideal thermoelectric materials because of their low thermal conductivity and high Seebeck coefficient.

Bismuth telluride (Bi_xTe_y) nanowires were electrodeposited from aqueous acidic solutions containing different $Bi^{3+}/HTeO_2^+$ (20/20 mM, 20/10 mM) concentration ratios. The polarization plots predicted that combined solutions exhibit more noble reduction potentials than individual solutions. Optimized deposition potentials were obtained from the combined electrolyte polarization plots. An anomalous codeposition behavior caused increase in Te concentration for depositions in the kinetic region of bismuth telluride; otherwise decreasing Te concentrations with increased deposition potentials was observed from composition analysis. X-ray diffraction showed a dominant (110) orientation for nanowires at low deposition potentials. N-type nanowires were obtained from both electrolytes, while p-type nanowires were only obtained from the 20/10 electrolyte for low Te (< 30%) concentrations. An intrinsic to extrinsic transition was observed for nanowires deposited from 20/10 electrolyte. The highest measured Seebeck coefficient was -318.7 μV/K and 117 μV/K for n-type and p-type nanowires, respectively. The Seebeck coefficient dependence on resistivity and composition of the nanowires is discussed.

Figure 1 shows the polarization behavior of the two studied combined electrolytes the 20/20, the 20/10, and their individual counterparts. Figure 1a illustrates the overall current profile of the 20/20 combined electrolyte, in which two distinct mass transport regions could be identified corresponding to the bismuth and tellurium components. From the partial current profiles the bismuth limiting current was reached at -150 mV. The overall current profile in the 20/20 combined electrolyte shows a shift toward the more noble potential region. Figure 1b shows the overall current of the 20/10 electrolyte and their partial currents. In this case the individual tellurium limiting current was observed at -250 mV. The overall current profile in the 20/10 case maintained the same behavioral trend as the 20/20 electrolyte, noticing a negative shift in limiting current potentials.

The current behavior in the 20 mM Bi^{3+} individual solution showed a limiting value of -29 mA/cm^2 at -150 mV. In the individual electrolyte solutions, the $HTeO_2^+$ component limiting current was observed for low concentrations indicating a diffusion effect. For 20 mM $HTeO_2^+$ no clear limiting current was observed, while a limiting current density of -20.6 mA/cm^2 was observed at -250 mV for 10 mM $HTeO_2^+$. The equilibrium reduction potential of the combined electrolyte was found to be more

positive compared to the individual electrolytes due to the mutually induced codeposition mechanism. (24, 26) Addition of Te in the combined electrolyte shifted reduction potentials to more positive region. For instance, the reduction potential for combined electrolyte with 10 mM $HTeO_2^+$ plus 20mM Bi^{3+} (20/20) starts at 19 mV, while for 20 mM $HTeO_2^+$ plus 20mM Bi^{3+} (20/10) electrolyte starts at 34 mV. To be noted that the current in the combined electrolytes follows a similar trend in Bi^{3+} individual electrolyte. A limiting current was observed in the combined electrolyte when the individual kinetic region Bi current is less than the Te counterpart.

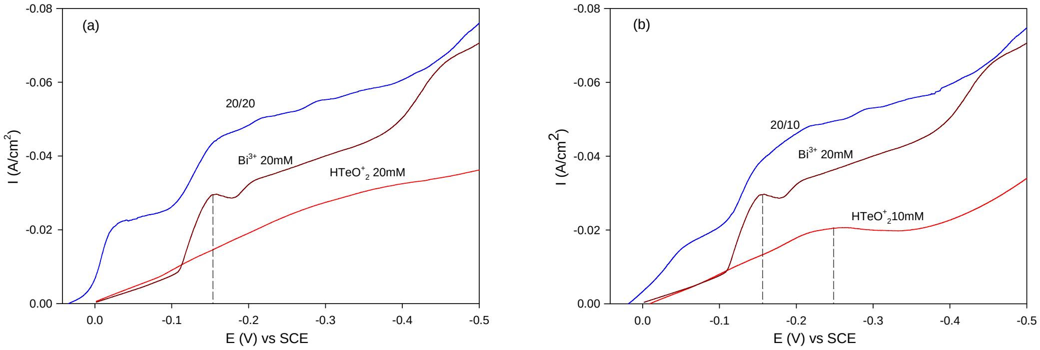


Figure 1a. Polarization curves of $HTeO^+_2$ (20Mm), Bi^{3+} (20mM), combined (20/20) electrolytes at a scan rate of 5 mV/s. Figure 1b. Polarization curves of $HTeO^+_2$ (10Mm), Bi^{3+} (20mM), combined (20/10) electrolytes at a scan rate of 5 mV/s.

Figure 2 shows XRD pattern of the nanowires deposited in AAO membrane at potentials -5 mV, -100 mV, and -300 mV from the 20/20 electrolyte. The nanowires deposited at -5 mV and -100 mV show a preferential (110) orientation, indicating that nanowires are polycrystalline with c-axis almost parallel to the nanowire length. However, the intensity of (110) peak decreased for nanowires deposited at higher overpotentials (-100 mV) and the (110) peak was strongly diminished for the sample deposited at even higher overpotential (-300 mV). Crystallite size calculations using the Scherer equation in JADE™ showed crystallite sizes of 210 Å, 150 Å, and 950 Å for nanowires deposited at -5 mV, -100 mV, and -300 mV, respectively. The XRD data suggests that the crystallite size is directly proportional to the deposition potential; higher the deposition potential larger the crystallite size.

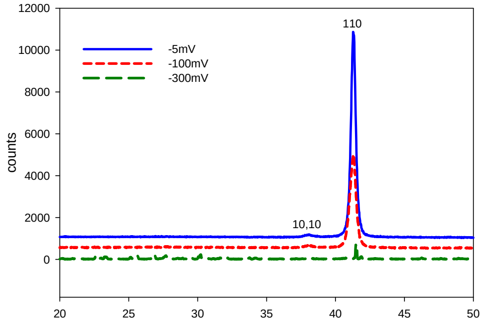


Figure 2. XRD of Bi_xTe_y nanowires deposited in AAO membranes at different potentials from 20/20 electrolyte.

b. Nanoparticle Composites (Stokes, Swart, Nolting)

We have prepared nanostructured Bi_2Te_3 and $Bi_{0.5}Sb_{1.5}Te_3$ powders. Briefly, elemental constituents (bismuth, tellurium and antimony) are loaded into a stainless-steel vial with stainless steel balls. The elements were purchased from ESPI; all elemental metals were 5N pure. We optimized the synthetic protocol by varying the length of ball-milling time as well as the ratio of the mass of the steel balls to mass of constituent material. We were able to obtain pure phases of both Bi_2Te_3 and $Bi_{0.5}Sb_{1.5}Te_3$. Figure 1 shows the powder x-ray diffractograms of the two compounds. Optimum conditions to obtain phase-pure samples were a ball-to- material ratio of 10:1 and ball-milling times of 25 to 40 hrs. Phase evolution was monitored at intermediate time intervals to establish the ball-milling protocols.

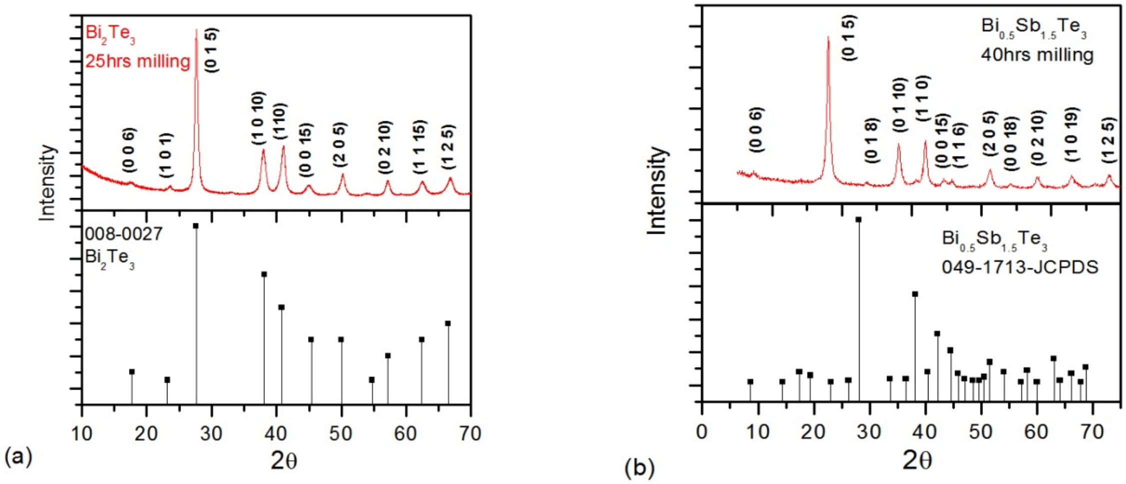


Fig. 1. X-ray diffraction patterns of (a) bismuth telluride and (b) bismuth antimony telluride powder samples. A comparison to Joint Committee on Powder Diffraction Standards (JCPDS) data is given in the lower graphs.

A representative scanning electron microscope (SEM) image of the ball-milled powders is shown in Fig. 2. The powders consist of large particles, on the order of several hundred microns. However, each large particle is an agglomeration of much smaller, nanometer-sized grains. These smaller, nanoscale structures are evident in the transmission electron microscope (TEM) image of the same powder shown in Fig. 3.

We have begun a preliminary study of the thermoelectric properties of these composites. The powders were consolidated in a uniaxial hot press. We were able to produce high-density pellets, 10 mm in diameter of both Bi_2Te_3 and $Bi_{0.5}Sb_{1.5}Te_3$. The density of the $Bi_{0.5}Sb_{1.5}Te_3$ sample was found to be 6.6 g/cm^3. This consistent with the density of the bulk alloy: The density of pure Bi_2Te_3 is 7.7 g/cm^3 and that of Sb_2Te_3 is 6.5 g/cm^3. A photograph of one of the pellets is shown in Fig. 4.

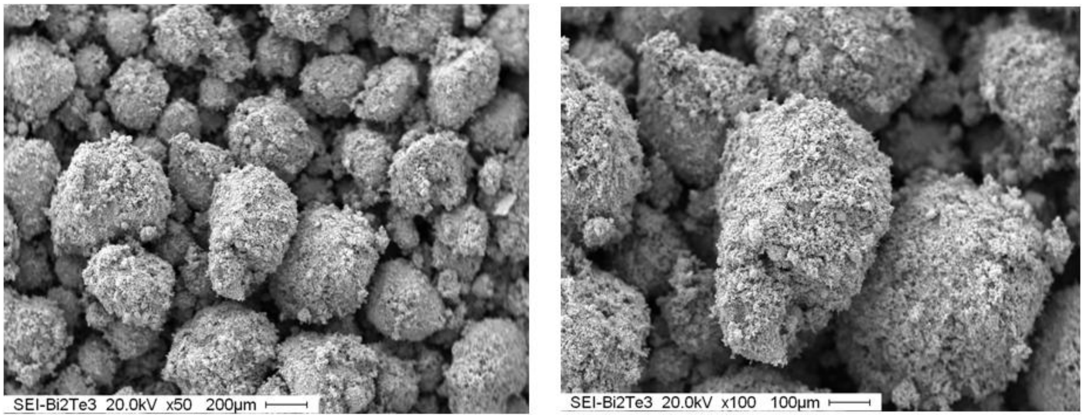


Fig. 2 Scanning electron micrographs (SEM) images of the ball-milled bismuth telluride powder.

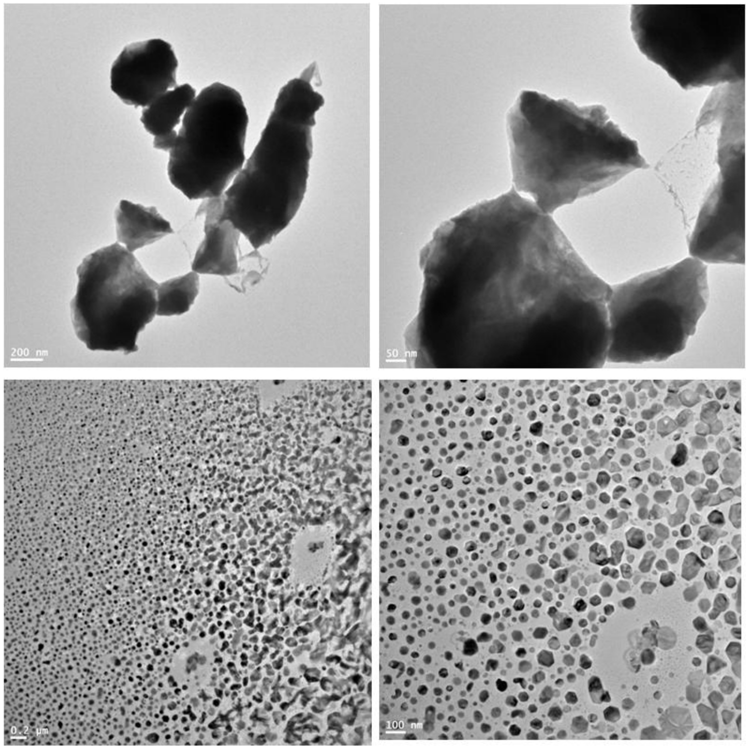


Fig. 3 Transmission electron micrographs (TEM) images of the ball-milled bismuth telluride powder.

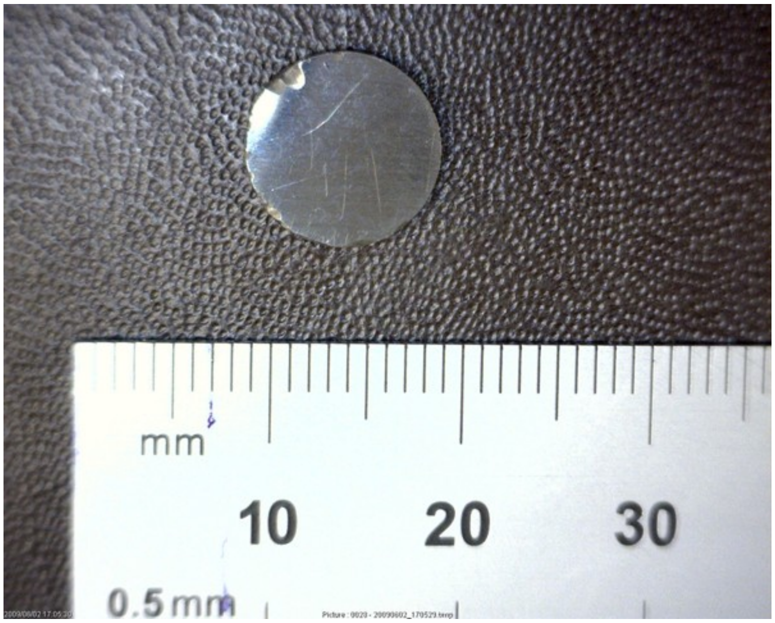


Fig. 4 Pellet of Bi_2Te_3 consolidated from ball-milled powder. The powder was pressed in a uniaxial press under a pressure of 50 MPa at 400°C for 1 hour.

c. Thermoelectric Transport in Wires (Champagne, Karki, Walker andYoung)

Our research has focused on the synthesis and characterization of novel intermetallic systems in reduced dimensions. By measuring the magnetotransport behavior of these materials in reduced dimensions, we gain insight into the physics driving the transport properties between the films and the bulk. We have just begun our initial investigation of the thermoelectric properties of films and fibers of MoN and Mo_3Sb_7, which have never been measured before. It's quite possible that the thermal conductivity in these advanced architectures can be reduced, thereby improving the materials overall thermoelectric performance.

Figure 1. New microfibers of $ZnNNi_3$.

In addition, we have begun a study of the intermetallic $Ag_{8+\delta}GeTe_6$ (Ag816). This material in bulk form has one of the lowest thermal conductivities of any material, and as such, warrants further investigation as a potential thermoelectric. Furthermore, it is a mixed conductor, possessing both electronic and ionic contributions to its electrical conductivity. In our thermal transport study of this material, we discovered that the electrical resistivity is a function of the local Ag-ion concentration, which can be altered via application of an electric field (current). This moves the Ag ions from one end of the sample to the other via a network of vacancies in the crystal structure, thereby creating a resistivity gradient across the sample. This produces a large non-uniform Joule heating effect which is reversible with current direction (see Figure 2). Large temperature differences between the two ends of the sample can be maintained, since the thermal conductivity of the material is so poor. Simply by switching the direction of the current, we can change the direction of the temperature gradient. In some samples with a current of 100 mA, we are able to maintain a 100 ^{o}C temperature difference across a 1-cm long sample.

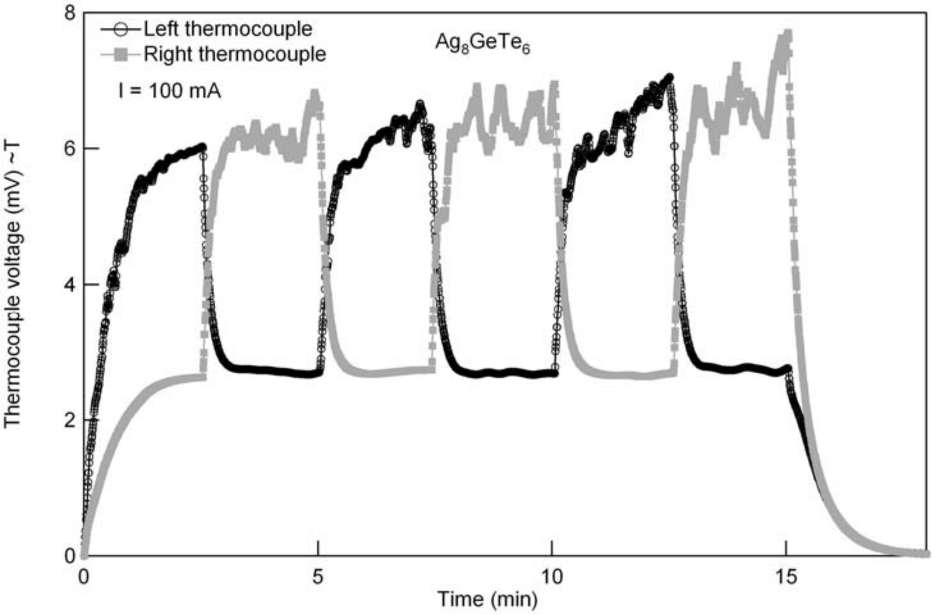


Figure 2. Plot of the thermocouple voltages attached to the two ends of a bar of Ag816. The left axis is proportional to temperature. Notice how the temperature gradient switches direction upon changing the direction of the current, for example, at 2.5 min and 5 min.

We have also made the Si version of the 218 material (Ag_8SiTe_6) as well as doped variants of the Ge compound, including: Se doping for Te and Cu doping for Ag. The hope is that through the chemical substitutions, we can reduce the electrical resistivity without adversely affecting the large Seebeck values and low thermal conductivity. There is a metal to semiconductor transition in the Mo_3Sb_7 system doped with Te. Good thermoelectrics tend to have carrier densities on the order of $10^{19}/cm^3$ By doping with Te, we can shift the Fermi surface toward a gap-edge in the density of states. We have begun the initial synthesis of this doped material. Our goal is to reduce the dimensions by synthesizing thin films via pulsed laser deposition (PLD).

This ongoing research program offers postdocs the opportunity to work on novel systems, provides graduate students with an avenue to perform dissertation directed research, and trains undergraduates in a variety of synthesis and characterization techniques. Overall, materials synthesis provides a natural bridge between teaching and research, especially for undergraduates. They are able to make real contributions in a relatively short amount of time. Nick Walker worked on this project last summer. He is an undergraduate biological science major from Nicholls State University and a participant in the Louisiana Biomedical Research Network (LBRN) Summer Research Program. Nick was an excellent student who made significant progress on the thermoelectric project in just several weeks. He presented his results during a poster session at the end of the program..

Considering the alternative energy aspects of thermoelectrics, and the new President's strong policy for increased funding in basic scientific research, new federal monies may emerge for thermoelectric research. We will pursue these opportunities in the upcoming year.

5. Work Products

d. Electrochemical storage materials (Gabrisch, Mohanty and Yi)

The main part of our research activities concerns the characterization of electrode material used in rechargeable Li-ion batteries by electron diffraction. During the past year we synthesized mixed transition metal oxides using a co-precipitation method and began a collaboration with Southern University for testing in Li-half cells. The combination of EELS and SQUID measurements proved a fruitful approach to better understand observed crystallographic transformations in Li_xCoO_2. The educational effort was realized by involving an undergraduate student in the research. A new undergraduate course : Introduction to Material Chemistry (CHEM 3610) has been developed by the PI and was taught for the first time in Fall 2008.

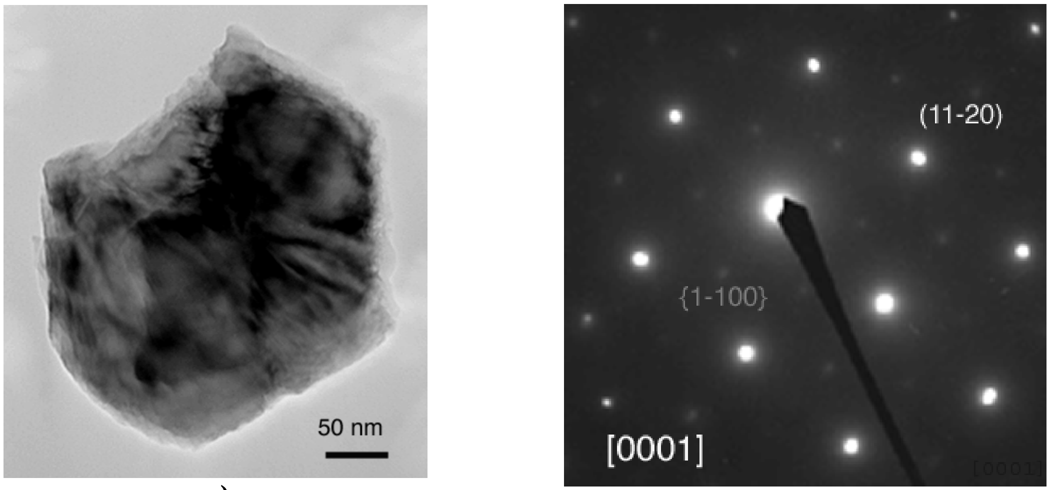
Experimental

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ was prepared by the hydroxide co-precipitation method. Stoichiometric amounts of $NiSO_4·6H_2O$, $CoSO_4·7H_2O$ and $MnSO_4·H_2O$ with a Ni:Co:Mn ratio of 1:1:1 were dissolved in distilled water separately to produce concentrations of 2 $molL^{-1}$. Then the solutions were precipitated by adding aqueous NaOH solution and proper amounts of NH_4OH solution under Argon atmosphere. The solution was kept in Argon atmosphere for 24 h at 50 ^oC while maintaining a pH of ~10-11. The precipitate was filtered, washed with water and kept in a glove box overnight at 50 ^oC. The obtained precursor was mixed with 5 % excess $LiOH·H_2O$ and thoroughly ground in a mortar. The powder was pressed into pellets and heated at 450^{o}C for 5h followed by heating at 650^{o}C for 9h. The disintegrated pellets were pressed again and calcinated at 850^{o}C for 18hrs to obtain $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. Chemical delithiation was performed under Argon atmosphere using NO_2BF_4 solution at a ratio TM : oxidant = 1 : 1.1 over 3 hours at room temperature. Subsequently portions of the delithiated powder were heat treated in air at 70ºC for 30 days. Commercial $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and cycled cathodes prepared of the powder were obtained from ENAX Inc (generation 2, powder prepared according to the method published in [8]). The cathodes underwent 520 charge discharge cycles between 3.0 and 4.3V and were stopped in the discharged state.

Electron diffraction experiments were performed using the JEOL 2010 Transmission Electron Microscope at the University of New Orleans operated at 200 kV. Experimental diffraction patterns were compared to patterns simulated with the software Desktop Microscopist using unit cells published in literature, a list can be found in [1].

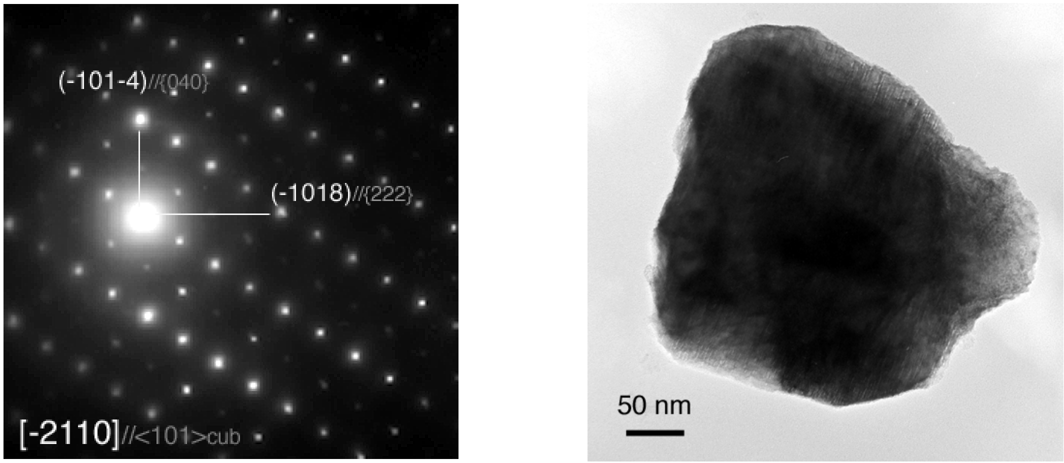
Results and Discussion

The in-house synthesized $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ showed no evidence of long range ordering, consistent with the low synthesis temperature of 850ºC. Out of 22 analyzed particles 20 were characterized by electron diffraction pattern typical for the O3 phase, which means that the TM ions are randomly distributed over the 3a lattice sites. A small fraction of particles (2 out of 22) showed spinel type reflections. Chemical extraction of Li from the synthesized particles did not introduce significant changes to the microstructure (estimated Li-content 0.75). This observation differs from observations in chemically delithiated Li_xCoO_2 where removal of small amounts of lithium results in the appearance of forbidden $\{1\bar{1}00\}$ reflections in the [0001] zone axis pattern. In $LiCoO_2$ O-Co-O slabs glide in the (0001) plane upon Li removal, which changes the stacking order and breaks the rhombohedral symmetry along the stacking direction of O-Co-O which gives rise to the observed $\{1\bar{1}00\}$ reflections. In $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ we observed very faint forbidden reflections, only in one out of 10 particles, see Fig. 1. This indicates an improved structural stability of the mixed TM compound in comparison to $LiCoO_2$. Annealing of the delithiated particles increased the amount of spinel phase to approximately 40%. Additionally after annealing the morphology changes in some particles to a lamellar structure, see Fig. 2. A comparison of the analyzed particles is given in table 1.



a.) **b.)**

Fig. 1 : $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ particle produced by chemical delithiation showing faint $\{1\bar{1}00\}$ reflections (see text).

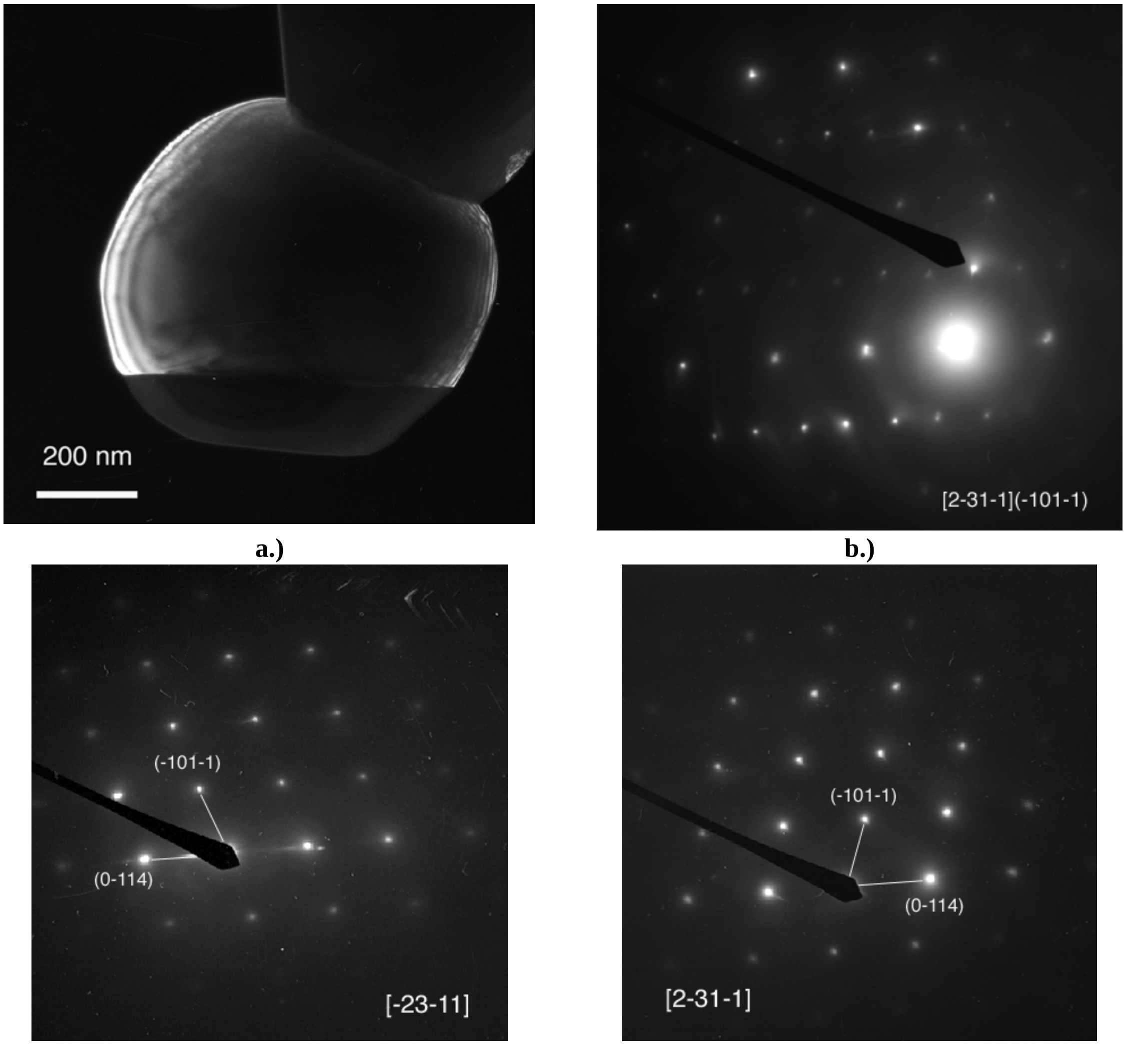


a.) **b.)**

Fig. 2 : $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ particle produced by chemical delithiation and annealing at 70ºC for 30 days. The diffraction pattern shows contributions of the O3 phase and fainter contributions of the cubic spinel phase, notice the morphology change near the particle surface.

<u>Table 1 :</u> Analysis of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ synthesized at UNO (The numbers reflect the count of each category, all particles were single crystal, the total number particles analyzed is give in brackets at the top of each column.)

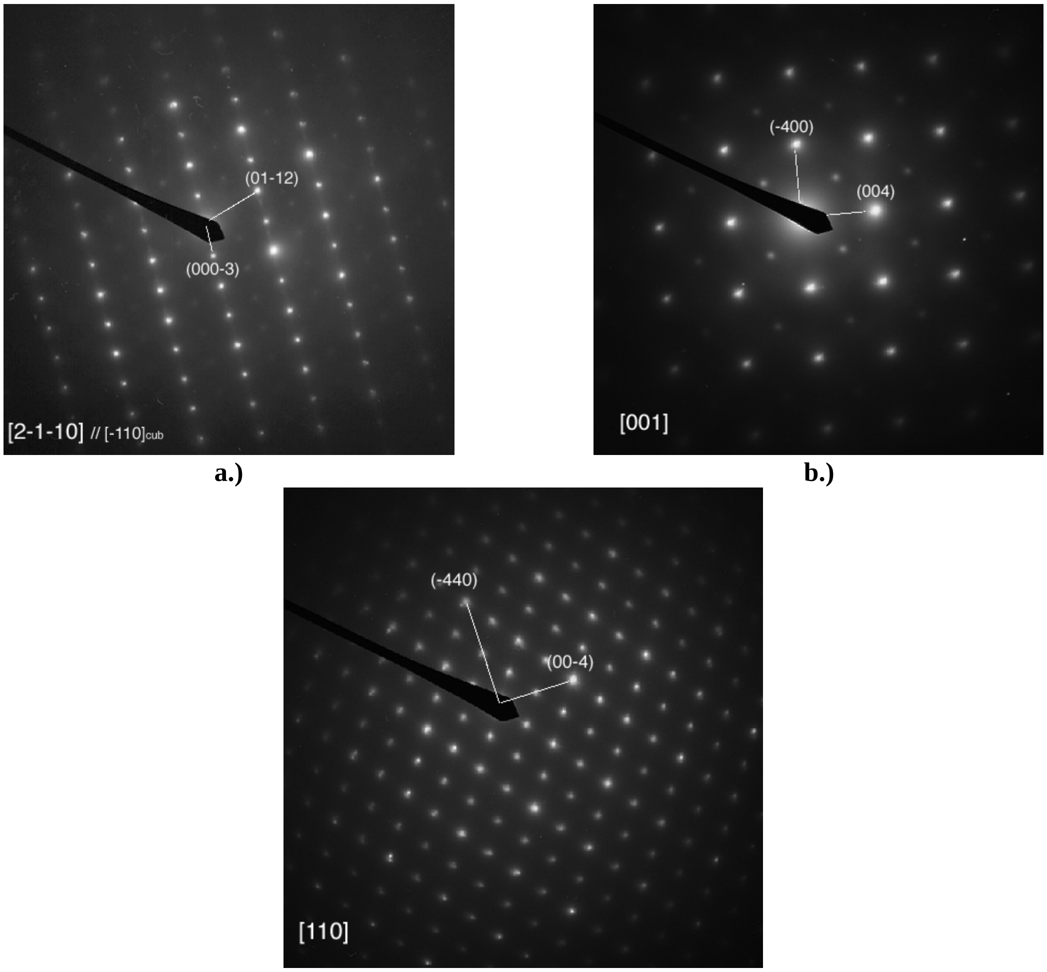
Classification	as synthesized (22)	delithiated (10)	delithiated, annealed (10)
O3	20	9	10
spinel	2	5	5
forbidden $\{1\bar{1}00\}$	0	1	0



a.) **b.)**

c.) **d.)**

Fig. 3 : Image and diffraction patterns taken from a pristine, commercial poly-crystalline particle. a.) dark field image taken with a reflection unique for the bright part in the image. b.) corresponding diffraction pattern, the reflection used for imaging is marked by the pointer. c. and d. show the diffraction patterns of the two crystals.



a.) **b.)**

c.)

Fig. 4 : Electron diffraction patterns showing spinel reflections of increasing intensity from a.) to c.) corresponding to a gradual cation rearrangement.

Table 2 : Analysis of commercial $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$: the numbers reflect the count of diffraction patterns in each category. Some particles were poly crystals, the total number of analyzed patterns is given in brackets at the top of each column, 25 pristine particles, 15 cycled particles were analyzed.

classification	pristine (31)	cycled (17)
O3	22	6
spinel	5	8
$\sqrt{3} \times \sqrt{3}$ R30°	3	2
other	1	1

The commercially produced $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ obtained from ENAX Inc. revealed a less homogeneous picture than our synthesized material. The material is however more homogeneous than the generation-I material supplied by the same company[1]. We found that the pristine material has about 20% polycrystalline particles and a small amount of in plane long-range ordering corresponding to the $\sqrt{3} \times \sqrt{3}$ R30° unit cell. In most cases the polycrystalline particles consisted of two crystals indexed as O3 phase that were related by a twin boundary (4 out of 5). An example is shown in Fig.3, where diffraction patterns of each crystal (Fig. 3c,d) are shown together with the superimposed pattern obtained from the whole particle (Fig. 3b) and a dark field image taken with a reflection unique to one crystal (Fig. 3a). The amount of poly-crystals was approximately constant in the particle population analyzed after cycling. Similarly the amount of long-range order remained constant before and after cycling, with 10% and 13% respectively. A change was however observed in the amount of spinel phase : during cycling the amount of spinel increased at the expense of O3 phase from 16% before cycling to 47% after cycling. In both samples the intensity of spinel reflections spans a wide range corresponding to a gradual change of the cation ordering between the two limiting phases : layered and cubic. This is illustrated in Figs. 4 a-c, where the typical spinel reflections are barely visible in Fig. 4a while they have an intensity identical to that of the fundamental reflections in Fig .4c. A summary of the analyzed particles of the commercial material is given table 2.

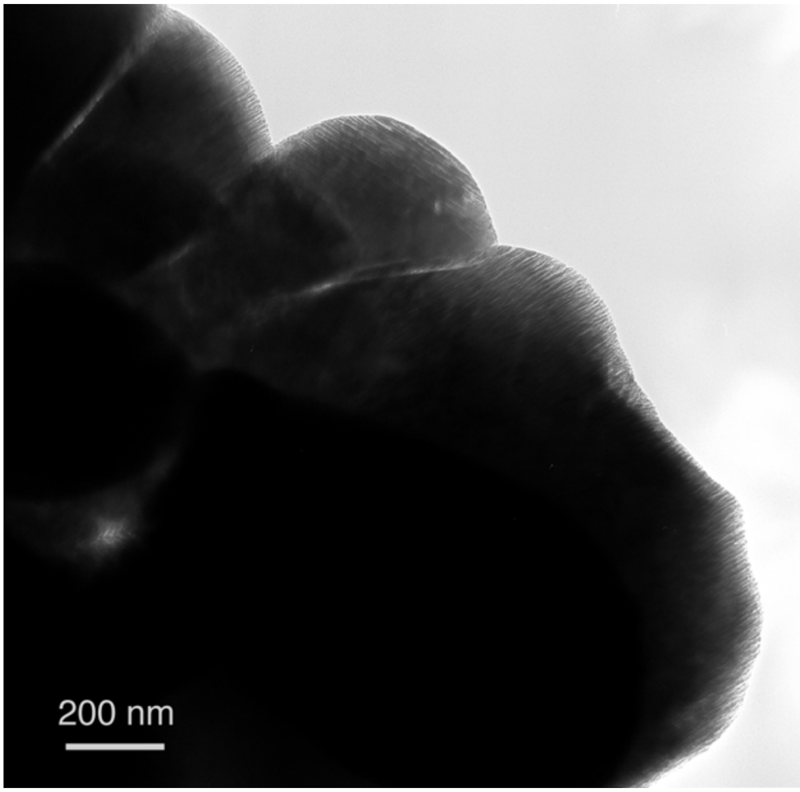
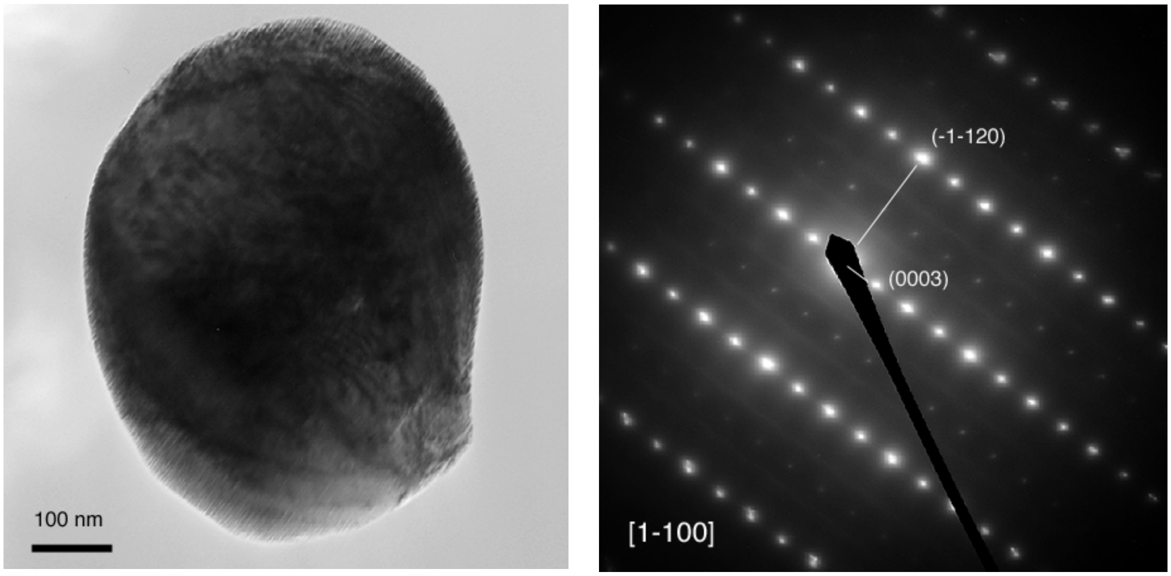
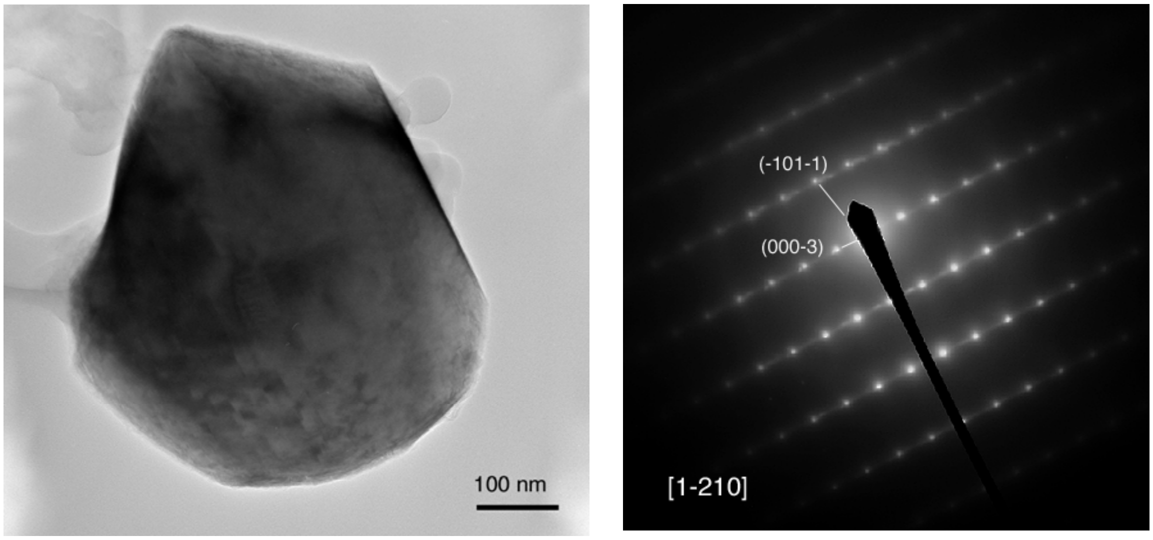


Fig. 5 : Transition Electron Microscope image showing an agglomerate of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ particles with a mile feuille morphology observed after charge discharge cycling or ageing.



a.) **b.)**

Fig. 6 : Image and diffraction pattern illustrating the orientation relationship between the lamella in the mille feullie morphology and the diffraction pattern.



a.) **b.)**

Fig. 7 : Image and diffraction pattern of a cycled particle.

The most striking observation in the cycled particles is the change in morphology in some particles that is similar to that observed in chemically delithated particles after heat treatment, see Fig.5. Apparently the particles start to disintegrate during cycling or anneal and form a lamellar morphology that we name “mille feuille”. In Fig. 6 a mille feuille particle is shown together with its diffraction pattern. The diffraction pattern can be indexed as O3 phase, however faint contributions of spinel and $\sqrt{3}\,\mathrm{x}\,\sqrt{3}\,\mathrm{R}30^{\mathrm{o}}$ ordering are also observed. A comparison between the directions in the diffraction pattern and in image illustrates that the lamellas form between (0001) planes, where bonding between adjacent layers is weak. A loser look at the intensity of fundamental reflections in Fig. 6b shows that the shape is not circular but streaked along the [0001] direction. Streaking indicates the presence of either stacking faults or very thin platelets in planes perpendicular to the streaking direction, which are the (0001) planes. At this point it is not clear whether the observed mille feuille morphology is responsible for the observed streaking. In Fig. 7 a cycled particle is shown that does not have the mille feuille morphology, but has high amounts of streaking in the diffraction pattern. Altogether we observed streaking in 6 out of 15 particles analyzed after cycling, but only in one out of 22 of the pristine material.

Conclusions

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ synthesized at 850ºC shows no in plane ordering and is structurally stable with respect to cation arrangement during chemical delithiation. After long-term anneal at 70ºC about 40% of the particles have a spinel structure and in some particles a the morphology has changed to a mille feuille type appearance. Commercial $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ synthesized at 1000ºC shows long-range ordering in about 10% of the analyzed diffraction patterns, a fraction that remains stable over charge discharge cycling. The pristine material consists to 70% of particles with random TM ions distribution on the 3a lattice sites, however after 520 charge discharge cycles a portion of these have transformed to spinel, so that about 47% spinel phase is observed after cycling. The mille feuille morphology is observed frequently after cycling. Streaking in the diffraction pattern of cycled particles indicates that microscopic defects have formed on (0001) planes.

Reference

[1] H. Gabrisch, T. Yi, and R. Yazami, Electrochemical and Solid-State Letter **11**(7) (2008) p. A119-A124.

e. Ferroic Materials (Malkinski)

This project deals with nonconventional methods of mutual conversion of electric to magnetic fields. One way of converting electric to magnetic field is developing multiferroic materials consisting of ferroelectric and ferromagnetic materials. More specifically, the ferroelectrics with superior electrostrictive properties can transfer over 90% of electric energy through elastic coupling to ferromagnetic materials with excellent magnetostrictive properties. The materials in the form of powders of ferroelectric PZT and PMN materials and ginat magnetostrictive Terfenol powder have been purchased to make composite materials. The first results showed that the elastic coupling between the grains of ferroelectric and ferromagnetic grains is essential for the performance of the composite. Two methods of binding have been explored: cold pressing and resin bonds. Both methods were found to have some disadvantages for the properties of composites. Cold pressing at smaller pressures cannot produce strong mechanical bonds between the hard grains. On the other hand, larger pressures change properties of the magnetostrictive material by inducing magnetic stress-anisotropy. These problems do not exist for resin bonding. However, in the case of indirect bonding the mechanical properties of the resin as well as the amount of the resin in between the grains are essential for the performance of the composite. It was found that too large amount of the resin absorbs the stresses and prevents efficient transfer of elastic energy between the grains of different kind. Another conclusion for the initial research is that the elastic properties of the resin should match those of the ferroelectric and ferromagnetic grains as close as possible. The research will be continued to optimize these parameters. In addition hot pressing and sintering will be explored.

Recently Dr. Malkinski has been working on developing a new concept of a composite of organic molecules and inorganic nanoparticles which will display the properties of multiferroic materials. The general idea is to embed elongated magnetic particles into nematic liquid crystals. The elongate molecules of the liquid crystal while directed by an applied electric field will drag magnetic nanorods and change the direction of the magnetic field produce by them.

Both kinds of the materials may lead to applications in voltage controlled magnets, which will be lighter and more energy efficient compared to electromagnets, which require large currents and produce significant losses of energy due to heat dissipation.

f. Nanoassembly of nanoparticles and tubule nanocontainers (Lvov)

Halloysite clay nanotubes were investigated as a nanotubular container for the corrosion inhibitor benzotriazole. Halloysite is a naturally occurring cylindrical clay mineral with an internal diameter in the nanometer range and a length up to several microns, yielding a high aspect ratio hollow cylindrical structure. Halloysite may be used as an additive in paints to produce functional composite coating material. Maximum benzotriazole loading of 9 % by volume was achieved for clay nanotubes of 50 nm external diameter and lumen of 15 nm. Variable release rates of the corrosion inhibitor were possible in a range between 5 and 50 hours as was demonstrated by formation of stoppers at tube openings. The anticorrosive performance of the sol-gel coating and paint loaded with 2-5 % of halloysite entrapped benzotriazole was tested on copper and on 2024-aluminum alloy by direct exposure of the metal plates to corrosive media. Kinetics of the corrosion spot formation at coating defects was analyzed by the scanning vibrating electrode technique with essential damping of corrosion development demonstrated.

Halloysite / paint nanocomposite coating In Fig. 1, SEM micrograph of halloysite nanotubes in scratched paint layer is shown. Nanotubes are exposed to external environment at paint scratch or cracks. Benzotriazole loaded halloysite will start enhanced release of the inhibitor when a crack the occurred, protecting the metal underneath from corrosion development.

Fig. 1. SEM micrograph of paint scratch containing 5 wt % of halloysite nanotubes in it

Halloysite is readily mixed with a variety of metal protective coatings which is an important advantage for this material. Water contact angle for halloysite pressed in the tablet was found as low as 10 ± 3° but it still was easily wet with paint, probably due to its highly porous surface. Surprisingly, for paint droplet the contact angle was even less, of ca 3 °. Paint droplets spontaneously spread over the halloysite tablet, which is an indication of good wettability of the halloysite surface by paint. The reason for this could be due to specific chemical interactions (like Van Der Waals interaction) between surface OH groups and paint CH groups.

Addition of nanotubes into industrial oil based paint significantly improved the strain – stress characteristics of the metallic coating as it is demonstrated in Fig 2. Threefold increase of paint tensile strength was observed with addition of 5 wt % of halloysite (0.7 MPa for pure paint versus 1.9 MPa for 5 wt % halloysite loaded paint). Halloysite fillers also increases the hardness of the paint. An elastic modulus of the dry paint samples was 16.3 MPa for the layer of pure paint and 23.1, 34.6, 69.3 MPa for 2 wt %, 5 wt %, and 10 wt % composite of halloysite with paint, respectively. However, paint films became brittle with loadings greater than 5 wt % halloysite. These data correspond to results on halloysite clay / polymer bulk composites. For example, incorporation of 5-13 % of halloysite in polypropylene resulted in 30-50 % strength increase. Therefore, from the point of view of paint cover strength, an optimal loading is approximately 5 wt %.

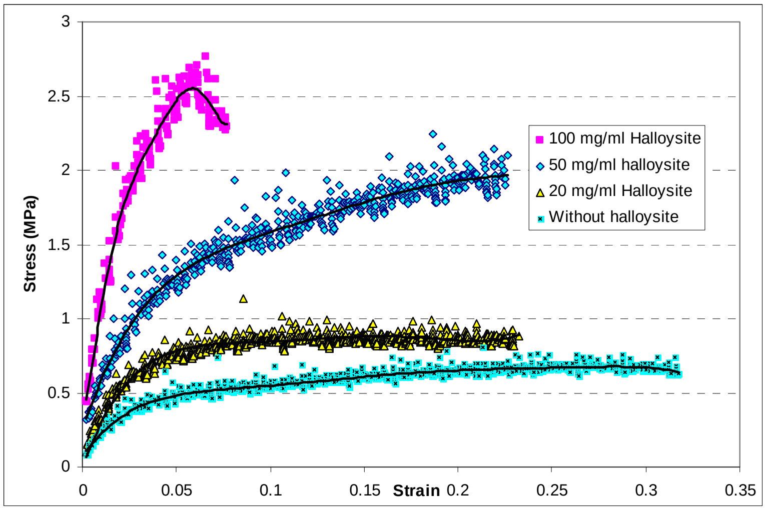


Fig.2. Stress strain relationship of industrial oil based blue paint. Concentration of halloysite is shown in milligrams of added halloysite per milliliters of wet paint.

Enhanced corrosion protection with benzotriazole loaded hallosyite The initial stages of corrosion development in metal coatings and self-healing ability of the halloysite-doped film were analyzed with scanning vibrating electrode technique on 2024-Al alloy (taken as a substrate), which contains 4 wt % copper. Alloy plates were coated by dip-coating procedure with ZrOx-SiOx sol-gel layer and artificially scratched. Both samples with and without inhibitor-loaded halloysites were immersed in corrosion solution and corrosion development was observed over 24 hours as maps of the corrosion current. Anodic corrosion activity on the aluminum alloy coated by simple sol-gel layer was high and rapidly increased within several hours in the scratched area. This indicates a fast pitting corrosion process taking place at the artificially introduced defect(s). In case of alumina coated with sol-gel containing halloysite tubes filled with benzotriazole, the rate of corrosion at the defect points is strongly reduced in the first moment of corrosion and almost no corrosion current (both cathodic and anodic) was observed. Compared to the pure sol-gel coating, maximal current density in this case was 6 times smaller (ca. 3 μA/cm² for inhibitor containing sol-gel and 18 μA/cm² for pure sol-gel after 24 hours of immersion), which points out very strong anticorrosion self-healing effect caused by controlled release of the inhibitor from the halloysite nanotubes in the cracked area.

Summary: Halloysite nanotubes are a promising material for entrapment of corrosion inhibitors into paint due to its viability and compatibility with variety of water or oil based coatings. Benzotriazole was loaded in 50 nm diameter halloysite tubes and admixed to paint coating in the amount 2-5 wt %. A tensile strength of such nanocomposite paint coating increased approximately in 2 times. Benzotriazole release from raw halloysite nanotubes extended for ca 5 hours, and its kinetics was fit with power function model. Corrosion inhibition efficiency of halloysite nanocontainers for aluminum and copper samples was demonstrated by monitoring the localized corrosion current density on scratched as well visually by exposure of scratched metal sample to highly corrosive environment showing significant reduction in metal corrosion rate.

C. Opportunities for Faculty Recruitment, Retention and Development Post-doc, Graduate and Undergraduate Student Training

- Seven graduate students and four undergraduate students are currently involved in training under this project, (five from La Tech/IfM, three from UNO and three from LSU).
- Undergraduates who were trained in the project: Michelle Sibille, Enkhjin Bayarsaikhan, and Chris Chain. Michelle Sibille has been accepted to medical school for fall 2009. Master's level graduate students: Raj Masvekar, Jessica Wasserman, and Dustin Green. Raj Masvekar and Dustin Green have been accepted into Ph.D. programs away from Tech for fall 2009 and Jessica Wasserman has been accepted into the Ph.D. program in Biomedical Engineering at Tech for Fall 2009. Post doc Dr. Mangilal Agarwal worked for the project for one year.

D. Partnership Activities

- Stokes (UNO) has partnered with Nanohmics, Inc. (Austin, TX) and United Technologies Research Center on a project concerning flexible thermoelectric devices.
- Drs. Lvov and Decoster –AMRI annual conference in February 2009, and discussed results with AMRI researchers. Two joint reports were presented at AMRI Mardi Gras symposium. With Prof. Kevin Stokes, we are working on preparation of the project on clay nanotube smart nanocontainer for anticorrosion coating.

E. Problems Encountered

- Second year funding for LaTech/IfM was delayed for six months and money received in December 2008, therefore, again we will need extension till December 31, 2009.

3. **Contributions:**

- Constructed a sample holder that will allow us to measure the Seebeck coefficient of thin films. The holder is designed to fit on a transport puck from the Quantum Design PPMS system, so that the temperature dependent thermopower can be measured.
- Constructed a "ZT-meter", which utilizes Harman's method to directly measure the thermoelectric figure of merit of a material. Currently, the meter can be used at room temperature. Having this device available will greatly facilitate in the screening of many new materials for improvement in their thermoelectric properties.
- "Clay Nanotubes for Controlled Release of Corrosion Inhibitors," NASA-EPSCOR LA BoR, pre-proposal, PI, $200,000, Jan 2010-Dec 2011.
- "Clay Tubule Nanocontainer for Responsive Corrosion Protection," NSF-nanomanufacturing, PI, $270,000, Sept- 09- Aug 20012
- 'Microfluidic Device for Directed Assembly of Nanoparticles and Polyelectrolytes on in situ Generated Templates," NSF-Nanomanufacturing, PI, $280,000, Sept- 09- Aug 20012
- "Materials Synthesis in Clay Nanotubes," PI, NSF, $340,000, Sept 2009- Aug 2012
- "Clay Tubule Nanocontainer for Responsive Corrosion Protection," NSF-nanomanufacturing, PI, $270,000, Sept 09- Aug 2012
- 'Collaborative Research: Microfluidic Device for Directed Assembly of Nanoparticles and Polyelectrolytes on in situ Generated Templates," NSF-nanomanufacturing (with Virginia Tech), PI, $280,000, Sept- 09- Aug 20012

4. **Project Revision**

- Dr. Despina Davis replaced as co-PI Kody Varahramyan with responsibility for the thermoelectrics project at IfM.

5. **Work Products:**

Papers:

A.B. Karki, D.P. Young, P.W. Adams, E.K. Okudzeto, and J.Y. Chan, "Critical current behavior of superconducting MoN and Mo3Sb7 microfibers", *Phys. Rev. B* **77**, 212503 (2008).

A.B. Karki, Y. M. Xiong, D.P. Young, and P.W. Adams, "Superconducting and magnetotransport properties of ZnNNi3 microfibers and films", submitted.

J. Zhang, A. Kumbhar, J. He, N. Das, K. Yang, J.-Q. Wang, H. Wang, K.L. Stokes and J. Fang, "Simple Cubic Super Crystals Containing PbTe Nanocubes and Their Core-Shell Building Blocks," *J. Am. Chem. Soc.* **130**: 15203-15209 (2008).

N. Veerabadran, Y. Lvov, R. Price, "Organized Shells on Clay Nanotubes for Controlled Release of Macromolecules" *Macromolecular Rapid Commun.***,** v.24, 99-103, 2009. featured on the journal cover page.

T. Shutava, S. Balkundi, Y. Lvov, "Epigallocatechin gallate/gelatin layer-by-layer assembled films and nanocapsules," *J. Colloid Interface Science,* v.330, 276-283, 2009

R. Mannam,M. Agarwal, A. Roy, V. Singh, K. Varahramyan, D. Davis, "Electrodeposition and Thermoelectric Characterization of Bismuth Telluride Nanowires," *J. Electrochemical Society* **156**, 8, 2009

Presentations:

1. “Nanostructured Thermoelectric Materials,” K.L. Stokes, Dept. of Chemistry and Physics Seminar, Southeastern Louisiana University, Apr. 3, 2009. (invited)
2. Q. Xing, S.Chen, M. DeCoster Y. Lvov, “Porous 3D Cellulose Fiber Based Microscaffold for Cell Culture,” TERMIS-NA 2008 (Annual Conference of Tissue Engineering & Regenerative Medicine International Society), San Diego, Dec 10, 2008.
3. S. Madisetti, Z. Zheng, Y. Lvov, L. Que, “Layer-by-Layer Nanoscale Coating of Microparticles with Droplet Microfluidic Device,” 4th Annual International Conference on Nano, Micro Engineering and Molecular Systems, IEEE-NEMS'09, Shenzhen, China, Jan 8-12, 2009
4. D Fix, Y. Lvov, H. Möhwald, “Inhibitor Loaded Halloysite Nanotubes for Corrosion Protection,” International Conference NanoMaterials-2009, Lisboa, Portuguese, April 5-8, 2009.

PKSFI Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04

Matthew A. Tarr
(PKSFI Broader Impacts, 2008-2009)

Broader Impacts (Educational and Commercial Outreach)

1. **Personnel:** List all key personnel and other staff who provided *significant* contributions to the project. Provide information about the types of contributions made by each listed participant and controls in place to ensure that these contributions are adequate to the project's requirements.

Matthew Tarr, Professor, Dept. of Chemistry, University of New Orleans – planned and coordinated academic year outreach activities (ScienceReach program) with subcontractor, Communities In Schools of New Orleans (CISNO); reviewed CISNO quarterly reports; presented program updates at quarterly meetings; conducted site visit to CISNO to evaluate subcontractor progress; coordinated planning and recruiting for summer outreach program (10 high school student participants for the summer 2008 program and 12 participants for the summer 2009 program). Supervised by project PI, Dr. Charles O'Connor.

Sara Massey , Director, Communities In Schools of New Orleans – directed all activities carried out by CISNO including academic year outreach programs in two New Orleans public or charter schools. Responsible for hiring and supervising ScienceReach program coordinator. Evaluated via quarterly reports submitted to Dr. Tarr and by site visits conducted by Dr. Tarr.

Brittany Morgan, ScienceReach Coordinator, Communities In Schools of New Orleans – implemented academic year outreach activities. Directly supervised and evaluated by Sara Massey.

2. **Activities and Findings:**
   - Describe major research and educational activities undertaken in this reporting period

The major focus of this project during the first project year has been on developing an academic year outreach program that targets New Orleans public or charter schools.

During this project year, the ScienceREACH program worked in four schools; McMain Secondary School, Sarah T. Reed High School, Martin Luther King, Jr. Charter for Science and Technology, Fischer Elementary. The programs implemented included; Rocketry Program, Forensics After School Program, Engineering Activities, Presentations, College STEM Major Lunches, Field Trips, In-Class Assistance, a College Day, a Science Fair, College Assistance and Tutoring/Mentoring, which combined reached a total of 204 students across 225 sessions.

(1) **Rocketry Program:** The Rocketry was an afterschool program at McMain Secondary School. Students built rockets under the supervision and guidance of David Koscielniak as part of the Team America Rocketry Challenge (TARC). The program served a total of 40 students across 26 sessions.

(2) **Forensics After School Program:** The Forensics Program was another component of the afterschool program at McMain Secondary School. In the Forensics Program students were exposed to the many STEM fields working within forensics including; Computer Forensics, DNA Analysis, Chemical Forensics, Forensic Anthropology, Forensic Pathology, and handwriting analysis. The forensics program engaged various professional from New Orleans Universities; Forensic Anthropologist John Verano from Tulane University, Dr. Golden Richard and Dr. Jaime Nino from the Computer Sciences Department at the University of New Orleans, and Dr. Paula Gregory and Dr. Dana Troxclair from the LSU Health Sciences Center all worked with the program to maximize the experience for the ScienceREACH students. The Forensics Program served a total of 40 students across 14 sessions.

(3) **Engineering Activities:** Engineering Activities were a third component to the after school program at McMain. There were 2 sessions devoted to exposing students to the basic principles of engineering and careers in the field. In one session students worked to build structures from simple materials such as spaghetti and marshmallows, and in the other students heard a presentation on civil engineering and bridge construction from Patrick Ibert, a civil engineer. This is Patrick Ibert's second year working with ScienceREACH. He also gave presentations to ScienceREACH students in the 2007-08 school year. A total of 22 students were served.

(4) **Presentations:** For the 2008-09 Program Year there were 13 college student and professional scientist presentations. Students in general chemistry at Tulane University gave 6 presentations on different areas within chemistry, including two presentations on atmospheric gases, two presentations on polymers, and two presentations on endothermic and exothermic reactions to 35 students at McMain. There were also three presentations at McMain given by graduate students at Tulane University; one student gave a presentation on Evolutionary Biology to 34 students, one student gave a presentation on Ornithology to 15 students, and another student in Evolutionary Biology and Ecology gave a presentation to 20 students on his research on insects in Costa Rica. There were also two presentations at McMain given by UNO Students in the STARS Program who talked to the science club and Mr. Lewis's Computer Science Class about different areas of computer science. Jost Goettert also gave a presentation to 30 students at Sarah T. Reed High School. His presentation focused on nanotechnology, and was given to chemistry classes.

(5) **College STEM Major Lunches:** There were 5 College STEM Lunches at McMain, which exposed 91 students to college students in the STEM Fields. The lunches served as an opportunity to connect high school and college students, and provided high school

students with the opportunity to ask candid questions about college life. The College STEM Major Lunches engaged college students from UNO, who talked about Computer Sciences, Xavier University students, who talked with about Pharmacy, Chemistry, Accounting, and Marketing, and Tulane University Students who talked about Evolutionary Biology and Ecology.

(6) **Field Trips:** Students involved in ScienceREACH went on a total of 7 field trips. Students from Sarah T. Reed High School took a field trip to the NASA Facilities at Michoud. Students at McMain attended 6 field trips to; UNO Computer Sciences Labs, WWL-News 4 Weather Center, NASA Facilities at Michoud, NASA Facilities in Stennis, Mississippi, an Allied Health Fair at Delgado Community College, and the Tulane University Neuroscience Labs. All field trips incorporated elements of the program, such as the rocketry program and NASA, or were a result of student interest and intended to further expose students to opportunities in the STEM fields.

(7) **In-Class Assistance:** Kathleen Darce, a UNO Education and Chemistry Major, worked in Mrs. Ryes Chemistry class at McMain Secondary to teach lessons, perform experiments, and assist Mrs. Ryes with other elements that contributed to an improvement in the class experience and quality. Kathleen worked with 17 students in Mrs. Ryes class for 1-2 hours per session for a total of 8 sessions.

(8) **College Day:** On January 17, 2009 ScienceREACH and Communities In Schools hosted a College Day in association with the Martin Luther King Jr. Day of Service at Loyola University. The ScienceREACH Coordinator planned the program, which included 34 high school students and over 30 volunteers from UNO, Dillard University, Xavier University, Tulane University, and Loyola University. The day was an opportunity for high school students to meet in small groups with college students and ask candid questions about college life, as well as review the Common Application and the college admissions process, and listen to college student's experiences. The high school students also received tours of Tulane University and Loyola University, as well as attended a panel with admissions counselors from UNO, Tulane, Dillard, and Loyola.

(9) **Science Fair:** ScienceREACH assisted Reed High School with its science fair, providing materials and assistance to students as they planned their projects, and then the ScienceREACH Coordinator, along with Jon Larson, the Americorps member assisting with the ScienceREACH Program, judged the projects.

(10) **College Assistance:** The ScienceREACH Coordinator has also helped students enrolled in the program with the college admissions, search, and ACT Registration process. The coordinator worked with 2 students to help them register for the ACT, as well as worked

individually with students to help them pick colleges that had the science majors they were interested in, and helped them map out their college classes and requirements.

(11) Tutoring/ Mentoring: Jon Larson, the ScienceREACH AmeriCorps member has tutored students in science and math at Reed, McMain, MLK and Fischer Elementary. In total he has tutored students for 212 hours.

a. Reed - 44 students for a total of 90 hours on 22 days
b. MLK - 1 students for a total of 22 hours on 22 days,
c. McMain - 3 students for a total of 12 hours on 12 days
d. Fischer - 5 students for a total of 88 hours on 33 days.

In addition to individual tutoring and mentoring, Jon has also worked in Mr. Judson's AP Physics Class, helping students on their labs. CIS provided AP Physics study guides to Reed High School with funding from a California funding group, for the students in the class had no textbooks and the teacher had only the preparation test teacher guide from which to work.

Number and type of interactions with UNO personnel: 48
There have been 15 interactions with UNO Personnel. The ScienceREACH Coordinator continues to cultivate the relationship with the UNO STARS Program. Dr. Jaime Nino was connected with a student at McMain Secondary School who has been accepted to UNO and intends to major in computer sciences. The coordinator has also worked with 8 students involved in the STARS program; Blandon Helgason, Andrew Case, Danielle Showmake, Therese Landry, Rupal Shah, Nathan Simpson, Jeremy Lay, and Andrew Cristina. Kathleen Darce has also worked with ScienceREACH at McMain, helping with science club and provided in-class assistance to Mrs. Ryes Chemistry Class. The coordinator also worked with Andy Benoit from the Admissions Office in order to plan for a UNO Admissions counselor to be present at the college day, and with Lynn Dupont from the Geography Department for GIS consultation. The ScienceREACH Coordinator also gave a presentation at the AMRI Mardi Gras Symposium on the Outreach Efforts of UNO and AMRI through the program.
ScienceREACH also continues to work with Lynette Bates of UNO's Upward Bound Program to provide the STEM enrichment portion of the Upward Bound Summer Program. In addition, we have worked with Juana Ibanez who works in the Geography Department. Juana has helped connect ScienceREACH to Marko Allain, who will be volunteering with Communities In Schools and ScienceREACH in our GIS Summer Program.

- Describe and provide data supporting the major findings resulting from these activities

This project reached a total of 204 students across 225 different sessions. Details of the number of students in each sub-program are presented in the section above.
Results: Student Reflections and a sample of the ScienceREACH Survey can be found at the end of the report.
For the 2008-2009 School Year the ScienceREACH Coordinator created a survey for students in order to track the effectiveness of the program. The results of the survey were as follows;

-100% of students know at least 10 Careers or more in the sciences as a result of the program
-100% of students said that they have learned more about STEM Professions and what type of education is required to reach them since being involved in the Program
-90% of students have reported that the program has increased their interest in Science
-Each student involved in the program has gained interest in at least 2 new areas of science, with most students now interested in careers in Engineering/Physics, Chemistry, and Computer Sciences
-100% of students want to go to college
-90% of students believe that the college lunches and talks with college students have helped to answer their questions about college
-Students also wrote reflections on the program, which supported this information. Students commented on how they were exposed to many different science careers, were supported in further exploring the careers that they were already interested in, and either increased or maintained their desire to pursue STEM Fields in college.

Efforts to expand funding and partnerships

CIS wrote two funding proposals which were not funded this year; however both funders have been cultivated and have encouraged submission of another application next year. The first was the Coypu Foundation to whom CIS wrote a proposal for $50,000 to fund the development and implementation of the Science of Natural Disasters program. Coypu did not fund any education-oriented projects in that round. The second was to the Environmental Protection Agency to expand upon the popular Sunship Earth program provided by Teaching Responsible Earth Education that would have guided 7th graders through a careers component. CIS continues to seek funding opportunities to expand its experiential offerings to students, as we continue to believe that exposure to careers in the STEM fields is one of the best ways we can bring relevance of academic work in the classroom to the attention of students.

Under development are two additional components: exposure to GIS mapping skills and the science of sports. These initiatives will take additional funding to develop.

- Describe the opportunities for faculty recruitment, retention and development, as well as post-doc, graduate and undergraduate student training provided by your project

There have been 15 interactions with UNO Personnel. The ScienceREACH Coordinator continues to cultivate the relationship with the UNO STARS Program. Dr. Jaime Nino was connected with a student at McMain Secondary School who has been accepted to UNO and intends to major in computer sciences. The coordinator has also worked with 8 students involved in the STARS program; Blandon Helgason, Andrew Case, Danielle Showmake, Therese Landry, Rupal Shah, Nathan Simpson, Jeremy Lay, and Andrew Cristina. Kathleen Darce has also worked with ScienceREACH at McMain, helping with science club and provided in-class assistance to Mrs. Ryes Chemistry Class. The coordinator also worked with Andy Benoit from the Admissions Office in order to plan for a UNO Admissions counselor to be present at the college day, and with Lynn Dupont from the Geography Department for GIS consultation. The ScienceREACH Coordinator also gave a presentation at the AMRI Mardi Gras Symposium on the Outreach Efforts of UNO and AMRI through the program.

ScienceREACH also continues to work with Lynette Bates of UNO's Upward Bound Program to provide the STEM enrichment portion of the Upward Bound Summer Program. In addition, we have worked with Juana Ibanez who works in the Geography Department. Juana has helped connect ScienceREACH to Marko Allain, who will be volunteering with Communities In Schools and ScienceREACH in our GIS Summer Program.

- Describe the nature and scope of partnership activities

  CISNO served as the primary agency for design, coordination, and implementation of all academic year outreach activities as described above.

- Describe any problems encountered during the last year of project activities.

  No problems were encountered.

3. **Contributions:** Summarize efforts made to build research and education capacity, secure external federal and private-sector funding, build infrastructure, contribute to economic development, and ensure project sustainability over the long term.

Academic year outreach programs were designed to attract high school students into college study in science and engineering fields. All schools targeted in this study have student bodies that are majority African-American. Furthermore, these schools have a high percentage of students receiving reduced or free lunch. Developing these human resources will provide a stronger base for science and technology development within the state of Louisiana.

A preproposal was submitted to the National Science Foundation's IGERT (Integrative Graduate Education and Research Traineeship Program) program. This program provides funding for training of graduate students in science and technology fields. If funded, this project will provide a unique training experience to graduate students which will develop within them a broad understanding of how science and technology fits into economic, social, and international issues. The proposal is pending as of submission of this report (June 2009).

4. **Project Revision:** Provide a listing of and explanation for any significant changes in the work plan for upcoming year, including any changes in the amount of investigators' time devoted to the project. If you made significant changes to the project design as outline in the proposal during the past year, please list and explain the changes, the purposes for the changes, and the results.

Several programs developed by CISNO will continue to be implemented in project year three. Refining of these programs will be undertaken in order to make them more efficient, but no major changes are foreseen. Efforts will be made to increase the number of undergraduate students involved in the project.

5. **Work Products:** List any tangible products (e.g., research publications and/or presentations, patents, licensing agreements etc.). Please combine all products into one document.

“Effects of atrazine on embryonic development and hatching of Japanese medaka (Oryzias latipes),” Theriot, J.; John, T.; Tarr, M. A.; Rees, B. B. 237th ACS National Meeting, Salt Lake City, UT, March 22-26, 2009.

PKSFI Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04
Leszek M. Malkinski
(PKSFI-ESIP Clean Room, 2008-2009)

Title: Nanodevice Processing Laboratory

1. Personnel:

Leszek Malkinski, Associate Professor of Physics and Materials Science. Dr. Malkinski is in charge of design and management of this part of the project.

2. Activities:

The aim of this project is to provide research support for AMRI and collaborating institutions with the cleanroom facilities and technology to do competitive research in the field of nanofabrication. The evaluation of the purity of the air is based on number of dust particles in a unit volume. “Class 1000” cleanroom is the minimum requirement for the research activities on nanotechnology. This requirement was exceeded by designing a higher class purity cleanroom with re-circulating air. Due to this design the air is filtered several times before leaving the cleanroom and the number of particles present in the unit volume dropped to below 100, which elevates the rank of the cleanroom to “class 100”.

In the period from July 2008 to June 2009 the following activities have been performed in relation to the Nanodevice Laboratory:

- UNO Services prepared room SC2041 for the installation by removing old floor tiles and leveling the floor, preparing the electrical and plumbing installations and repairing the roof.
- CEI Manufacturing Inc., selected through a bid process, started installation in the middle of July and major construction works have been completed by the end of September.
- Initial testing by independent company ENV Services, showed that the Nanodevice Processing Laboratory meets requirements of cleanroom “class 100” in terms of air purity. However, the pressures in the laboratory and the ante-room slightly exceeded acceptable standards.
- Corrections have been made in the airflow circulation to adjust the pressures to the acceptable levels. This work was completed in December 2008
- Following these modifications the laboratory was re-tested and on December 12, 2009 and a Certificate of Compliance was issued by the ENV Services stating the laboratory meets ISO Class 5 standards, which translates into “class 100”. At this moment the payments were made for the CEI for the installation.
- Particle monitoring system has been purchased and installed for continuous monitoring of the air purity in the laboratory. During the certification process the readings of our particle monitoring system were compared and found consistent with the readings of the instruments used by the ENV Services.
- In January of 2009 we began moving and installing and testing the equipment in the Laboratory. In particular the mask aligner and UV exposure station as well as spin-coater/ hot plate were assembled and tested. Installation of the ion milling system was completed by the technician form the AJA International Co. in April 2009. At this moment the Nanodevice Processing Laboratory was open for the qualified users.

- At the beginning of June 2009 a series of training sessions for the users began. The sessions will prepare several students and postdoctoral researchers how to follow cleanroom procedures and to use equipment in the laboratory for their research.

The remaining budget will be used to purchase necessary “100 class” furniture, supplies and standard cleanroom instruments.

The views of the Nanodevice Processing Laboratory are presented in Figs 1 and 2.

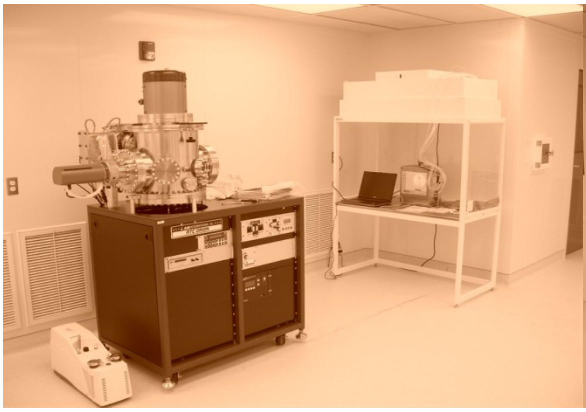


Fig1. Ion milling system and a particle monitoring system (inside the vertical flow-bench in the Nanodevice Processing Laboratory

Fig 2. Mask aligner/ UV exposure station mounted on anti-vibration table.

Project Revision

The design of the clean laboratory using recirculating air made it possible to exceed the originally planned standards of the cleanroom class1000. As a result, the Nanodevice Processing Laboratory meets standards of higher class 100 cleanroom (or ISO class 5).

Annual Report for Year 1 (ending 6/30/2008)

A Center for Advanced Materials and Nanotechnology in AMRI at the University of New Orleans

Louisiana Board of Regents Contract
LEQSF(2007-12)-ENH-PKSFI-PRS-04

Annual Progress Report - 2008

June 30, 2008

SUMMARY

The purpose of this report is to provide an annual progress report for the LA Board of Regents funded project entitled: "A Center for Advanced Materials and Nanotechnology in AMRI at the University of New Orleans" through LA Board of Regents Contract LEQSF(2007-12)-ENH-PKSFI-PRS-04 during the first year of the project from June 1, 2007, through June 30, 2008. Included are progress reports from the three Focus Research Groups (FRGs) and the Broader Impacts group which comprise the organization of the overall project. Included also is progress report on the Clean Room Project which received ESIP funds for development of a Nanodevice Processing Laboratory to support ongoing research projects in nanotechnology at UNO.

The first year of this project was very productive and has been successfully completed. A research consortium organization for this project has been established and includes the University of New Orleans and the following five partner institutions: Louisiana State University, Tulane University, Louisiana Tech University, Children's Hospital, and Communities in Schools of New Orleans, Inc. All subcontracts from the University of New Orleans to the five collaborating partner institutions (Louisiana State University, Tulane Universtiy, Louisiana Tech University, Children's Hospital, and Communities in Schools of New Orleans, Inc.) are in place and the work at these institutions is progressing well. The overall effort of the project is organized into three FRGs based on technical areas and one Broader Impacts group, which provides community outreach support for the project. These groups are: FRG-1: Nanomaterials for Biological Sensing and Imaging; FRG-2: Nanoscale Mechanical Devices; FRG-3: Nanomaterials for Energy Conversion and Storage; and the Broader Impacts (Educational and Commercial Outreach) group. All research activities within each group are progressing well.

Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04

Weilie Zhou
(PKSFI FRG 1, 2007-2008)

FRG-1: Nanomaterials for Biological Sensing and Imaging

1. Personnel: List all key personnel and other staff who provided *significant* contributions to the project. Provide information about the types of contributions made by each listed participant and controls in place to ensure that these contributions are adequate to the project's requirements.

A. AMRI personnel involves with this project

- **Weilie Zhou**- co-Leader of FRG 1. He is mainly responsible for overall management for biosensor part and coordination of AMRI tasks with other partners
- **Zhongming Zeng**-Postdoctoral Research Associate; Zhongming is in charge of nanowire assemble, e-beam nanolithography, surface modification and detection of antigen fabricated from Children Hospital of LSUHSC. Meanwhile he is integrating the microfluidic system to the nanosensor chips.
- **Hui Ma**-Ph.D student: She is fabricating magnetic nanocarriers for drug delivery and meanwhile she is helping Dr. Zeng to modify the nanowire surface for bio-detection.
- **Charles J O'Connor**-Principal investigator, investigating the whole project and looking for the new grant for whole teams. He is also directing magnetic nanoparticle synthesis.
- **Daniela Caruntu**-Postdoctoral Research Associate; She is in charge of magnetic nanoparticle synthesis for biomedical application.
- **Zeev Rosenzweig**-Professor in Chemistry, His group is fabricating quantum dots for biomedical imaging.

B. CAMD personnel involved with this project

- **Jost Goettert** – main responsibility is overall project management for CAMD part and coordination of CAMD tasks with partner efforts;
- **Yoonyoung Jin** – Research Associate (RA) 5; Jin is leading senior researcher at CAMD with expertise in lithography, thin films, system integration, and measurements; he was carrying out all lithography and thin film based efforts and was in charge of the rapid prototyping solutions for microfluidic;
- **Kyung-Nam Kang** – PhD student; he is supporting Jin with lithography and thin film deposition/etching related processing;
- **Proyag Datta** – Research Associate (RA) 5; he joined the team in the last 2 months providing expertise in molded microfluidic structures and fluidic system control and integration; he is currently molding hard plastic fluidic chips and works on chip integration with Si sensors.

C. LSUHSC Children Hospital involved with this project

- **Seth Pincus**-co-leader of this project. He is responsible for antigen engineering.
- **Chad Gustafson** (50%) – Bachelor's level Technician, working on the engineering
- **Grace Maresh** –Technician, working on quantum imaging.

D. Louisiana Tech personnel involved with this project

- **Mark DeCoster**-Professor in biochemistry; he is in charge of biocompatible testing and alive cell detection
- **James McNamara**-Ph.D student; he is in charge of alive cell culture and testing
- **Ruturaj Masvekar**- M.S student; he is responsible for toxicity test for magnetic carriers and nanowires

2. Activities and Findings:

I. Nanowire for biosensor application

A. Field effect transistor fabrication based on In_2O_3 nanowires

In the first year, we have successfully achieved high-quality In_2O_3 nanoparticles film by self-assembly method and aligned nanowires by combing method. The sensors based on In_2O_3 nanoparticles exhibit high sensitivity and selectivity. The electrical properties of aligned nanowires were also characterized. Based on the work in the last quarter, the sensor mechanism of CuO nanowire arrays to H_2S was also studied.

The mechanism of FET sensors is based on carrier density changes when targeting molecules attach on the nanowires surface. Applying a gate voltage on the nanowire will simulate the carrier change process in the nanowire channels. So, the effect of gate voltage on the conductivity change of nanowire is an efficient benchmark on the sensitivity of nanowire based sensors. And the nanowire must have proper resistance to ensure the sensitivity. We have patterned In_2O_3 nanowires into FETs by e-beam lithography, metal evaporation and lift-off process. The basic electrical transport properties and biological response of In_2O_3 nanowire device were characterized.

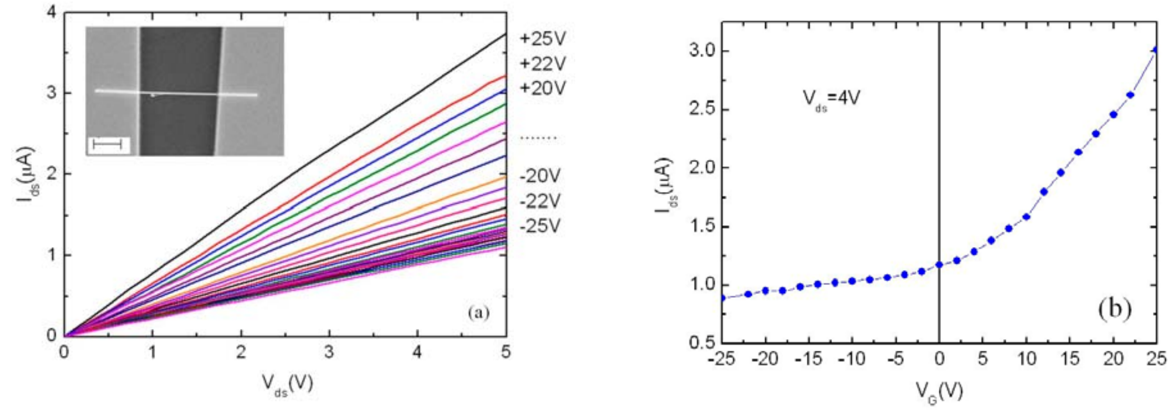


Figure 1 (a) I-V curves of a typical In_2O_3 device with respect to back-gate voltage (V_g = from -22 to +22V with a step of 2V). Inset: SEM image of the device, the scale bar is 2 μm. (b) The corresponding I_{sd}-V_g curve at V_{sd} of 4.0V.

B. Design and fabrication of micro-size electrodes

Research efforts have been directed towards exploring design and fabrication concepts for the anticipated sensor focusing in integration of nanowires into microfluidic channels. The biosensor consists of three principle functional components - fluidic channels for sample delivery, micro-size electrodes providing an electrical interface to the outside world, and integrated nanowires performing the selective interaction with sample molecules and delivering the original signal. The schematic of the sensor design is shown in Figure 2 shows.

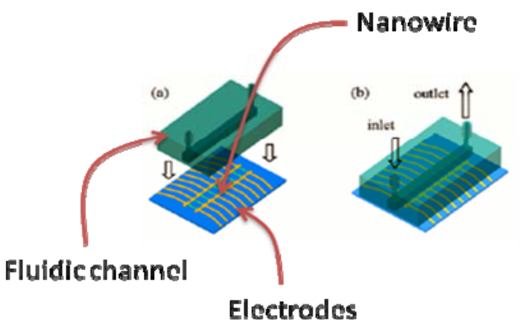
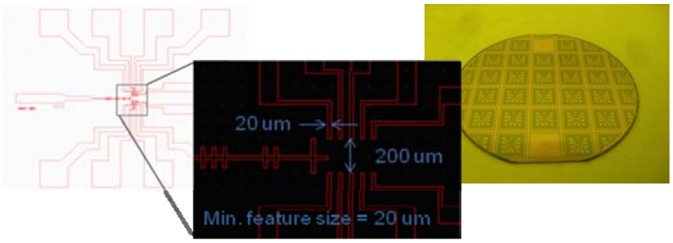


Fig. 2: Biosensor with fluidic channels, electrodes and embedded nanowires.



-Drs Zhou and Zong's Design -UNO

Fig. 3: Electrode design (left) and Si wafer with patterned electrode layer (right).

Au electrodes are patterned onto a silicon substrate covered with a thin silicon oxide insulation layer using UV lithography and wet-etching. UV optical masks contain the actual design information for both electrode and fluidic channel designs, and can easily be changed when exploring new, optimized layouts and configurations. Using UV lithography into thick SU-8 negative resist an inverse layout of the fluidic structure was generated which served as template for a PDMS casting process defined as rapid prototyping approach. These test devices were enabling early proof-of-concept experiments in a microfluidic environment. Issues with PDMS structures are low mechanical stability and thus unrepeatable performance when conducting fluidic experiments. However, the first results led to a good understanding of a suitable fluidic setup which is currently fabricated by hot embossing on a hard plastic fluidic chip ensuring very controlled fluidic experiments.

Initial electrical tests of embedded nanowires were done by pipetting fluid droplets to cover the nanowire and the adjoining area. In order to repeatable test the reaction of the nanowire to surface bonded molecules, it is necessary to flow fluids across the nanowire surface in a precisely controlled manner. This step is also an important step for further development towards packaged, user-friendly sensors with integrated microfluidics. We also finished the design the design of fluidic channels and nanowire integration design–rapid prototyping.

C. Nanowires - Passive adsorption studies

As a preliminary measure to determine the need for coupling chemistry and to determine whether antibody bound to nanowires in the absence of any chemical modification to the wire or genetic modification of the antibody, we performed passive adsorption studies. Indium oxide nanowires were incubated with either the anti-ricin monoclonal antibody RAC 18, or with the irrelevant protein bovine serum albumin. We then tested to see if the antibody was bound to the wire using either fluorescently labeled anti-mouse IgG or fluorescent ricin. Wires were examined using a confocal microscope. The results indicated that there was non-specific adsorption of the fluorescent proteins (Fig.4). The experiment was repeated, diluting the fluorescent proteins in a 100X excess of unlabeled protein, and binding was still observed. These results indicate an unexpectedly high degree of non-specific interaction of proteins with the nanowires, possibly through hydrophobic interactions.

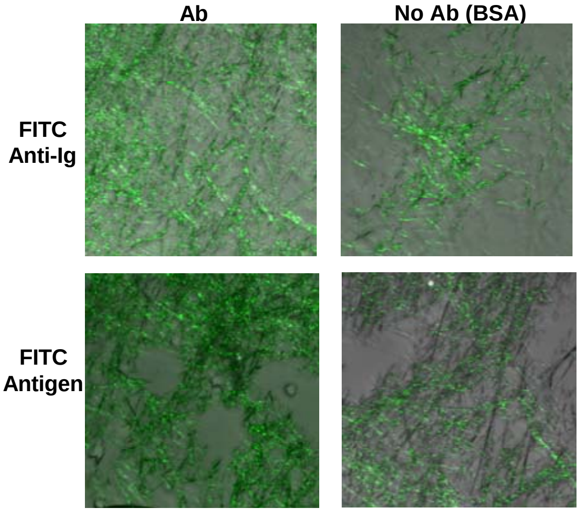


Fig. 4 Non-specific adsorption of the fluorescent proteins.

We have engineered two different antibodies so that they express a C-terminal 6X-histidine domain for metal binding. The two antibodies are directed against either HIV gp120 or against ricin A chain. Two different 6X-his forms of each antibody have been made: a full length antibody and an F(ab)’2. Figure 5 shows our PCR strategy and demonstrates that the polymerase chain reaction (PCR) was successful and produced amplicons of the correct length. We have inserted these amplicons into pcDNA-expression vectors and have successfully cloned all four of the constructs (full length and F(ab)’2 of the anti-RAC and anti-HIV antibodies). The plasmids have been sequenced to confirm that they are correct, large scale plasmid preparations have been made. These have been expressed in 293-F cells using a standard transient expression protocol. We have confirmed by enzyme-linked immunoassay (ELISA) that the two full length antibodies and F(ab)’2 fragments bind to ricin or HIV ENV, as appropriate, and contain the 6X-His tag (the latter was done using a rabbit anti-6X His antibody), Table 1. We have used SDS-PAGE and western blot with anti-6X His antibody to confirm the structures and the presence of the 6X-His tag (figure 6). Interestingly, the F(ab)’2 is predominantly found in its monomeric Fab form.

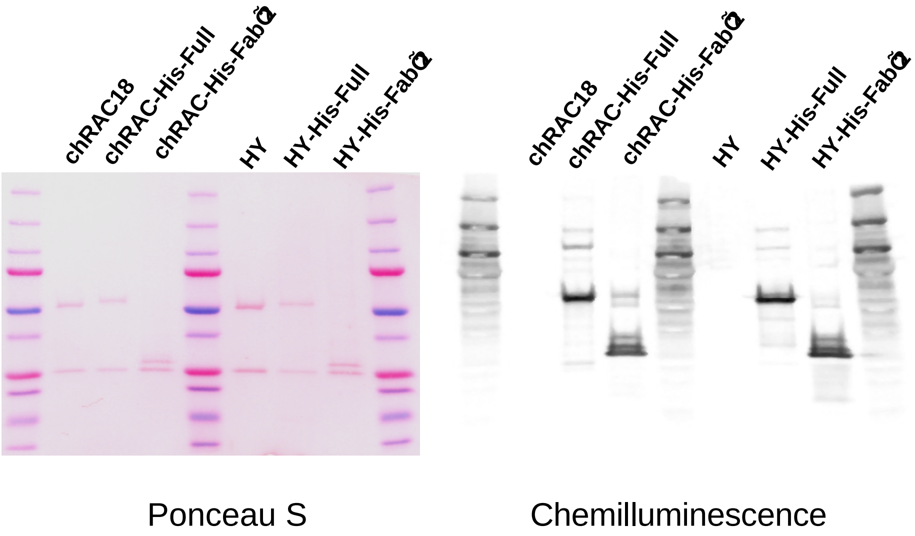


Figure 5. It shows a reduced gel blotted onto nylon and stained with Ponceau S (total protein), or blotted against anti-His antibody and detected with chemiluminescence. The His-Tag is found on the appropriate chains.

Table 1. Binding of Native and His-Tagged Antibodies to Antigen, and Detection with Secondary Anti-Human Ig and Anti-His Antibodies

RAC plate

Anti-Human			Rabbit anti-His+ Anti-Rab			Anti-Rabbit		
	Mean	SEM		Mean	SEM		Mean	SEM
ChRAC18			ChRAC18			ChRAC18		
3ug/ml	0.44	0.05	3ug/ml	0.438	0	3ug/ml	0.30	0.02
0.3ug/ml	0.33	0.00	0.3ug/ml	0.288	0.006	0.3ug/ml	0.21	0.01
0.03ug/ml	0.25	0.03	0.03ug/ml	0.215	0.004	0.03ug/ml	0.19	0.00
chRAC18-His-Full Length			chRAC18-His-Full Length			chRAC18-His-Full Length		
3ug/ml	0.84	0.11	3ug/ml	1.17	0.06	3ug/ml	0.34	0.01
0.3ug/ml	0.47	0.04	0.3ug/ml	0.46	0.02	0.3ug/ml	0.23	0.01
0.03ug/ml	0.26	0.02	0.03ug/ml	0.28	0.01	0.03ug/ml	0.18	0.00
chRAC18-His-Fab'2			chRAC18-His-Fab'2			chRAC18-His-Fab'2		
3ug/ml	0.26	0.00	3ug/ml	0.43	0.06	3ug/ml	0.17	0.00
0.3ug/ml	0.20	0.01	0.3ug/ml	0.26	0.03	0.3ug/ml	0.15	0.01
0.03ug/ml	0.19	0.01	0.03ug/ml	0.21	0.00	0.03ug/ml	0.16	0.01
Blotto	0.16	0.01	Blotto	0.17	0.01	Blotto	0.15	0.00

Gp120 plate

Anti-Human			Rabbit anti-His+ Anti-Rab			Anti-Rabbit		
	Mean	SEM		Mean	SEM		Mean	SEM
HY			HY			HY		
3ug/ml	0.82	0.05	3ug/ml	0.51	0.032	3ug/ml	0.53	0.05
0.3ug/ml	0.84	0.04	0.3ug/ml	0.4085	0.0545	0.3ug/ml	0.43	0.00
0.03ug/ml	0.62	0.03	0.03ug/ml	0.4045	0.0045	0.03ug/ml	0.40	0.02
HY-His-Full			HY-His-Full			HY-His-Full		
3ug/ml	0.92	0.17	3ug/ml	1.01	0.02	3ug/ml	0.42	0.01
0.3ug/ml	0.69	0.04	0.3ug/ml	0.58	0.03	0.3ug/ml	0.34	0.01
0.03ug/ml	0.55	0.01	0.03ug/ml	0.43	0.01	0.03ug/ml	0.34	0.01
HY-His-Fab'2			HY-His-Fab'2			HY-His-Fab'2		
3ug/ml	0.58	0.01	3ug/ml	0.71	0.00	3ug/ml	0.35	0.02
0.3ug/ml	0.48	0.02	0.3ug/ml	0.46	0.03	0.3ug/ml	0.32	0.00
0.03ug/ml	0.45	0.03	0.03ug/ml	0.38	0.00	0.03ug/ml	0.34	0.02
Blotto	0.49	0.02	Blotto	0.35	0.01	Blotto	0.33	0.00

II. Nanoparticles for biomedical application

A. Quantum Dots

Although it is possible to attach antibodies to QDs that have been coated with a polymer shell, this greatly increases the size of the quantum dots, thus limiting their utility for vital staining and other uses. Therefore we have sought to bind antibodies more directly.

Cadmium/selenium quantum dots with a zinc sulfide outer shell were reacted with 16-mercaptohexadecanoic acid to provide a hydrophilic surface (figure 2). These beads produced a homogenous suspension when in water (figure 3). However when placed into buffers that would allow for biological interactions, phosphate buffered saline or RPMI tissue culture medium, there was marked aggregation. The aggregates could be partially dispersed by sonication (figure 3)

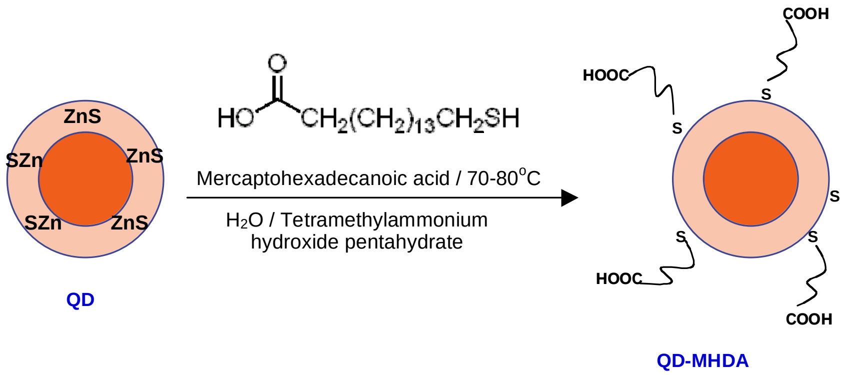


Figure 6. Coating of QDs to obtain a hydrophilic surface

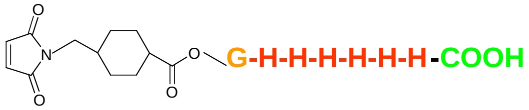


Figure 7. His-tagged peptide modified

In an effort to prevent this aggregation and to provide a means of attaching antibodies to the QDs, we utilized the metal-binding capability of 6X-histidine peptides to attach a gly-6X-his peptide to the quantum dot. The amino terminal of the peptide was blocked, and the carboxy-terminal derivatized with EDC (figure 4). The EDC allows binding to free amino groups of larger proteins or other molecules. We have attached two different monoclonal antibodies of matching isotypes: UCHL-1, directed against the cell surface marker CD45RO, and RAC18, directed against ricin A chain. We have also attached bovine serum albumin, as a control. The binding of these labeled antibodies has been measured on appropriate target cells by flow cytometry (figure 5). The results suggest that there is some binding of the antibody to the quantum dots, although there are some unexplained artifacts (why do only a portion of the cells bind). Confocal microscopy is being performed to confirm whether there is binding of the QDs to cells or whether we are observing aggregation of QDs. Further specificity controls will also clarify whether the binding is mediated by antibody.

B. Magnetic porous hollow silica nanoparticles

Fe3O4/CaCO3 composite particles were prepared by rotating packed bed (RPB) reactor first. Then the composite particles were used as templates to fabricate hollow structure and the magnetic nanoparticles remains in hollow core after the removal of CaCO3. The hexadecyltrimethylammonium bromide (CTAB) and Octane surfactants were used as second templates to form porous structure in the silica shells. To investigate their nanomedicine applications, ibuprofen was loaded into the MPHSNs to study their drug loading and releasing capabilities. The toxicity of MPHSN was also investigated.

C. Toxicity test

Biocompatibility/toxicity of porous silica nanoparticles were tested using the CRL-2199 brain cell line. In cultures treated with growth medium (Figures 3 A+B), as well as those treated with 50 µg/ml of the silica nanoparticles (Figures 3 E+F), cells continued to grow, showing no toxicity, in contrast to copper nanoparticles at the same concentration, which were toxic (Figures 3 C+D). This result indicates that the MPHSN may have potential bio-medical application due to the character of bio-compatibility.

For the nanosensor project, Dr Weilie Zhou is leading this project at AMRI. His group focus on nanowire synthesis and nanosensor patterning using e-beam nanolithography. The sensor initial testing was also performed. His group is teaming up with CAMD at LSU and Children hospital at LSUHSC and for microfludic and antigen detection. At CAMD of LSU, an inter-disciplinary team is working on the process and design related issues aiming to resolve the challenge of microelectronic-microfluidic integration using a hybrid integration approach. The fluidic stack based on molded polymer fluidic chips is an ideal platform for developing flexible, user-specific setups that allow well-controlled experiments. The micrscofludic system will be integrated with Dr Zhou's nanosensors for the living detection. Children is working on the antigen engineering and supply the antigens to AMRI and CAMD for the biodetection.

For the nanopartciels for biomedical application. Drs. O'Connor and Rosenzweig at AMRI are fabricating magnetic nanoparticles and quantum dots to supply to Dr Zhou at AMRI and Dr Seth at Childeren Hospital of LSU for drug delivery and imaging, respectively.

Some obstacles encountered during the last year are the delay of the active research (funds weren't allocated as promised) and in setting

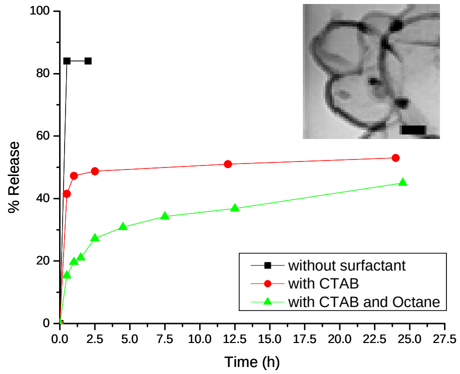


Fig.8 Drug release of ibuprofen from the MPHSNs showing slow release. The inset is a TEM image of MPHSNs. The scale bar is 20 nm.

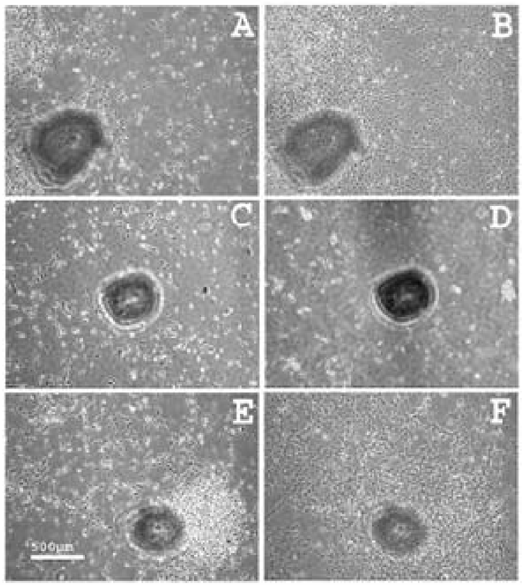


Fig.9 3 CRL-2199 cell toxicity: phase microscopy. Cells were treated with control media (A+B), or with 50 µg/ml of copper nanoparticles (C+D) or porous silica nanoparticles (E+F). Panels A, C, and E show cultures 5 minutes after treatment and panels B, D, and F at 20 hours after treatment. The large black dot in each figure is an orientation marker to ensure that the same area or cells is monitored over time. Scale bar indicated.

up a regular communication to make sure that all team members work effectively together towards the same goal.

Publications

1. "Porous Biocompatible 3D Microscaffold of Cellulose Fibers and Gelatin Composites for Cell Culture", Q. Xing, S. Chen, M. DeCoster, Y. Lvov, **Polymer Mater. Science and Engineering,** v.99, 151-152, 2008

2. "A large quantity synthesis of ultra-thin ZnO nanobelts induced from stacking faults" Kai Wang, Jiajun Chen, Yuxi Chen and Weilie Zhou, Journal of Nanoscience and Nanotechnology, (Communication) (accepted).

3. "Detection of H2S at room temperature by using individual indium oxide nanowire transistor", Zhongming Zeng, Kai Wang, Zengxing Zhang, Jiajun Chen, and Weilie Zhou, submitted to Nanotechnology (2008).

Presentations

1. "Nanotechnology: New Tools for studying brain cell function and disease", Mark DeCoster, Weilie Zhou, Hui Ma, James McNamara, Brittany Oliva, Matthew Tarr, DARPA UNO AMRI Review and Symposium, 31 January- 2008, New Orleans, LA

2. "Magnetic porous hollow silica nanospheres for biomedicine application", H. Ma, J. Zhou, M. A. DeCoster, J. McNamara, D. Caruntu, M.H. Yu, J.F. Chen, IEEE Intermag, May 4-8, 2008, Madrid, Spain

3. "In2O3 nanowire based field effect transistors for biological sensors", Zhongming Zeng, Kai Wang, and Weilie Zhou, American Physics Society Annual Conference March 10-14, 2008, New Orleans.

PKSFI Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04

John Wiley
(PKSFI FRG 2, 2007-2008)

FRG-2: Nanoscale Mechanical Devices

1. Personnel:

This focused research group consists of researchers from the University of New Orleans (UNO) and Tulane University (TU). The principal investigators are John Wiley (UNO), Bruce Gibb (UNO), Scott Whittenburg (UNO), Leonard Spinu (UNO), Vijay John (TU). and Hank Ashbaugh (TU). A number of graduate students are also contributing to the work: Jianxia Zhang (UNO), Yuan Yao (UNO), Haiying Gan (UNO), Ovidiu C. Trusca (UNO), Joy St. Dennis (TU), Bhanukiran Sunkara (TU), Piyush Wanjari (TU), and Ashish Sangwai (TU). In one project, photoactive polymers are being synthesized and tested as possible light driven actuators in mechanical devices (Zhang in Wiley's group). In another project, sets of host-guest molecules are being synthesized and characterized as possible tethers for the directed self-assembly of nanocomponents (Gan and Yao in the Gibb and Wiley groups). New carbon fibers have also be produced for potentials mechanical device components (Joy St. Dennis and Bhanukiran Sunkara in V. John's group). Both the Ashbaugh and Whittenburg groups have been modeling various properties of host-guest systems. Ashbaugh's group (Piyush Wanjari and Ashish Sangwai) is studying mixed solvent effects on solvent-mediated interactions between hydrophobic species and Whittenburg is studying Brownian dynamics simulations of host-guest interactions as well as micromagnetic simulation of the nanoparticles. The latter project involves joint project between Whittenburg, Spinu and Trusca.

2. Activities and Findings:

The activities and findings will be broken up into the various aspects of the program.

a. *Photoactive polymers.* We have synthesized and characterized a series of photoactive polymers. Nanowires of these polymers have been made and initial studies into their photoresponse carried out. The wire arrays show unusual contraction behavior. In previously reported work, films were shown to curl up on exposure to light. Here the wire arrays were anchored to a substrate, so that instead of curling, the mesh arrays could only form fissures in response to the photo-stimulus.

Another interesting aspect of this work is the discovery of an interesting solvent response seen in these materials. On exposure to specific solvents,

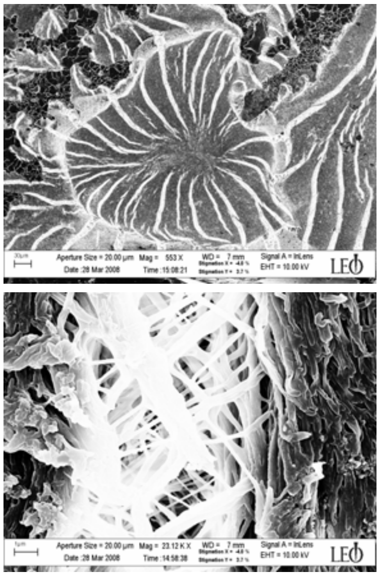
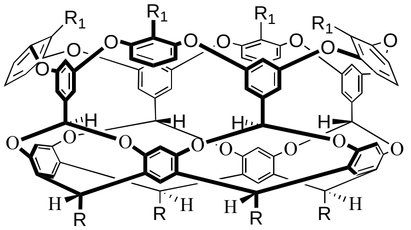


Figure 2-1. Top image shows low magnification image of polymer nanowires after UV light exposure. Bottom image is closs up of nanowire arrays.

certain polymer combinations show rapid and reproducible curling. It may be possible to exploit this behavior in mechanical systems as well as develop some sort of sensor system based on this response.

b. *Host-guest assembly.* This program of research focuses on the controlled assembly of nano-objects into complex nano-systems. The general approach involves the development of hosts (H1, H2 and H3) that bind complementary guests (G1, G2 and G3). Each host-guest pair is orthogonal, i.e. H1-G1 strongly associates, but for example H1-G2 or H3-G1 do not. Hence, one surface of a nano-object coated with H1 will stick to another object coated with G1. Moreover, with three, orthogonal host-guest pairs, it is theoretically possible to assemble complex objects by selectively coating different objects (or different parts of objects) with different hosts and guests. Our strategy is to utilize thioether-functionalized deep-cavity cavitand hosts (DCC) and complementary guests that bind strongly to gold surfaces. The design of the hosts **1** and **2** (below) was based on work reported by Reinhoudt for a smaller host.[1] Of importance is the choice of thioether feet for the DCC over long chain thiols. Reinhoudt has reported that better surface coverage is obtained using the thioether feet since they are able to fold back under the resorcinarene head group upon binding of the sulphur atom to the gold surface to more effectively pack the space under the receptor. This results in a densely packed, more organised monolayer that passivates the gold surface better.[2] Hosts **1** and **2** have been synthesized following Reinhoudt's procedure.

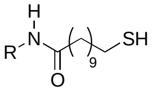
c.



1: R = $(CH_2)_{10}S(CH_2)_9CH_3$, R_1 = H

2: R = $(CH_2)_{10}S(CH_2)_9CH_3$, R_1 = CH_3

The corresponding hosts for **1** and **3** (**3** and **4** respectively), have also been synthesized.



3: R = 1-adamantane
4: R = cyclopentyl

Most recently, we have evaluated the association constants between **1** and **3**, and **2** and **4**. Complexation of **3** to **1** is slow on the NMR time-scale. The association constant is 95 M^{-1}. Disappointingly, the association of **3** and **4** (at least in organic solvents) is negligible. We are therefore going back to synthesize alternatives to **4** which we anticipate will be to bind to the host.

Further efforts have involved the attachment of the host and guest molecules to the surfaces of gold nanoparticles, nanowires, and metal films. Most of the effort has been on nanoparticles (5 and 10 nm). Here we believe we have successfully attached guest molecules to the surfaces. We will then start to look at the binding of these functionalized nanoparticle with free host molecules.

c. *Modeling of Host-Guest systems.* One project in the Ashbaugh group involves the study of water mediated interactions between hydrophobic host (cavitand) and guest (adamantane/cyclopentane) species in water and mixed solvents. To date, the student involved in this project is being trained in the programming of molecular dynamics simulations and how to use the simulation package AMBER to simulate thermodynamic trajectories for complex molecular species. The student has developed simulations of Lennard Jonesium in the microcanonical and canonical ensembles. They have also performed preliminary simulations of liquid water. In the immediate future, the student will begin to perform simulations of the self-association of simple hydrophobic species (like methane) in water to train him on the methodologies for evaluating intermolecular forces that ultimately drive complex formation. By the end of the summer we plan on simulating cavitands and candidate guest species in water to evaluate their hydration properties and water-mediated interactions. These simulations will be performed in collaboration with the Gibb and Wiley groups at UNO to help guide their research projects on cavitand recognition and directed nanoparticle assembly.

In another project, the study of the mechanisms underlying the size selectivity barrier of the nuclear pore complex. The selectivity barrier is moderated by natively unfolded proteins rich in hydrophobic phenylalanine and leucine amino acids. The selectivity barrier is found experimentally to be diminished by the addition of alcohols to the water swollen interior of the pore. To this end, we have performed simulations of phenylalanine and leucine side chain interactions in water and mixed alcohol systems. The alcohols studied include methanol, ethanol, propanol, isobutanol, 1,2-hexanediol, 1,6-hexanediol, and 1,2,3-hexanetriol. We find that as the proportion of the hydrophobic groups of the alcohol increases (notably for isobutanol and 1,2-hexanediol) the tendency for the hydrophobic side chains to aggregate into proto-micellar alcohol/hydrophobe aggregates increases. This suggests that the size selectivity barrier for the nuclear pore is diminished by aggregation of hydrophobic side chains, forming a “swiss cheese” like structure within the pore.

In Prof. Whittenburg’s efforts in the study of the Brownian Dynamics (BD) of the host-guest systems, he has worked to move his BD computer code to the LONI supercomputers. He has successfully compiled the code and has used it to conduct simulations on the binding of hydrogen bromide (as simple test case) to deep-cavity cavitands. The experimental work on this binding studies is done in collaboration with co-PI Gibb. Whittenburg has also written programs to enable visualization of the resulting BD trajectories. The next step involves adding the magnetic force field from his micromagnetics code to allow simulation of the three-dimensional controlled ordering of nanometer-sized structures. The magnetic phase of this work will be done in collaboration with Spinu and his student.

d. *Carbon Fibers.* Research and Educational Activities: Novel carbon materials, such as carbon nano-tubes, fullerenes and uni-dimensional carbon structures[3,4], and their applications in gas storage[5,6] and as photo-voltaic devices[7,8] have received significant attention in recent years. We have developed a class of novel carbon nanotubes through controlled pyrolysis of specific carbohydrates.

Data Supporting the Major Findings: Scanning electron microscopy (SEM) carried out at room temperature using a Hitachi 4800 High-resolution SEM (Figure 1) show long tubular "worm-like" carbon structures. We observed individual microtubules, approximately 1 μm in length, intertwined with each other to form masses of carbon.

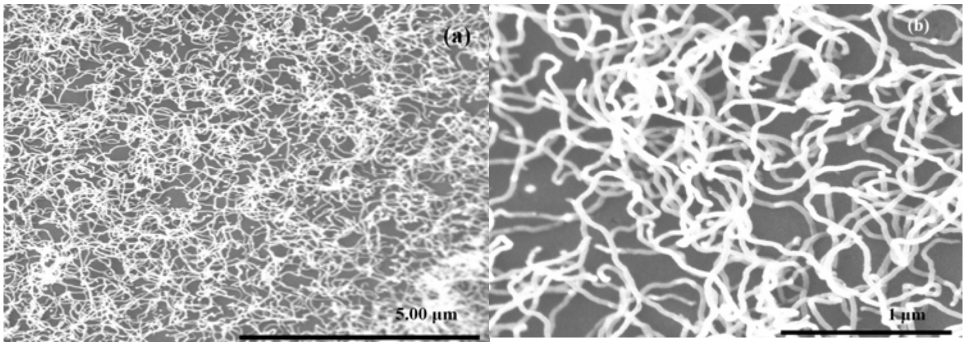


Figure 2-2: SEM's of carbons from selected sugars.

Transmission electron microscopy (TEM) was carried out using a JEOL 2010 Transmission Electron Microscope. The microtubules of carbon, measuring about 20-30 nm in width, were observed to be hollow and had walls measuring 1-2 nm in thickness (Figure 2). Further imaging reveals that the microtubules have nanoporous surface. The graphene sheets constituting the walls of these tubules were also observed under TEM. (Figure 3)

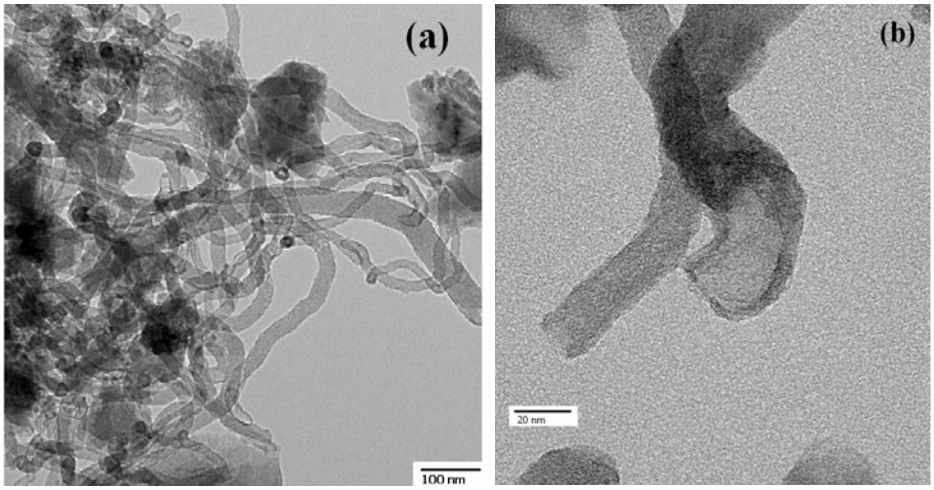


Figure 2-3 - TEM images of α-cyclodextrin after pyrolysis at low magnification (a), showing the intertwined microtubules and at high magnification (b) showing the hollow cylindrical tubes.

While we have shown that there is some evidence of self assembly of cyclic oligosaccharides at elevated temperatures, it has also been demonstrated that pyrolysis for extended time scales lead to formation of graphitic structures. The graphitic morphologies and porous surfaces of these microtubules make them competent materials for applications in gas storage as well as electrode materials for battery applications and in photovoltaic devices. We are also starting a program to blend these easily made carbon nanotubes with polymers to realize nanocomposite materials with high strength and resiliency properties.

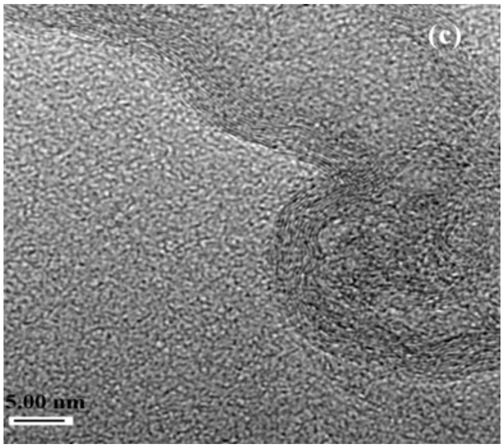


Figure 2-4: High resolution TEM showing graphitic planes

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All of these projects offer extensive opportunities for the training of students and postdocs. Further, all the faculty involved in the project have greater opportunities for collaboration, beyond that outlined above, and this will lead to greater efforts in faculty retention as well as opportunities for successfully securing of joint funding. The success demonstrated by these faculty will serve to attract other highly motivated scientists and engineers to the New Orleans area.

The nature and scope of these projects are outlined above.

There have been no problems encountered over the last year.

3. Contributions:

Initially the focus has been on building the research group, attracting student, initiating the research, and building the collaborations. Some of the PI's (Wiley, Gibb, Spinu) have successfully secured funding for a scanning probe microscope that will serve to support this research. In other cases (V. John), aspects of this project have been promoted to NASA, Sandia Laboratories and Los Alamos Laboratories where agencies are examining application potential;

also, a confidential disclosure has been submitted. In another case (Whittenburg), the PI is writing the response to a major RFP which will be submitted at the end of May. Another PI (Ashbaugh) has presented aspects of this work during seminars at Purdue, UPenn, and the University of Maryland.

4. Project Revision:

None

5. Work Products:

"Fabrication of photosensitive polymer nanowires," Jianxia Zhang, Jin-Hee Lim and John B. Wiley, 235th American Chemical Society National Meeting, New Orleans, LA, April 6-10, 2008.

"Carbons from sugars: Morphology, microstructure and applications to gas storage," J. E. St.Dennis, Pradeep Venkataraman, Vijay T. John, Gary McPherson, Jibao He, Camille Y. Jones, Stephen J. Obrey, and Robert P. Currier, 235th American Chemical Society National Meeting, New Orleans, LA, April 6-10, 2008.

PKSFI Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04

Kevin L. Stokes
(PKSFI FRG-3, 2007-2008)

FRG-3: Nanomaterials for Energy Conversion and Storage

1. Personnel:

Davis, Despina. Researcher, LaTech–Thermoelectrics
Gabrisch, Heike. Co-PI, UNO/AMRI – Battery materials.
Karki, Amar. Graduate Research Assistant, LSU/Physics – Thermoelectrics
Lvov, Yuri. Co-PI, LaTech– Hydrogen storage materials
Malkinski, Leszek. Co-PI, UNO/AMRI – Ferroic composites
May, Garrett. Graduate Research Assistant, UNO/AMRI – Thermoelectrics
Mohanty, Debasish. Graduate Research Assistant, UNO/AMRI – Battery materials.
Stokes, Kevin L. Co-PI, UNO/AMRI – Thermoelectrics
Swart, Donald. Graduate Research Assistant, UNO/AMRI – Thermoelectrics
Varahramyan, Kody. Co-PI, LaTech–Thermoelectrics
Yi, Tanghong. Graduate Research Assistant, UNO/AMRI – Battery materials.
Young, David P. Co-PI, LSU/Physics – Thermoelectrics

Dr. Kevin Stokes reviews quarterly progress reports from LSU and La Tech to ensure that these contributions are adequate to the project's requirements.

2. Activities and Findings

A. Major Research and Educational Activities Undertaken

This focused research group (FRG) is applying the science and engineering of nanometer-scale materials to several areas of energy conversion and storage. Stokes, Varahramyan, Davis and Young are investigating various aspects of nanocomposites thermoelectric materials and microdevices, Gabrisch is investigating novel electrode materials for electrochemical storage applications (rechargeable batteries); Malkinski is researching novel magnetic to electrical power conversion composites for micropower applications and Lvov is developing techniques for the nanoassembly of nanoparticles and tubule nanocontainers for possible hydrogen storage applications. There are six principle investigators, one senior researcher and five graduate students (total) from the University of New Orleans, Louisiana State University and Louisiana Tech. The results for June 2007 to June 2008 are summarized below.

B. Major Findings and Results

a. Electrodeposition of bismuth telluride (Davis, Varahramyan)

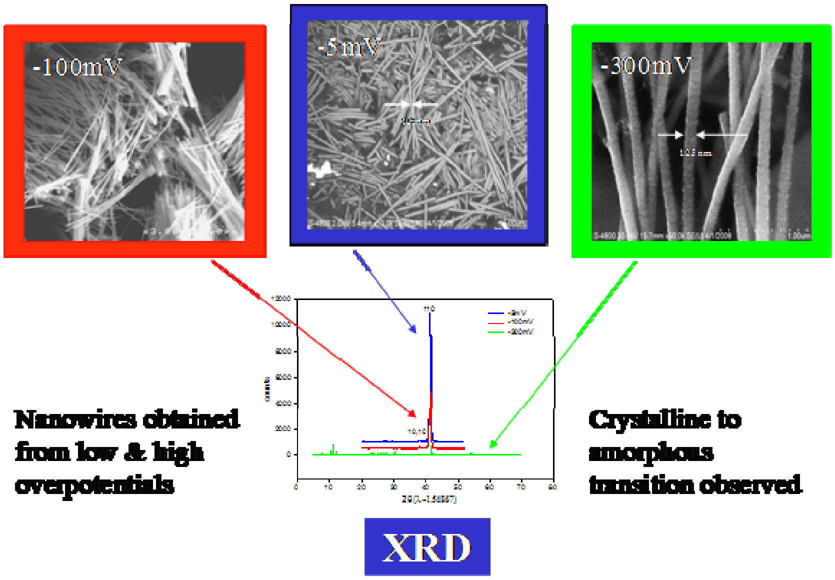
Nanostructured bismuth-telluride (Bi_2Te_3) materials are the focus of intensive research since this thermoelectric material combines a high power factor and a low thermal conductivity. Thermoelectric (TE) materials can generate electricity from heat and can act as cooling devices when a voltage drop is applied. The thermo-electric phenomena provides a way to locally control temperature. GMR sensors are damaged by the heat dissipation during sensing. This project is to cap GMR nanowires with thermoelectric (bismuth telluride) nanostructured material, which will act as a nano-heat-sink (cooler), and absorb the generated heat. The novelty of its architecture [(Bi_2Te_3)bottom/(GMR)multilayers/(Bi_2Te_3)top] could make this nanomaterial a superior sensitive magnetic sensor. Moreover, thermal control is a requirement to all space flight missions. Heat rejection is critical to the operation of the focal planes used in space-based telescopes used by NASA. Efficient coolers may contribute to the implementation of new bolometric detectors for ultra-low-noise observations of the early universe.

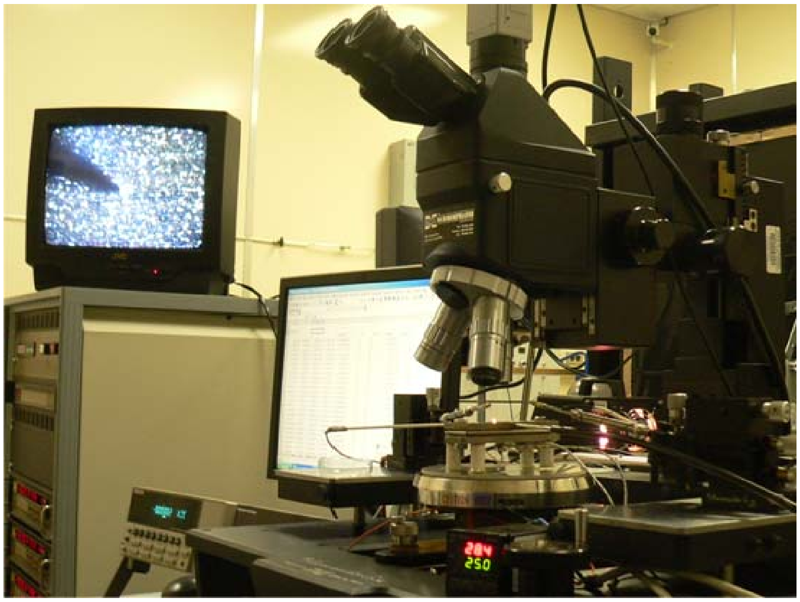
Implementation Strategy: Bi_2Te_3 nanotubes and nanowires are to be electrodeposited using a variety of pore size polycarbonate membranes (100-500 nm pore diameter). The Bi_2Te_3 electrolyte concentration will be varied; the initial concentration will be doubled, quadrupled and the ratios of bismuth oxide and tellurium oxide will be varied in order to study the concentration effect on the Seebeck coefficient measurements. Electron microscopes (SEM and TEM) will be utilized to observe the electrodeposited nanotubes after the supporting PC membrane will be dissolved in dichloromethane. Seebeck coefficient will be measured and optimized for both the n-type (Te rich) and p-type (Bi rich) nanotubes.

Electrodeposition of thin film Bi_2Te_3 alloy: Using potentiostatic electrodeposition on pure copper substrates start electrodeposition of Bi_2Te_3 thin film alloy. For various thin film compositions utilize the potentials previously identified from the singe electrolyte polarization curves (apply constant voltages in the vicinity of the Bi and Te mass transport peaks for a fixed deposition time).

Bi_2Te_3 Alloy Nanowires Electrodeposition:

- Using the electrodeposition potentials that yielded the highest Seebeck coefficients in the thin films deposits, start electrodeposition inside the PC membrane (6 μm in thickness, 200 nm pore diameter).
- Measure Seebeck coefficients of the nanostructured Bi_2Te_3 alloy. Compare these values to the thin film measurements obtained at the same potentials.
- Using different size pore diameter membranes, both Bi rich and Te rich alloy nanotubes will be deposited at the improved previous conditions. Seebeck coefficients and composition analysis will conclude if different pore sizes have an effect on the nanotubes thermoelectric properties. Varying the electrolyte composition deposit nanotubes at the conditions that previously yielded the highest Seebeck coefficient. Optimize electrolyte recipe and deposition conditions to improve the nanotubes Seebeck coefficients.





Thermoelectric cooling device electrodeposition: Figure 1 shows a schematic of the proposed thermo-cooling device. In a single supporting membrane both Bi-rich (p-type) and Te-rich (n-type) nanotubes structures will be connected on one side to a voltage source and on the other side to the object to be cooled (Peltier cooling). This device manufacturing idea using selective sputtering and electrodeposition of distinct p and n type nanotubes regions on the same membrane is unique and extremely cost effective.

b. Nanoparticle Composites (Stokes, Swart)

We have successfully created a p-type solid material from consolidation and low-temperature sintering of chemically-synthesized PbTe nanoparticles. The PbTe nanoparticles were synthesized using Pb acetate and a tellurium-trioctylphospine (Te:TOP) complex in squalane at ~160°C. We used excess tellurium (3:1 Te:Pb mole ratio) to achieve p-type materials. Several samples of this type were produced with varying synthesis conditions For the two samples reported here, 3 mmol of lead acetate were dissolved in squalane at 70°C with oleic acid. The amount of oleic acid was different; 6 mmol oleic acid was added to sample 1 and 3 mmol added to sample 2. After stirring under vacuum at 70°C for 2-3 hours, the temperature was increased to 180°C. 12 ml of 0.75 M Te:TOP solution (9 mmol) was injected; the temperature immediately decreased to 150°C. The reaction proceeded for 8 minutes, then cooled to room temperature in a water bath. The sample was washed with methane/hexane solution and the particles resuspended in hexane.

The two main problems in creating an electrically-conducting sample from chemically-synthesized nanoparticles are 1. removal of the bulky organic ligands and 2. repair of the native oxide layer surrounding each nanoparticle. The high-resolution transmission electron microscope image in Figure 2 shows a distinct amorphous layer surrounding a PbTe particle; this layer is presumed to be an oxide. We used a treatment in formic acid to precipitate the particles and remove the oleic acid. In addition, the formic acid is a mild reducing agent and serves to remove (or repair) the oxide coating. After washing three times in formic acid/1-propanol, the particles were suspended in formic acid and stirred overnight. Then the particles were placed in a vacuum oven at 80°C for 10-12 hours to dry. The resulting particles were loaded into a die and pressed (uniaxially) at a pressure of 1.25 GPa. The pellets were 9 mm (3/8") in diameter and between 0.25 mm and 0.50 mm thick, as shown in Fig. 3. The pellets where then sintered at 200°C for two hours in a 8%H_2:92%Ar gas flow.

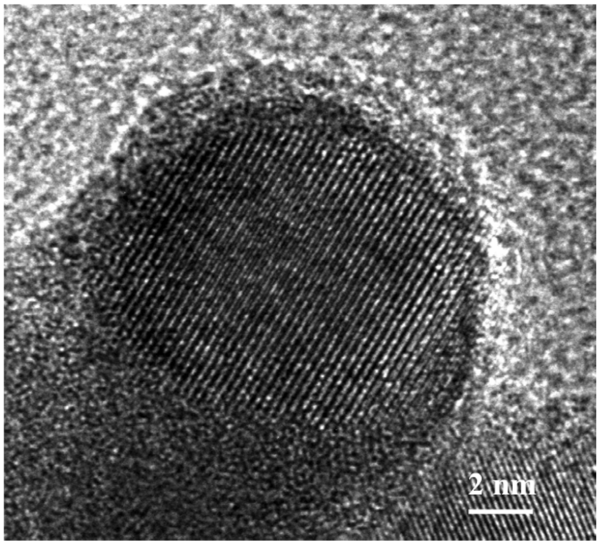


Figure 2. High resolution transmission electron microscope image of a PbTe nanoparticle. An outer amorphous layer (~1 nm, presumably oxide) is evident.

Both samples were found to be p-type. Resistivity was taken with a four-probe measurement apparatus (four in-line, spring-loaded probes) at constant currents of 0.1, 1.0 and 10. mA. After appropriate geometrical corrections to account for the finite size and thickness of the samples, the resistivity was found to be 100 Ω.cm for sample 1 and 3 Ω.cm for sample 2 (±20% for both samples). The Seebeck coefficient was measured in a standard differential geometry and was found to be +350 μV/K for Sample 1 and +370 μV/K (±5%).

We were also able demonstrate the heat-pumping capability of our the pressed nanoparticle material. A small current (±100 mA) was driven through the sample. This was enough to generate a reversible temperature gradient as shown in Fig. 4. The temperature difference across the sample was about 7°C with +100 mA applied and 3°C with -100 mA applied. The asymmetry is due to more efficient heat sinking one side of the sample.

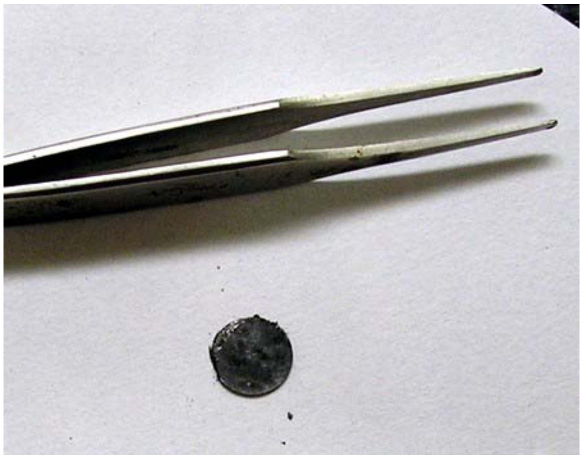


Figure 3. Photograph of the pressed pellet.

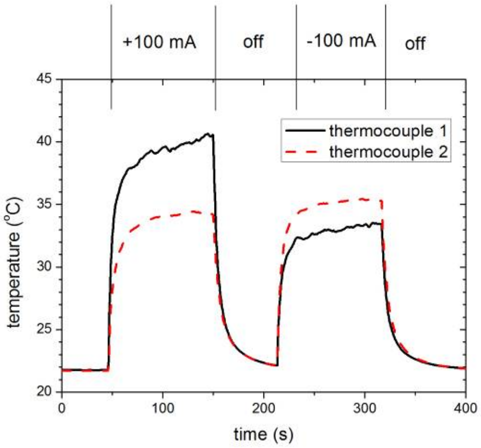


Figure 4. Temperature gradients generated by running a current through Sample 2. The gradient is smaller when the current is reversed because of asymmetrical heat sinking of the sample.

We have also developed a periodic technique for measuring the thermal conductivity of thin, disk-shaped samples. In samples of this type, temperature measurements must be made across the sample faces and are therefore subject to large error due to the interface resistance between the temperature sensor and the sample. The technique uses measurements of the amplitude and phase of the periodic temperature across both a reference sample and the unknown material at several different frequencies. Modeling of the heat flow in the sample allows the simultaneous determination of the thermal parameters of the sample as well as the interface resistance. This work was the subject of Mr. Garrett May's master's thesis (defended December 2007) and has resulted in a paper and presentation at a scientific conference.

c. Thermoelectric Transport in Wires (Karki, Young)

Our research has focused on the synthesis and characterization of novel intermetallic systems in reduced dimensions. We have had success at growing thin films in planar geometry and as coatings on the surface of carbon microfibers (see Figure 5).

Different intermetallic compounds, such as MgB_2, $MgCNi_3$, MoN, and Mo_3Sb_7, have been grown on the fibers. This allows the perfect geometry for characterizing the transport properties of these materials, and in particular, the critical current density, since these are all superconducting compounds. By measuring the magnetotransport behavior of these materials in reduced dimensions, we gain insight into the physics driving the superconductivity. Several of these intermetallics have an exotic pairing state which is driven by spin fluctuations. Funds for the subcontract did not become available until January 2008, so we have just begun our initial investigation of the thermoelectric properties of these films and fibers, which have never been measured before. It's quite possible that the thermal conductivity in these advanced architectures can be reduced, thereby improving the materials overall thermoelectric performance.

Fig. 5. 800 Å of $MgCNi_3$ grown on the surface of a 7-μm diameter solid carbon fiber.

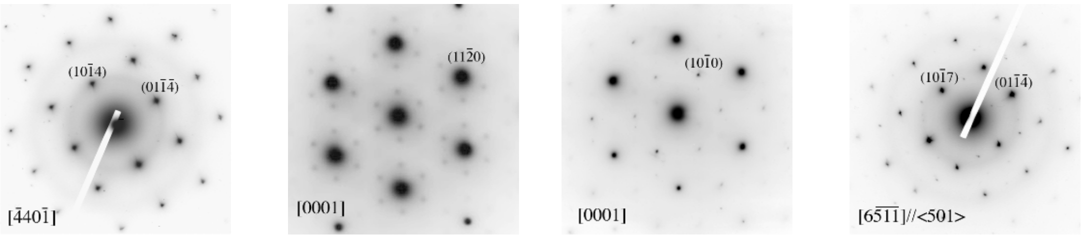
There is a metal-to-semiconductor transition in the Mo_3Sb_7 system doped with Te. Good thermoelectrics tend to have carrier densities on the order of $10^{19}/cm^3$. By doping with Te, we can shift the Fermi surface toward a gap-edge in the density of states. We will attempt to synthesize this system on carbon fibers and then measure their thermoelectric properties.

d. Electrochemical storage materials (Gabrisch, Mohanty and Yi)

The main part of our research activities concerns the characterization of electrode material used in rechargeable Li-ion batteries by electron diffraction. We have so far focused on commercially available material that was characterized in the pristine state and after thermal ageing or charge to high voltage. The educational effort was realized by teaching two new graduate students principles of electron diffraction, operation of a transmission electron microscope, evaluation of single crystal electron diffraction pattern, use of simulation software. Parallel to this, a new course has been developed by the PI and was taught for the first time in spring 2008, *Characterization Techniques in Material Chemistry* (CHEM 6610).

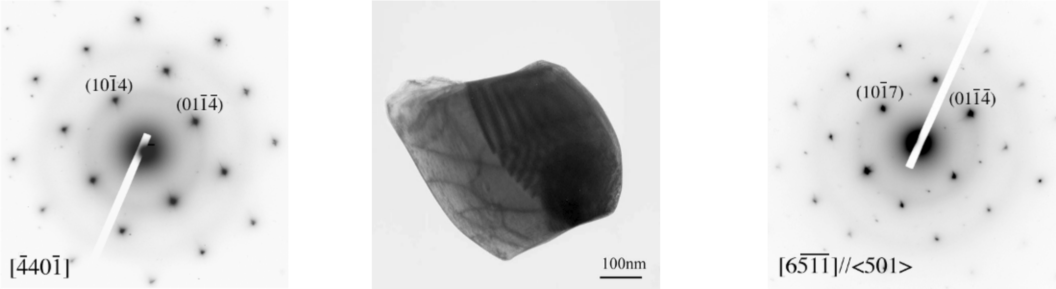
We analyzed 25 particles of the starting material, 16 aged particles, and 17 particles subjected to charge to 5.2V. In all samples the majority of diffraction patterns can be indexed completely in the unit cell of the O3 structure. Possible interpretations of O3 type diffraction patterns are given in the discussion section. A few particles of each sample have reflections typical of the cubic spinel phase located halfway between fundamental reflections of the O3 phase. In the pristine powder additional extra reflections of different origin are observed in 46% of diffraction patterns. They can be classified into three categories, including the $\sqrt{3} \times \sqrt{3}$ R 30° in-plane ordered unit cell suggested by Ohzuku. The intensity of extra reflections varies from faint to strong indicating fluctuations in the degree of cation ordering. However for statistical purpose we do not distinguish between faint and strong intensity. We count the number of diffraction patterns of each configuration in each cell (starting material, aged, high voltage discharge), which is higher than the number of particles due to the occurrence of polycrystals. The percentage of patterns with extra reflections other than those due to spinel type ordering decreases from 46% in the pristine sample to 16% after ageing balanced by an increase in particles having O3 or spinel diffraction patterns. After charge to 5.2V only O3 and spinel phases are observed. The rearrangement of cations during ageing is accompanied by changes in particle morphology. The fraction of bi and tri-crystals in the starting material and in particles subjected to high voltage is comparable at values of 16% and 18% respectively. After ageing in the charged state about 44% of the analyzed particles are polycrystals.

Pristine LiNi1/3Mn1/3Co1/3O2 powder : 21 out of 25 analyzed particles show uniform diffraction patterns across single crystalline particles or across the grains in a polycrystalline particle. The polycrystalline particles include 1 bi-crystal that is part O3 and part spinel phase separated by a grain boundary and one tri-crystal formed by three O3 crystals having a well-defined orientation relationship. The diffraction patterns of these 21 particles can be classified into five categories: a.) diffraction patterns indexed completely as O3 phase b.) diffraction patterns with $\{10\bar{1}0\}$ reflections that are forbidden in the O3 structure , c.) diffraction patterns with superlattice reflections corresponding to the $\sqrt{3}$ x $\sqrt{3}$ R 30º superlattice , d.) diffraction patterns with sets of three extra diffraction spots halfway between fundamental $\{11\bar{2}0\}$ or $\{1\bar{1}01\}$ reflections. The spacing between the extra spots is d/6 (d=distance between two fundamental reflections), suggesting that a full set of these reflections consists of 5 spots. In all observed cases only three reflections are present. We call this configuration "triplet", e.) diffraction patterns representative of the cubic spinel phase with extra reflections halfway between fundamental diffraction spots. Figure 6 gives an overview on typical diffraction patterns observed in the pristine material. Figure gives an example of a bi-crystal consisting of spinel and O3 phase separated by a straight grain boundary.



a.) b.) c.) d.)

Figure 6. Diffraction patterns of the pristine material. a.) O3 type phase b.) superlattice reflections typical of a $\sqrt{3}$ x $\sqrt{3}$ R 30º in-plane ordering. c.) appearance of forbidden $\{10\bar{1}0\}$ reflections, d.) diffraction pattern of spinel phase.

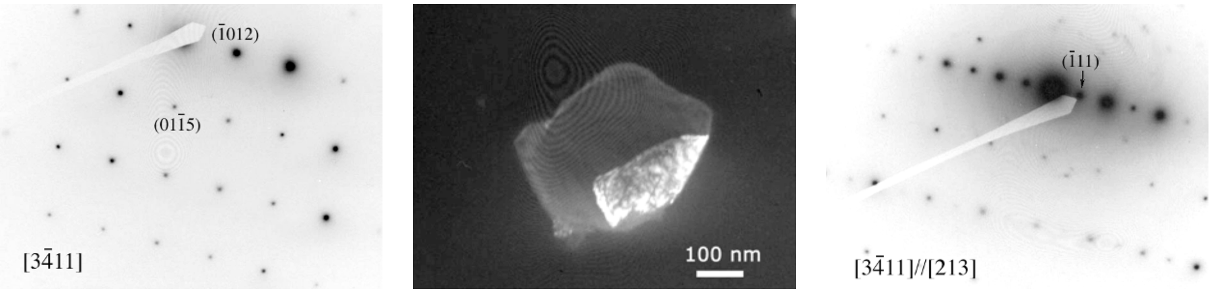


a.) b.) c.)

Figure 7. Pristine material. a.) O3 type diffraction pattern observed in left crystal b.) Image of a bicrystal formed by O3 type phase neighboring spinel phase. c.) spinel type diffraction pattern of right crystal.

Thermally aged and overcharged $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ *powders*

The main diffraction types observed after ageing are O3, spinel and forbidden $\{10\bar{1}0\}$ reflections. In one case the forbidden $\{10\bar{1}0\}$ reflections are superimposed with very faint reflections of the $\sqrt{3}$ x $\sqrt{3}$ R 30º in-plane ordering. Compared to the starting material the fraction of polycrystals has increased from 4 out of 25 (starting material) to 6 out of 16 (or 44%) after ageing. The cubic spinel phase is most often found in bi-crystals neighboring O3-type crystals. The oxygen lattice of the two crystals is aligned parallel resulting in the orientation relationship (0001)//{111} and $[1\bar{1}00]$//<110>. Other bi-crystals and tri-crystals could be indexed completely as O3 phase (3 out of 7 polycrystals). Similar configurations were observed in the starting material, however at a much lower rate (1 out of 25 analyzed particles compared to 3 out of 16 in the aged sample). Figure 8 gives an example of a bi-crystal in the aged material that consists of O3 and spinel phase.



a.) b.) c.)

Figure 8. Diffraction patterns and image of an O3/spinel bicrystal taken from the aged cathode. a. Diffraction pattern indexed completely as O3 phase. b. Dark field image taken with a $(\bar{1}11)$ reflection of the cubic spinel phase. c. Diffraction pattern of the cubic spinel phase.

After charge to high voltage only patterns of the O3 phase and of the spinel phase are observed. We observe streaking of (0003) reflections in some O3 patterns, accompanied by contrast variations in the image parallel to (0001) planes. Spinel-type reflections are very weak and are found either in single crystals or in bi-crystals adjacent to a crystal of O3 phase (2 bi-crystals). Of the 17 analyzed particles 3 were polycrystals (18%).

e. Ferroic Materials (Malkinski)

This project deals with nonconventional methods of mutual conversion of electric to magnetic fields. One way of converting electric to magnetic field is developing multiferroic materials consisting of ferroelectric and ferromagnetic materials. More specifically, the ferroelectrics with superior electrostrictive properties can transfer over 90% of electric energy through elastic coupling to ferromagnetic materials with excellent magnetostrictive properties. The materials in the form of powders of ferroelectric PZT and PMN materials and ginat magnetostrictive Terfenol powder have been purchased to make composite materials. The first results showed that the elastic coupling between the grains of ferroelectric and ferromagnetic grains is essential for the performance of the composite. Two methods of binding have been explored: cold pressing and resin bonds. Both methods were found to have some disadvantages for the properties of composites. Cold pressing at smaller pressures cannot produce strong mechanical bonds between the hard grains. On the other hand, larger pressures change properties of the magnetostrictive material by inducing magnetic stress-anisotropy. These problems do not exist for resin bonding. However, in the case of indirect bonding the mechanical properties of the resin as well as the amount of the resin in between the grains are essential for the performance of the composite. It was found that too large amount of the resin absorbs the stresses and prevents efficient transfer of elastic energy between the grains of different kind. Another conclusion for the initial research is that the elastic properties of the resin should match those of the ferroelectric and ferromagnetic grains as close as possible. The research will be continued to optimize these parameters. In addition hot pressing and sintering will be explored.

Recently Dr. Malkinski has been working on developing a new concept of a composite of organic molecules and inorganic nanoparticles which will display the properties of multiferroic materials. The general idea is to embed elongated magnetic particles into nematic liquid crystals. The elongate molecules of the liquid crystal while directed by an applied electric field will drag magnetic nanorods and change the direction of the magnetic field produce by them.

Both kinds of the materials may lead to applications in voltage controlled magnets, which will be lighter and more energy efficient compared to electromagnets, which require large currents and produce significant losses of energy due to heat dissipation.

f. Nanoassembly of nanoparticles and tubule nanocontainers (Lvov)

In the first year of the project, we report pioneering research on halloysite clay nanotubules, studying them as possible nanocontainer for loading protective materials and as nano-reactor for synthesis of asymmetrical nanoparticles. Halloysite is an economically viable clay material that can be mined from deposits as a raw mineral. Halloysite ($Al_2Si_2O_5(OH)_4 \times nH_2O$) is a two-layered (1:1) aluminosilicate chemically similar to kaolin which exhibits a tubule morphology. From a technical perspective, the most interesting halloysite structures are cylinders with a very small inner diameter, and for loading/release studies one uses halloysite nanotubules with a diameter of 50 nm and a lumen of 15 nm. Halloysite is a hydrophilic material with a bulk contact angle with water of 10°. Therefore, to mix it with hydrophobic polymers requires mediating molecules at the interface. These may be molecules with amphiphilic properties as was demonstrated for polypropylene loading. A more radical approach could be modification of the halloysite SiO_2 surface with silane compounds. In our experiments, we have been able to achieve contact angles of 70° using this method. A range of metals including iron, copper, cobalt, permalloy and nickel may be utilized to form conductive and magnetic cores in the halloysite clay. We concentrate here on the description of halloysite as a tubular substrate for the entrapment and controlled release of functional species which may be used in coatings for oxidation corrosion protection, and for hydrogen storage.

Loading and Sustained Release. To entrap hydrophilic molecules, halloysite is mixed as a dry powder with a saturated solution of a chosen active agent in water, ethanol, acetone, or another solvent and then exposed to high vacuum. The release profiles of drugs and the corrosion inhibitor benzotriazole from halloysite in comparison to that of the microcrystals are shown in Figure 1c. The release from the halloysite tubules takes 50-100 times longer than that from the microcrystals. No macromolecules were inserted between halloysite clay layers in the roll, and it was confirmed by the preserved 7.2 Å packing X-ray reflection. The amount of exogenous active agent is difficult to determine. We cannot exclude some of the active agents being attached to the outer surface of the halloysite, especially in natural gap-defects on the cylinder surface at the end of the rolled clay sheet (it is a natural pocket on the tubule surface). The typical 5-10 % initial release burst observed may be related with dissolution of this material. Halloysite is a biocompatible material but due to the aluminosilicate chemistry should not biodegrade.

Corrosion protection: As an anti-fouling biocide, we have studied iodobutylpropyl carbonate (IBPC) and its release curves were similar to those described above. As anticorrosion protection, we are studying loading and release of benzotriazole. face chemistry, allowing for a range of surface treatments. Common quaternary surfactants, as well as functional silanes, may render the clay easily wet by common polymers. Unlike platy clays, halloysite does not need exfoliation prior to use. In addition, unlike common nanoclays, the functionality of the halloysite as a controlled delivery system or as conductive filler expands the range of polymeric applications, permitting greater variability in product design. The unique feature of halloysite tubules are chemically different outermost and innermost surfaces, which allows for separate chemical modification. Halloysite is also a "green" material and due to the fact that it is a natural product will not add risk to the environment as other nanomaterials may have the potential to do.

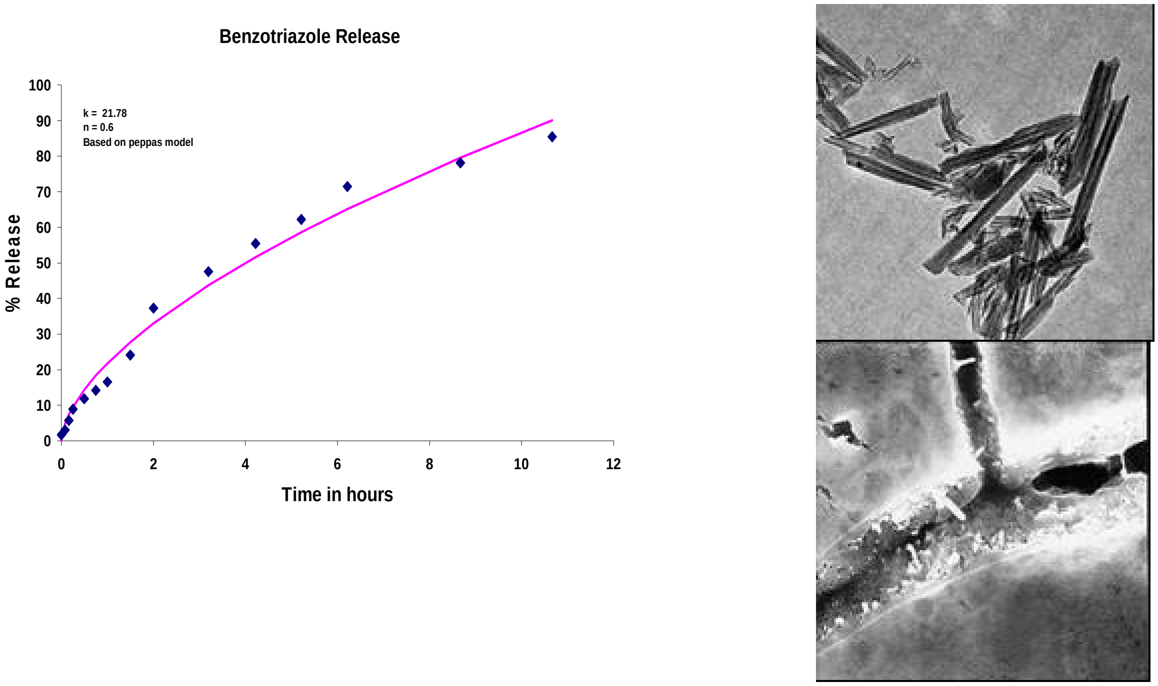


Figure 2. Release curves of anticorrosion agent benzotriazole (a). TEM images of halloysite nanotubes dispersed in water and their cross-section (insert) (b) ;image of cracks in a dry layer of paint with inclusion of halloysite nanotubules containing an antifouling agent (c).

C. Opportunities for Faculty Recruitment, Retention and Development Post-doc, Graduate and Undergraduate Student Training

- Educational effort was realized by teaching two new graduate students principles of electron diffraction, operation of a transmission electron microscope, evaluation of single crystal electron diffraction pattern, use of simulation software.
- A new course has been developed by Gabrisch (UNO) and was taught for the first time in spring 2008, *Characterization Techniques in Material Chemistry* (CHEM 6610).
- One postdoc (M. Agarwal) was hired for 6 months with 50% load. While no undergraduates are directly the IfM has 5 undergraduates as well as 6 other graduate students which indirectly benefit and contribute to the project, for example through weekly lab group meetings and feedback.
- One MS Thesis was completed with partial support from this PKSFI (G. May, UNO).
- Six graduate students are currently involved in training under this project, (two from La Tech/IfM, three from UNO and one from LSU).

D. Partnership Activities

- Gabrisch/UNO collaborates with R. Yazami at Caltech, where Li-half-cells are being assembled and tested. UNO then disassembles the half- cells and retrieve the active material

for our studies. The scope is to combine the knowledge about the electrochemical behavior that is obtained in tests at Caltech with knowledge on the microstructure that we generate at UNO. The combination will allow to better understand the correlation between performance and microstructure.
- Dr. Lvov (La Tech) visited Stokes (UNO) in May 2008 for updates and discussion on the research contributions and future of the collaboration
- Stokes (UNO) has partnered with Nanohmics, Inc. (Austin, TX) and submitted a proposal to the Army Research Office on flexible thermoelectric devices.
- Young (LSU) visited UNO in October 2007 and delivered a seminar on his current research activities.

E. Problems Encountered

- Gabrisch (UNO) had difficulty in recruiting a graduate student for the first ½ of this year. Subsequently, this left $10,000 in student support funds unused. We have received approval from the Board of Regents to transfer this money to travel funds. This will allow Dr. Gabrisch and a student to travel to a DOE sponsored national user facility which has more sophisticated instrumentation (not available locally) and can be used to resolve new and interesting questions which have arisen from our basic characterization which were performed at UNO.
- Subcontracts for LSU and La Tech were not initiated until December 2007. Therefore, they had no funding until that time effectively giving them only 6 months of funding for the first year. We anticipate that now that systems are in place, combined with the long-term nature of this project, that year 2 funding and ordering will be more effective. This has also affected support for graduate students, which again we anticipate will be more effective in Year 2.

3. Contributions:

- Y. Lvov (with M. Decoster) submitted IGERT-NSF pre-proposal: Multi-Scale Integration of Biomimetic Systems, and Lvov submitted one NSF proposal on the project topic.
- Stokes (UNO) is a co-PI on a proposal lead by Nanohmics, Inc. (Austin, TX) on flexible thermoelectric devices which was submitted to the Army Research Office.
- Gabrisch submitted a LINKS proposal for travel to a research facility where the education in the use of different microscopy techniques can be continued. At the same time the visit (if approved) will generate additional data that will be beneficial for a proposal to a federal funding agency planned for later in 2008.
- Young (LSU) has constructed a sample holder that allows measurement of the Seebeck coefficient of thin films. The holder is designed to fit on a transport puck from the Quantum Design PPMS system, so that the temperature dependent thermopower can be measured. Young (LSU) has also constructed a "ZT-meter", which utilizes Harman's method to directly measure the thermoelectric figure of merit of a material. Currently, the meter can be used at room temperature. Having this device available will greatly facilitate in the screening of many new materials for improvement in their thermoelectric properties.

4. Project Revision

- Dr. Kody Varahramyan (La Tech/IfM) has resigned from La Tech effective June 2008. His work on the project will be continued by Dr. Despina Davis. The nature of the work on the electrodeposition on thermoelectric materials is described in section 2.B.a above.

5. **Work Products:**

Papers:

H. Gabrisch, T. Yi, and R. Yazami, *"Transition Electron Microscope Studies of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ before and after long term ageing at 70ºC"*, Electrochemical and Solid-State Letters Volume 11, 7, in print (2008).

A.B. Karki, D.P. Young, P.W. Adams, E.K. Okudzeto, and J. Y. Chan, "Critical current behavior of superconducting MoN and Mo_3Sb_7 microfibers,"*Phys. Rev. B* (in press).

Y. Lvov, H. Mohwald, R. Price, "Clay Nanotubes for Controlled Release of Bioprotective Agents," ACS Nano **2**, 814-820 (2008).

Q. Xing, S. Chen, M. DeCoster, Y. Lvov "Porous Biocompatible 3D Microscaffold of Cellulose Fibers and Gelatin Composites for Cell Culture, Polymer Mater. Science and Engineering, **99**, 151-152 (2008).

G.T. May, D.R. Swart and K.L. Stokes, "Periodic Technique for the Measurement of Thermal Properties of Nanocomposites," *Proc. EPD Congress 2008, TMS 2008 Annual Meeting* (Minerals, Metals and Materials Society, Warrendale, PA, 2008). pp. 361-370.

Presentations:

H. Gabrisch, T. Yi, R. Yazami, "Development of the Microstructure of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ subjected to Ageing", *Focused Battery Technology Workshop III- Material Challenges for High Energy Density and Long-Life-Lithium-Ion Cells*, Pasadena, Ca, February 18-19 2008.

A.B. Karki, P.W. Adams, and D.P. Young, "Magneto-transport properties of MoN and Mo_3Sb_7 thin films and microfibers," American Physical Society March Meeting, New Orleans, LA, March 2008.

K.L. Stokes, G.T. May and D.R. Swart, "Periodic Technique for the Measurement of Thermal Properties of Nanocomposites," presented at *TMS2008-The Minerals, Metals & Materials Soc. 137th Annu. Conf.,* New Orleans, LA, March 11, 2008.

PKSFI Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04

Matthew A. Tarr
(PKSFI Broader Impacts, 2007-2008)

Broader Impacts (Educational and Commercial Outreach)

1. **Personnel:** List all key personnel and other staff who provided *significant* contributions to the project. Provide information about the types of contributions made by each listed participant and controls in place to ensure that these contributions are adequate to the project's requirements.

Matthew Tarr, Professor, Dept. of Chemistry, University of New Orleans – planned and coordinated academic year outreach activities (ScienceReach program) with subcontractor, Communities In Schools of New Orleans (CISNO); reviewed CISNO quarterly reports; conducted site visit to CISNO to evaluate subcontractor progress; coordinated planning and recruiting for summer outreach program (10 high school student interns for summer 2007 program). Supervised by project PI, Dr. Charles O'Connor and presented program updates at quarterly meetings.

Sara Massey , Director, Communities In Schools of New Orleans – directed all activities carried out by CISNO including academic year outreach programs in two New Orleans public or charter schools. Responsible for hiring and supervising ScienceReach program coordinator. Evaluated via quarterly reports submitted to Dr. Tarr and by site visits conducted by Dr. Tarr.

Davina Allen, ScienceReach Coordinator (Aug – Dec 2007), Communities In Schools of New Orleans – designed and implemented academic year outreach activities. Directly supervised and evaluated by Sara Massey.

Brittany Morgan, ScienceReach Coordinator (Jan 2007 -), Communities In Schools of New Orleans – implemented academic year outreach activities. Directly supervised and evaluated by Sara Massey.

2. **Activities and Findings:**
   - Describe major research and educational activities undertaken in this reporting period

The major focus of this project during the first project year has been on developing an academic year outreach program that targets New Orleans public or charter schools.

The ScienceREACH program worked in three schools; New Orleans Charter for Science and Math High School (NOCSM), O. Perry Walker High School, and McDonogh 35 High School. The programs implemented included; ACT Prep Program, After School/Rocketry Program, College STEM Major Lunches, In-Class Presentations, and In-Class Mentoring, which combined reached a total of 85 students across 20 different sessions.

(1) **ACT Prep Program:** The ACT Prep program ran at New Orleans Charter for Science and Math high school and included six 2.5 hour sessions. Four volunteers from Tulane University worked with students each week in order to help them prepare for the ACT tests held in April and June. On average eighteen students participated in the sessions. In these sessions students were introduced to ACT practice tests, as well as testing strategies. On average student scores on the ACT increased by five points.

During the ACT sessions also the NOCSM students got to interact with the Tulane University volunteers, all of whom were engineering majors. The high school students used this opportunity to ask questions about college life, class requirements, and different types of majors. It was at these sessions that a need for college student-high school student interaction was observed. Thus, we began to implement the College STEM Major Lunches at Science and Math High School.

(2) **College STEM Major Lunches:** The College STEM major lunches have introduced 23 students at NOCSM to college students in STEM fields. The students gained access to first hand information about college life, classes, and majors. The first lunch presentation was given by Tulane students in the field of Biomedical Engineering. At this lunch many of the high school students who attended were introduced to the field of Biomedical Engineering for the first time. The second lunch was with Pre-Pharmacy students from Xavier University. Three Pre-Pharmacy students spent time talking about their major and college life to potential pharmacy students. Because the lunch went so well, the Pre-Pharmacy students stayed an extra hour talking with two students who will be attending Xavier in fall 2008.

The students have shown a desire for more STEM Major Lunches in the future, perhaps weekly, wherein they are able to continue to talk candidly to students about college life and explore different major areas and professions.

(3) **After School/Rocketry Program:** This program continued from last quarter, and was conducted at NOCSM as well as at McDonogh 35 High School. The program worked with five students, and met for a total of three mentoring sessions during the defined time period.

(4) **In-Class Presentations:** The in-class professional scientist presentations are meant to supplement class teachings and help the students understand how what they are learning in the classroom applies to the real world. One of these sessions was implemented at Walker High School to a class of nineteen students. Mr. Patrick Ibert, a civil engineer, gave a presentation to a physics class about his work building bridges, and then explained to the students how what they were learning in physics related to his work. The students were given the challenging task of building their own bridge out of paper and paperclips. Mr. Ibert assisted the students in their bridge building and helped them apply their knowledge of forces and tension to their projects. At the end of the session, students were able to make the clear connection of how their class work was relevant in the real world. Mr. Ibert gave the extra materials that he brought to the teacher so that he could use them

as teaching tools in future classes. Students were very involved in the presentation and are eager for future presentations.

(5) **In-Class Mentoring:** In-class mentoring pairs teachers with a college student who assists them in their classes. Between February and April 2008 a freshman from Xavier University worked in Mrs. Porea's Geometry class at New Orleans Charter for Science and Math High School. The volunteer worked in the classroom of ten students for three classes, each of which were each two hours long. The students received one-on-one attention and assistance from the volunteers. We would have liked to have more sessions; however, spring break and LEAP Testing were barriers. Next year with LEAP testing being later in the school year, there should be time for more sessions.

(6) **College Club:** ScienceREACH has also been involved with the College Explorers Club at NOCSM. Through College Club ScienceREACH has given students the opportunity to explore colleges in Louisiana, and learn more information about the different programs at these schools. A total of ten students are involved in the club, and six of them are potentially interested in the STEM fields. ScienceREACH took eight students on a daytrip to several colleges in Louisiana. They were given information about STEM majors and programs at the schools. The ScienceREACH Coordinator has developed relationships with these students, and has worked to help them find schools with their potential interests, as well as expose them to different areas of study.

- Describe and provide data supporting the major findings resulting from these activities

This project reached a total of 85 students across 20 different sessions. Details of the number of students in each sub-program are presented in the section above.

In its first year ScienceREACH has faced the initial challenge of recruiting a core group of students to work with the program. However, as the first year comes to a close there is a clear presence and relationship between the ScienceREACH Coordinator and approximately ten students at New Orleans Charter for Science and Math High School. Now that these relationships have begun to form the Coordinator will be better able to offer supportive services to the students. One barrier we were able to remove was that originally we offered programs after school. These were hard for students to attend because of transportation issues. Hence, in February we integrated programming into the school day, with dinners becoming lunches, and science professionals being brought directly into the classroom. This removed the transportation barriers, and also gave teachers some extra support. Working within the school day also helped the ScienceREACH Coordinator to foster relationships within the school.

We have found that when a school is receptive to ScienceREACH, CIS is able to provide more programming. Because of the willingness of NOCSM to participate in ScienceREACH, we have been able to get a lot of traction there. The ScienceREACH Coordinator has developed relationships with Delaney French, the Guidance Counselor, Stella Allen, the Dean of Science, and Mr. Solet, the Disciplinarian. The ScienceREACH Coordinator works out of the school in either the Guidance Counselor's office, the Student Support Services Room, or directly in the classrooms, and through this has developed relationships within the school. Students at NOCSM are aware of the Coordinator's presence, and have approached her with ideas for STEM related projects that they would like to see at their school, such as a school wide recycling day for old notes and uniforms.

We approached Walker High School for the first time in April regarding ScienceREACH programming. They were very receptive to ScienceREACH, thus making it easy for CIS to provide services to Walker students. We look forward to providing more programming to Walker students in the future. We are evaluating our opportunities with McDonough 35 for 2008-09.

Number and type of interactions with UNO personnel: 3

CIS has had three interactions with UNO personnel. Golden Richard has connected ScienceREACH and the UNO Stars Program. We expect to work with approximately ten UNO STARS students who will work in some capacity with high school students. This collaboration will help ScienceREACH develop more interactions with UNO Students in the future as they work within the STARS and ScienceREACH programs. ScienceREACH has also worked with Sourav Chakraborty, a PhD student at UNO. Due to time constraints, however, he was unable to give an in-class presentation. We are hoping he will be available next school year. CIS has also connected with Jim Mesa, the Dean of the College of Education. We intend to include more UNO personnel in ScienceREACH in the coming academic year.

In addition to UNO, CIS continues to cultivate relationships within the New Orleans community. The Community Action Council of Tulane University Students has contributed to ScienceREACH with four volunteers who have run the ACT Prep Program, as well as two students who have participated in a College STEM Major Lunch. Three Xavier University students have worked with ScienceREACH -- one with the In-Class Mentoring/Teacher Assistance, and all three in a College STEM Major Lunch. Patrick Ibert, a civil engineer who owns his own company, as well as a Emery Meyer, a member of the American Society of Civil Engineers, have also worked with ScienceREACH to do the In-Class Presentation at Walker High School.

Potential future partners include Mad Science, which is a national program aimed at introducing students to science. The program works in first through fifth grades with assemblies, as well as providing teachers with materials to support their assemblies and presentations. Mad Science works within the state science curriculum. Through collaboration between ScienceREACH and Mad Science, high school students will have the opportunity to intern with Mad Science and assist Mad Scientists (who are college students) in the elementary school presentations. The Mad Science interns will be learning more about science through teaching, and will be developing a relationship with a college student at the same time.

ScienceREACH continues to develop and expand. Through other Communities in Schools Initiatives, we have been able to bring the ScienceREACH concept to PK-8 students. The CIS Site Coordinator at Ben Franklin Elementary ran a Science Club on Fridays which was regularly attended by 18 students. Tulane University Students facilitated experiments for the students. The CIS Site Coordinator at Dr. Martin Luther King Jr. Charter School held a Science Fair at MLK, which the ScienceREACH coordinator helped to judge. The fair was a great success. Students at MLK were also treated to field trips to the Botanical Gardens. These trips were funded by the Vincent Memorial Fund, which donated $15,000. The ScienceREACH program has also leveraged funding from the Greater New Orleans Foundation which totaled $5,500.

- Describe the opportunities for faculty recruitment, retention and development, as well as post-doc, graduate and undergraduate student training provided by your project

  One graduate student participated in this portion of the project. The student had two roles: 1) to meet with CISNO personnel to learn about and become involved in their activities and 2) to conduct research on oxidation of nanoscale low density lipoprotein (LDL) aggregates. The graduate student received training by learning from CISNO personnel about ongoing projects. The graduate student also received research training by working with the PI as well as scientists at Children's Hospital of New Orleans. Several undergraduate students have been involved in the project as described above.

- Describe the nature and scope of partnership activities

  CISNO served as the primary agency for design, coordination, and implementation of all academic year outreach activities as described above.

- Describe any problems encountered during the last year of project activities.

  No problems were encountered.

3. **Contributions:** Summarize efforts made to build research and education capacity, secure external federal and private-sector funding, build infrastructure, contribute to economic development, and ensure project sustainability over the long term.

Academic year outreach programs were designed to attract high school students into college study in science and engineering fields. Both schools targeted in this study have student bodies that are majority African-American. Furthermore, these schools have a high percentage of students receiving reduced or free lunch. Developing these human resources will provide a stronger base for science and technology development within the state of Louisiana.

A proposal was submitted to the National Science Foundation's IGERT (Integrative Graduate Education and Research Traineeship Program) program. This program provides funding for training of graduate students in science and technology fields. If funded, this project will provide a unique training experience to graduate students which will develop within them a broad understanding of how science and technology fits into economic, social, and international issues. The proposal is pending as of submission of this report (June 2008).

4. **Project Revision:** Provide a listing of and explanation for any significant changes in the work plan for upcoming year, including any changes in the amount of investigators' time devoted to the project. If you made significant changes to the project design as outline in the proposal during the past year, please list and explain the changes, the purposes for the changes, and the results.

Several programs developed by CISNO will continue to be implemented in project year two. Refining of these programs will be undertaken in order to make them more efficient, but no major changes are foreseen. Additional involvement of the graduate student with CISNO programs will be undertaken in project year 2. Efforts will be made to increase the number of undergraduate students involved in the project.

5. **Work Products:** List any tangible products (e.g., research publications and/or presentations, patents, licensing agreements etc.). Please combine all products into one document.

"LC-MS/MS mapping of the oxidation of apoB in low density lipoproteins," Sourav Chakraborty, Yang Cai, and Matthew A Tarr, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, Mar. 2008.

"Oxidative mapping of apoB in human low density lipoprotein using LC-MS/MS," Sourav Chakraborty, Yang Cai, and Matthew A Tarr, Gordon Research Conference on Oxygen Radicals, Ventura Beach, CA, Feb. 2008.

"Oxidative mapping of amino acids in human low density lipoprotein using hydroxyl radical and LC-MS/MS analysis," Sourav Chakraborty, Yang Cai, and Matthew A Tarr, Society for Free Radical Biology and Medicine National Meeting, Washington, DC, Nov. 2007.

PKSFI Report for LEQSF(2007-12)-ENH-PKSFI-PRS-04

Leszek M. Malkinski
(PKSFI-ESIP Clean Room, 2007-2008)

Title: Nanodevice Processing Laboratory

1. **Personnel:**
   Leszek Malkinski, Associate Professor of Physics and Materials Science. Dr. Malkinski is in charge of design and management of this part of the project.
2. **Activities:**

The aim of this project was to provide research support for AMRI and collaborating institutions with the cleanroom facilities and technology to do competitive research in the field of nanofabrication.

Fabrication and assembly of nanodevices involves integration of components with distinctly different sizes in the nano-, micro- and macro-scales into one functional device. These multi-step technological processes, as well as testing of the devices, require ultra clean environment, since the finest features of the devices are typically much smaller than the average size of dust particles. The evaluation of the purity of the air is based on number of dust particles in a unit volume. "Class 1000" cleanroom is the minimum requirement for the research activities on nanotechnology.

The following activities have been performed in relation to the Nanodevice Laboratory:

- The space in the Science Building on UNO main campus has been identified and approved by the Dean of the College of Sciences, Dr. J. King to accommodate the laboratory. The room SC2041 selected for the lab has an approximate area of 24'x34'.
- The best design of the laboratory has been worked out through discussions with multiple leading companies specializing in cleanroom building, including Cleanroom International Inc., Terra Universal Inc., Clean Air Products, Liberty Industries Inc. The important features of the cleanroom are as follows:
  a) Modular cleanroom is designed as a "closed loop" recirculation system to provide lower particle counts and greater control of temperature and humidity. The recirculating design is important to improve HEPA filter life by continuously recriculating air without allowing contaminates to enter from outside. Unlike a "once thru" type design, pre-filters inside the low-wall return air grilles act as a "second trap" to remove impurities before they can be introduced.
  b) The lab will be entered through a secure door to the class 1000 anteroom (gowning room)
  c) The cleanroom is made from smooth hard walls from galvanized steel, with antistatic coating to prevent accumulation of dust. They support a ceiling grid in which filters and lights with yellow cups are mounted. HEPA filters (#12805 SAM24 MicroSound GS Fan/Filter Modules) have fans with adjustable speed. The filters are replaceable from the interior of the cleanroom.
  d) The laboratory height is 8 feet. A top ceiling plenum cap from painted metal for recirculating air storage is be placed 2'above the ceiling. The space between the

ceiling and the plenum will be attached to the existing air conditioning system to control temperature inside the cleanroom.

e) The southern wall has transparent double walls with yellow coating to filter UV light.

f) The Magnehelic panel with 3 gauges is used to control pressure in the laboratory

g) Samples and materials can be transferred to the laboratory from anteroom through a pass-thru cabinet with mechanical interlock without opening of the cleanroom doors.

- The company Cleanroom Technology which will build the cleanroom has been determined by the bid process.
- The cleanroom has been purchased for the amount of $192k. The price includes installation and testing of air quality by independent company which will issue a certificate.
- UNO Facilities Services has been preparing the room for the installation. Specifically the existing suspended ceiling, air conditioning ducts, cabinets and sinks are being demolished. The old floor has been removed and new floor that meets the requirements of the cleanroom is installed. The preparation will be finished by 6/30/2008
- All components of the cleanroom will be delivered to UNO by the Cleanroom Technology by 06/30/2008
- The installation of the laboratory will be completed by August 15, 2008
- Testing and certification will be completed by August 30, 2008.
  Drawings of the cleanroom have been approved and first payments made.

In addition to building the laboratory, the following equipment has been purchased:

- **Mask Aligner/UV Exposure** system has been purchased by $100k from Newport Inc. as a sole source. Some unique features of the system include:

a) The exposure station uses 500 wt HgXe Short Arc Lamp which provides the deep ultra violet light with wavelengths of 220 to 260 nm which can be converted to 350 to 450nm through dichroic mirror. Digital exposure controller maintains the stability of the lamp as it ages to within +/- 1%, and time exposures from 10 ms to 9999 hours in 0.1 second intervals.

b) The system is equipped with the splitfield microscope mounted on X-Y Stage with illumination kits to illuminate both high reflective and non-reflective substrates/wafers; 5x and 10x objectives and microscope video kit.

c) Mask alignment fixture with easy 3-Step Alignment to accommodate wafers/substrates from 1 in OD or 1 x 1 in up to 6 in OD or 6 x 6 in; 5 x 5 in mask holder and custom 4 in wafer holder to hold both a 4 in OD and 3 in OD wafer; mounted on a Precision Translation Slide with 24 in travel.

d) The system is mounted on patented table with active vibration damping to enable maximum resolution of the alignment and exposure.

Parts of the mask aligner system have been received and partial payments made.

- **Ion Milling** system for patterning of nanostrcutures has been purchase form AJA International for $217k as a sole source. Important features of the system include:

a) Stainless steel high vacuum chamber pumped by oil-free roughing pump and a turbopump, which provide base vacuum better than 10^{-7} Torr.
b) The RF ion plasma source system must capable of ion milling metals, semiconductors and insulators as well as magnetic materials. The system is also capable of the reactive ion etching RIE. It has a dedicated gas line with mass flow controller for RIE.
c) A water-cooled substrate holder accommodates substrates up to 3" can be tilted by 80 degrees and rotates with up to 20 revolutions per minute.

The blueprints of the system have been approved and partial payments made.

- A **Spin Coater/ Hot Plate** have been requested as a sole source for $20k. The system will be used for coating substrates with photo-resists and curing the resist after exposure.

The important specifications of the system include:

a) All stainless steel construction
b) 700 Recipes/20 Steps
c) 0.1 Second Resolution for Step Times
d) Spin Speed up to12,000 RPM and spin speed repeatability and resolution better than 0.2RPM
e) System can accommodate substrates with different sizes from 10mm to 200mm
f) Hotplate temperature up to 400°C, resolution: 0.1 °C and 0.3% temperature uniformity across working surface
g) Three automated bake methods (contact, vacuum & proximity)

Project Revision

The design of the clean laboratory using recirculating air made it possible to exceed the originally planned standards of the cleanroom class1000. As a result, expected performance of the cleanroom should meet standard of higher class 100.

Certain delays in realization of the project have been caused by bid process. The bidders requested more information about the specifications and technical details which resulted in multiple addenda and extension of the bid opening. Also, realization of the equipment for the Nanodevice Process Laboratory (ion milling system and mask aligner) will take more time because of superior parameters of the ordered equipment and technical complexity of the systems.