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.

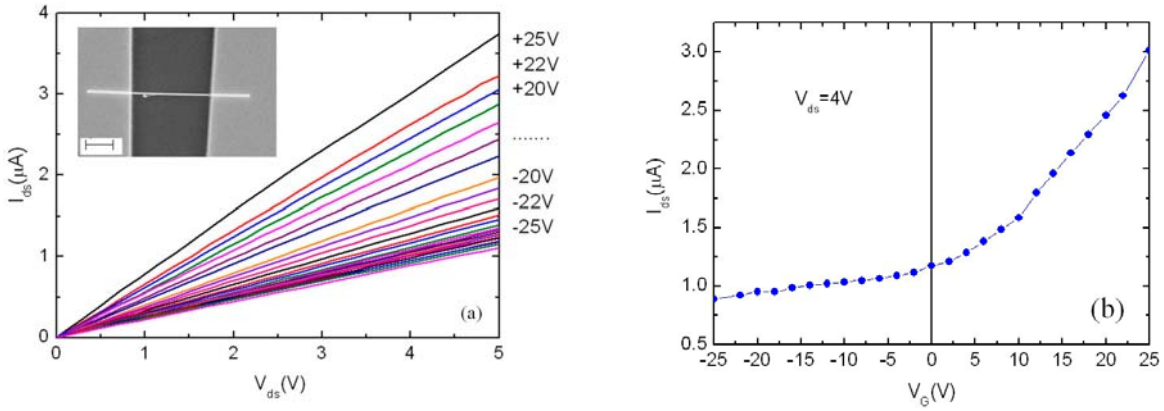


Figure 1 (a) I-V curves of a typical In_2O_3 device with respect to back-gate voltage (V_g = from -22 to +22V with a step of 2V). Inset: SEM image of the device, the scale bar is 2 μm. (b) The corresponding I_{sd}-V_g curve at V_{sd} of 4.0V.

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.

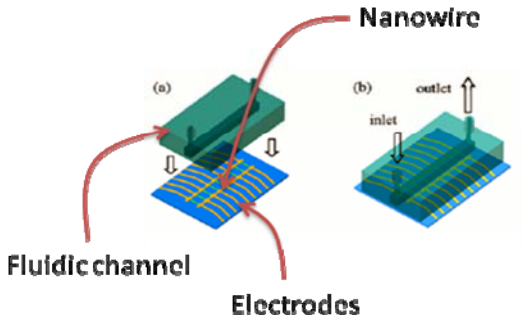


Fig. 2: Biosensor with fluidic channels, electrodes and embedded nanowires.

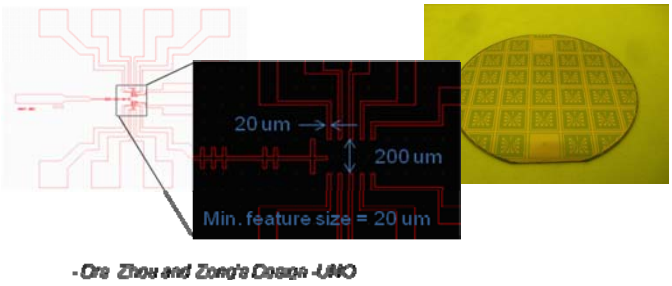


Fig. 3: Electrode design (left) and Si wafer with patterned electrode layer (right).

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.

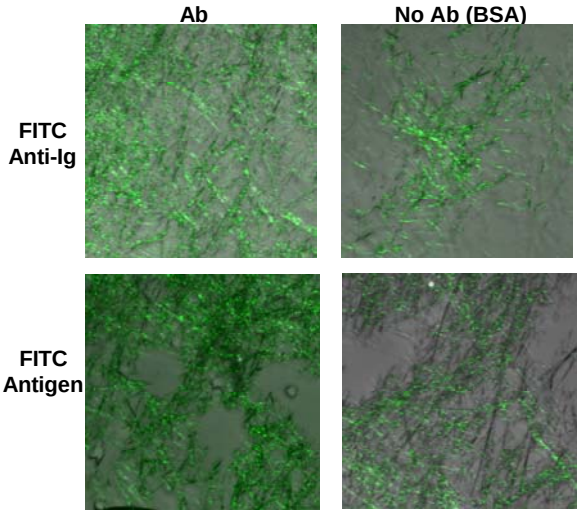


Fig. 4 Non-specific adsorption of the fluorescent proteins.

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.

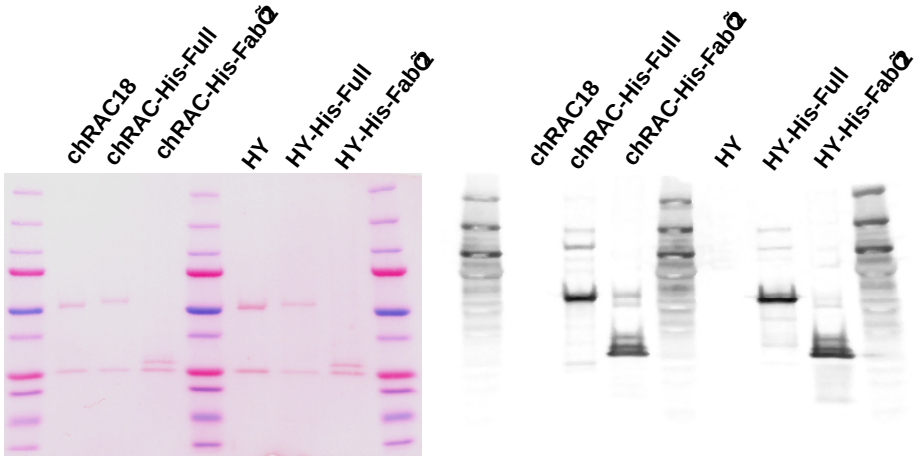


Figure 5. It shows a reduced gel blotted onto nylon and stained with Ponceau S (total protein), or blotted against anti-His antibody and detected with chemiluminescence. The His-Tag is found on the appropriate chains.

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	Mean	SEM
ChRAC18		
3ug/ml	0.44	0.05
0.3ug/ml	0.33	0.00
0.03ug/ml	0.25	0.03
chRAC18-His-Full Length		
3ug/ml	0.84	0.11
0.3ug/ml	0.47	0.04
0.03ug/ml	0.26	0.02
chRAC18-His-Fab'2		
3ug/ml	0.26	0.00
0.3ug/ml	0.20	0.01
0.03ug/ml	0.19	0.01
Blotto	0.16	0.01

Rabbit anti-His+ Anti-Rab	Mean	SEM
ChRAC18		
3ug/ml	0.438	0
0.3ug/ml	0.288	0.006
0.03ug/ml	0.215	0.004
chRAC18-His-Full Length		
3ug/ml	1.17	0.06
0.3ug/ml	0.46	0.02
0.03ug/ml	0.28	0.01
chRAC18-His-Fab'2		
3ug/ml	0.43	0.06
0.3ug/ml	0.26	0.03
0.03ug/ml	0.21	0.00
Blotto	0.17	0.01

Anti-Rabbit	Mean	SEM
ChRAC18		
3ug/ml	0.30	0.02
0.3ug/ml	0.21	0.01
0.03ug/ml	0.19	0.00
chRAC18-His-Full Length		
3ug/ml	0.34	0.01
0.3ug/ml	0.23	0.01
0.03ug/ml	0.18	0.00
chRAC18-His-Fab'2		
3ug/ml	0.17	0.00
0.3ug/ml	0.15	0.01
0.03ug/ml	0.16	0.01
Blotto	0.15	0.00

Gp120 plate

Anti-Human	Mean	SEM
HY		
3ug/ml	0.82	0.05
0.3ug/ml	0.84	0.04
0.03ug/ml	0.62	0.03
HY-His-Full		
3ug/ml	0.92	0.17
0.3ug/ml	0.69	0.04
0.03ug/ml	0.55	0.01
HY-His-Fab'2		
3ug/ml	0.58	0.01
0.3ug/ml	0.48	0.02
0.03ug/ml	0.45	0.03
Blotto	0.49	0.02

Rabbit anti-His+ Anti-Rab	Mean	SEM
HY		
3ug/ml	0.51	0.032
0.3ug/ml	0.4085	0.0545
0.03ug/ml	0.4045	0.0045
HY-His-Full		
3ug/ml	1.01	0.02
0.3ug/ml	0.58	0.03
0.03ug/ml	0.43	0.01
HY-His-Fab'2		
3ug/ml	0.71	0.00
0.3ug/ml	0.46	0.03
0.03ug/ml	0.38	0.00
Blotto	0.35	0.01

Anti-Rabbit	Mean	SEM
HY		
3ug/ml	0.53	0.05
0.3ug/ml	0.43	0.00
0.03ug/ml	0.40	0.02
HY-His-Full		
3ug/ml	0.42	0.01
0.3ug/ml	0.34	0.01
0.03ug/ml	0.34	0.01
HY-His-Fab'2		
3ug/ml	0.35	0.02
0.3ug/ml	0.32	0.00
0.03ug/ml	0.34	0.02
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)

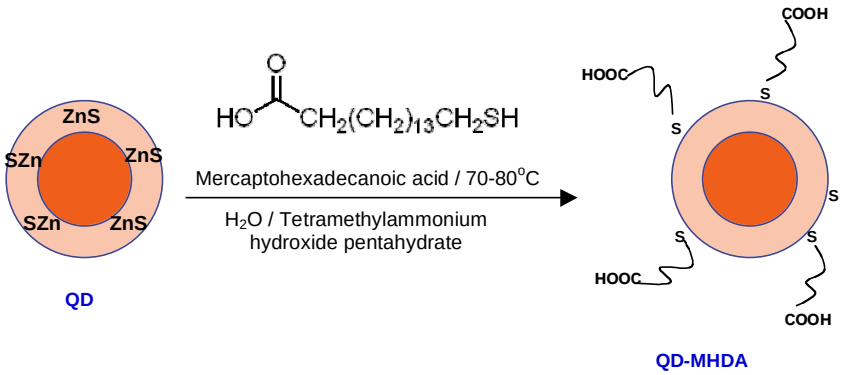


Figure 6. Coating of QDs to obtain a hydrophilic surface

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.

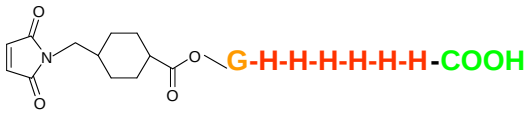


Figure 7. His-tagged peptide modified

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

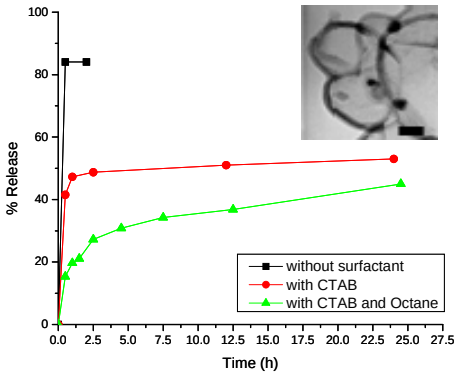


Fig.8 Drug release of ibuprofen from the MPHSNs showing slow release. The inset is a TEM image of MPHSNs. The scale bar is 20 nm.

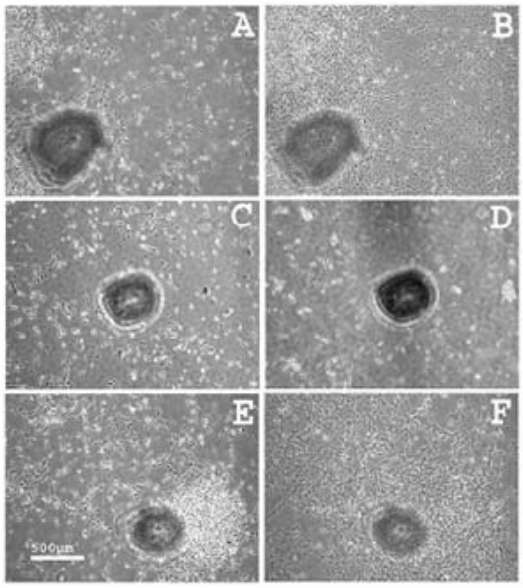


Fig.9 3 CRL-2199 cell toxicity: phase microscopy. Cells were treated with control media (A+B), or with 50 µg/ml of copper nanoparticles (C+D) or porous silica nanoparticles (E+F). Panels A, C, and E show cultures 5 minutes after treatment and panels B, D, and F at 20 hours after treatment. The large 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,

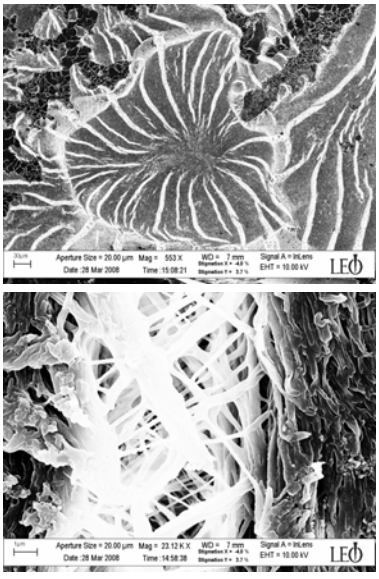
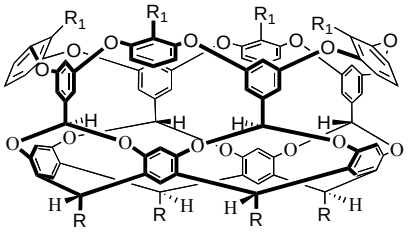


Figure 2-1. Top image shows low magnification image of polymer nanowires after UV light exposure. Bottom image is closs up of nanowire arrays.

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.

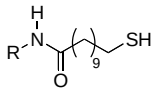
b. *Host-guest assembly.* This program of research focuses on the controlled assembly of nano-objects into complex nano-systems. The general approach involves the development of hosts (H1, H2 and H3) that bind complementary guests (G1, G2 and G3). Each host-guest pair is orthogonal, i.e. H1-G1 strongly 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.

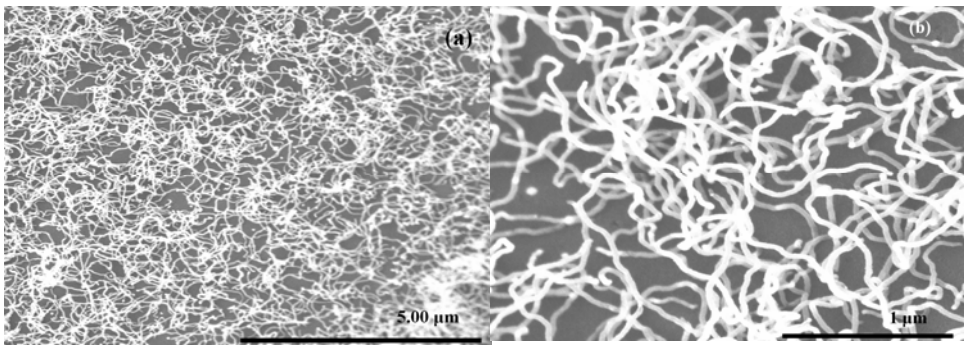


Figure 2-2: SEM's of carbons from selected sugars.

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)

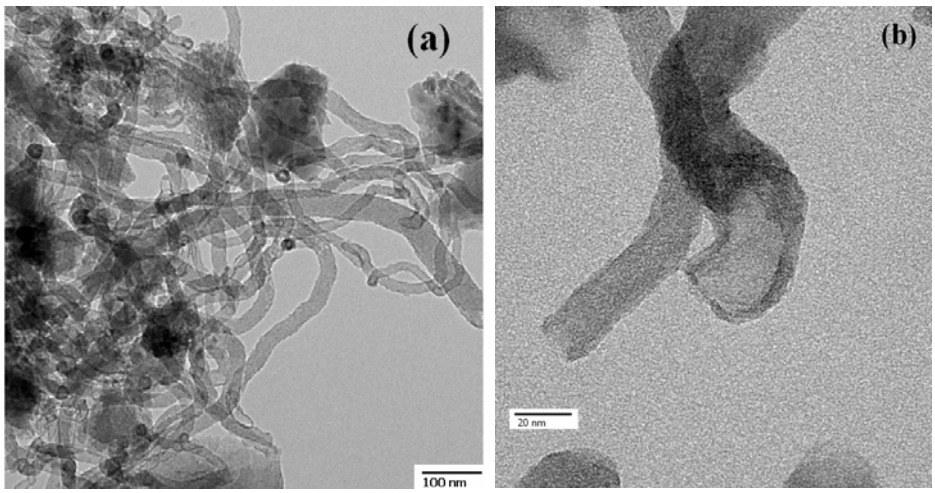


Figure 2-3 - TEM images of α-cyclodextrin after pyrolysis at low magnification (a), showing the intertwined microtubules and at high magnification (b) showing the hollow cylindrical tubes.

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.

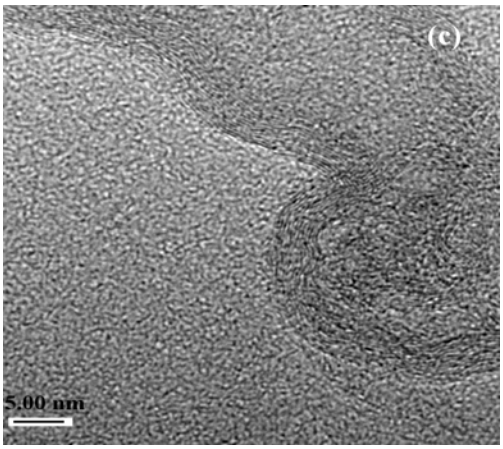


Figure 2-4: High resolution TEM showing graphitic planes

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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

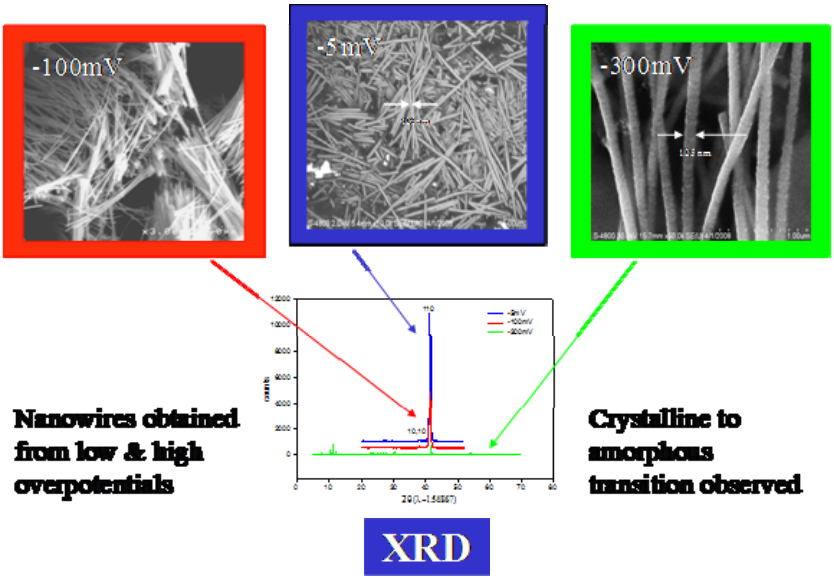
act as a nano-heat-sink (cooler), and absorb the generated heat. The novelty of its architecture [(Bi_2Te_3)bottom/(GMR)multilayers/(Bi_2Te_3)top] could make this nanomaterial a superior sensitive magnetic sensor. Moreover, thermal control is a requirement to all space flight missions. Heat rejection 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.

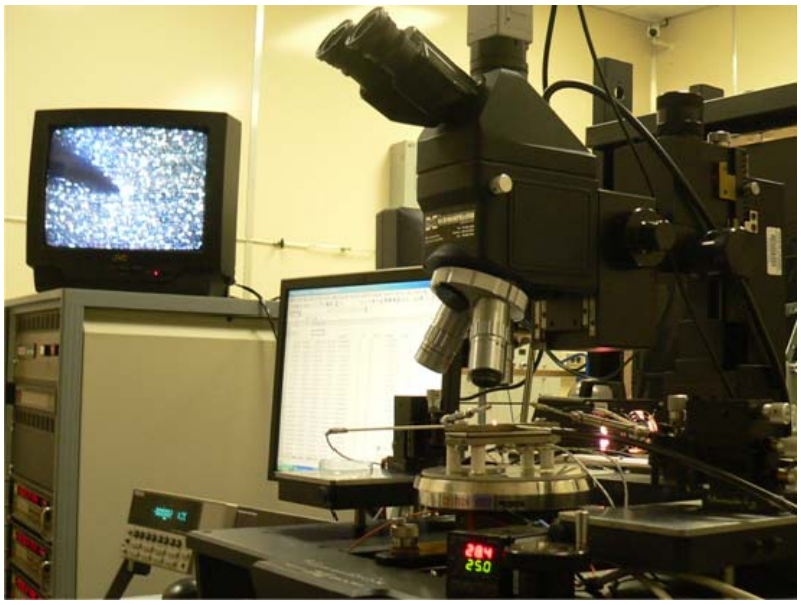
*Implementation Strategy***:** Bi_2Te_3 nanotubes and nanowires are to be electrodeposited using a variety of pore size polycarbonate membranes (100-500 nm pore diameter). The Bi_2Te_3 electrolyte concentration will be varied; the initial concentration will be doubled, quadrupled and the ratios of bismuth 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.

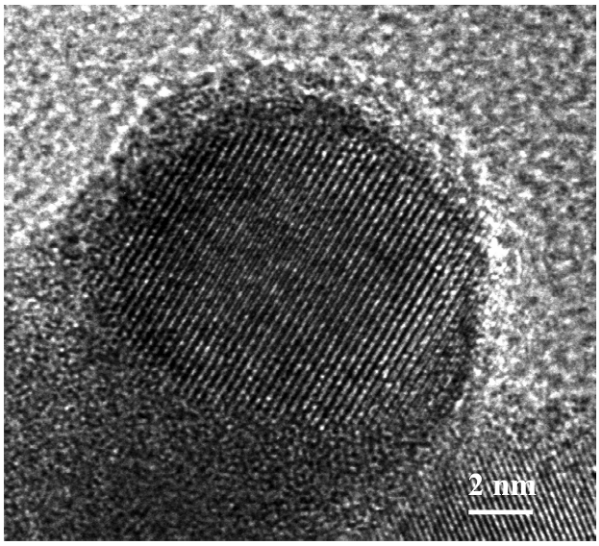


Figure 2. High resolution transmission electron microscope image of a PbTe nanoparticle. An outer amorphous layer (~1 nm, presumably oxide) is evident.

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.

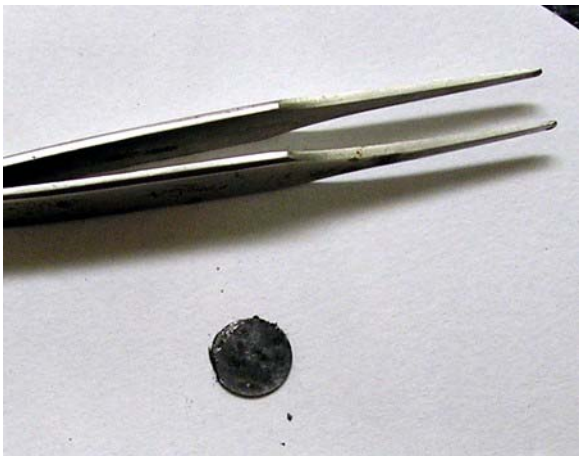


Figure 3. Photograph of the pressed pellet.

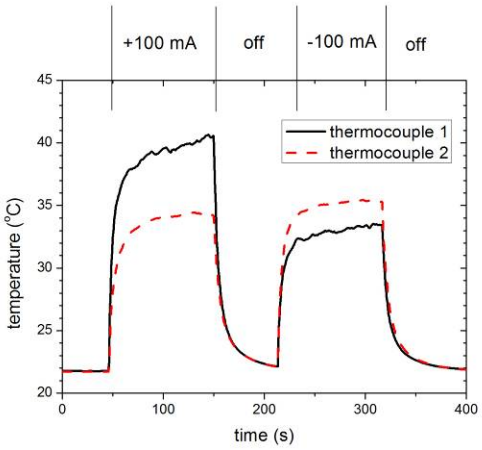


Figure 4. Temperature gradients generated by running a current through Sample 2. The gradient is smaller when the current is reversed because of asymmetrical heat sinking of the sample.

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.

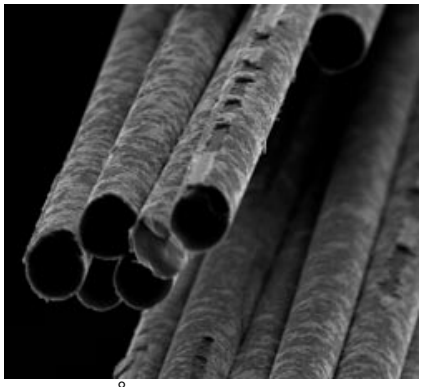


Fig. 5. 800 Å of $MgCNi_3$ grown on the surface of a 7-□m diameter solid carbon fiber.

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.

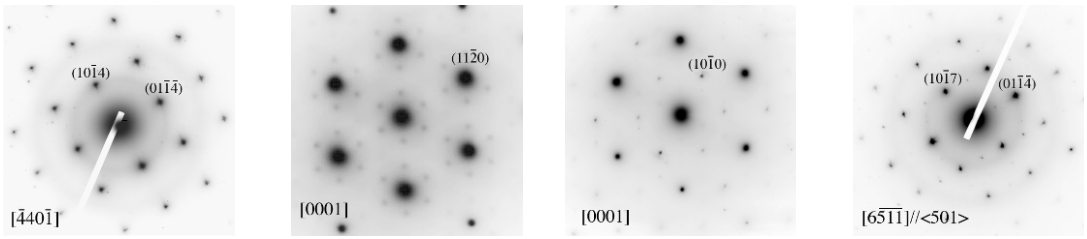
d. Electrochemical storage materials (Gabrisch, Mohanty and Yi)

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 $\sqrt{3}$ x $\sqrt{3}$ R 30º 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

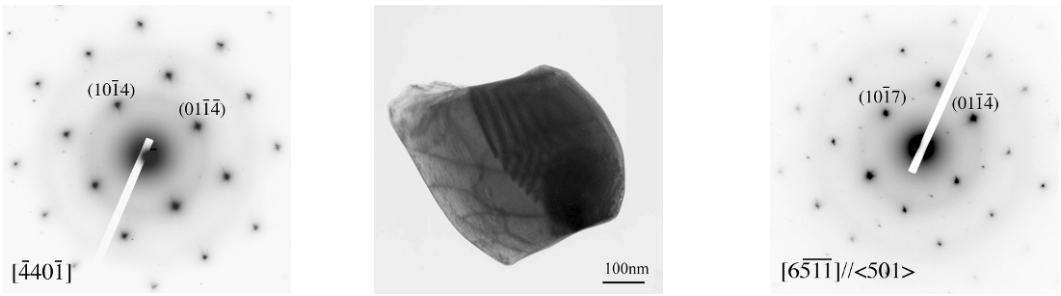
decreases from 46% in the pristine sample to 16% after ageing balanced by an increase in particles having O3 or spinel diffraction patterns. After charge to 5.2V only O3 and spinel phases are observed. The rearrangement of cations during ageing is accompanied by changes in particle morphology. The fraction 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.

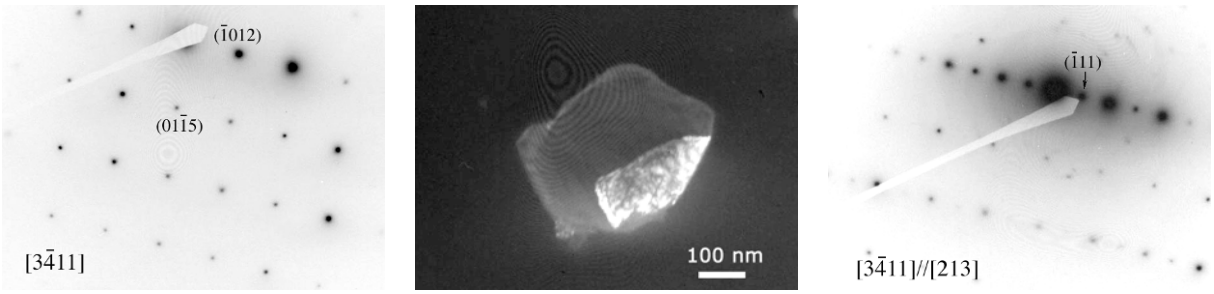


a.) b.) c.)

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.

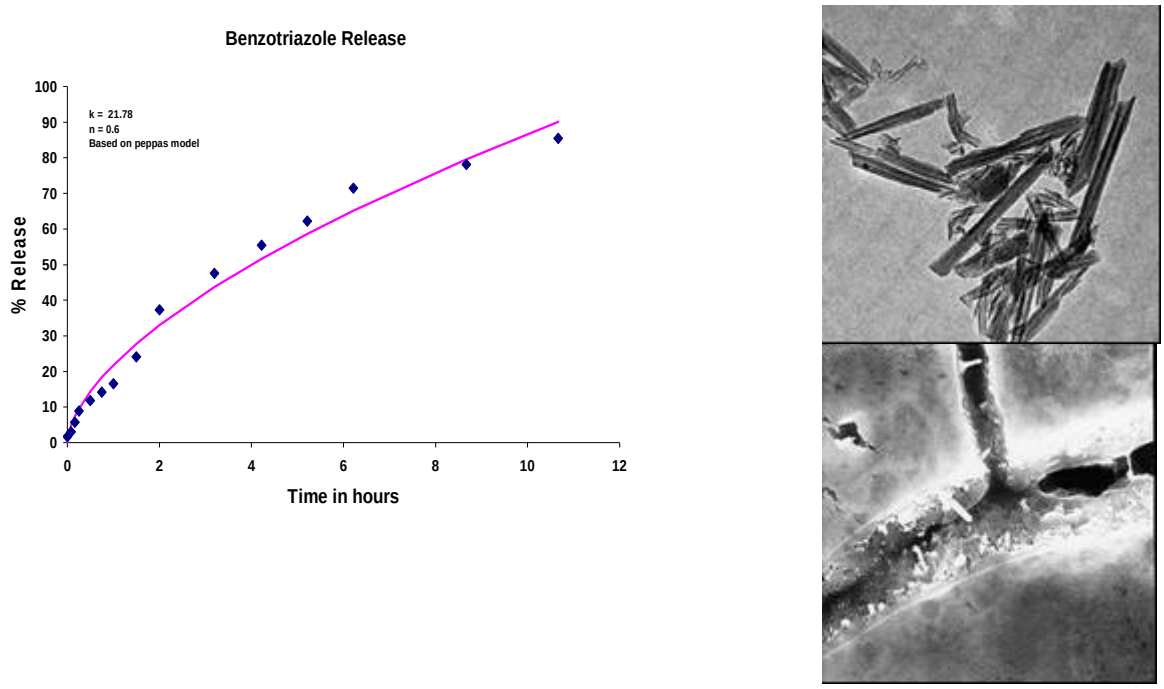


Figure 2. Release curves of anticorrosion agent benzotriazole (a). TEM images of halloysite nanotubes dispersed in water and their cross-section (insert) (b) ;image of cracks in a dry layer of paint with inclusion of halloysite nanotubules containing an antifouling agent (c).

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^{o}C, resolution: 0.1 ^{o}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.