**Project Title: Biomedical Engineering Bionanosystems Research at Louisiana Tech University**

**DoE Identification Number: DE-FG02-08ER64601**
**Budget after reductions:** $1,435,000

**Nature of the Project:** The nature of this project is to equip and support research in nanoengineered systems for biomedical, bioenvironmental, and bioenergy applications.

**Applicant/Institution:** Louisiana Tech University

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**DOE Office of Science Program Office:** Biological and Environmental Research

**DOE Office of Science Technical Program Manager:** Dr. Arthur Katz

# Introduction

Funds provided by the Department of Energy (DoE) under this Congressional Directive were used to support two ongoing research projects at Louisiana Tech University in biomedical, bioenvironmental, and bioenergy applications. Two major projects (Enzyme Immobilization for Large Scale Reactors to Reduce Cellulosic Ethanol Costs, and Nanocatalysts for Coal and Biomass Conversion to Diesel Fuel) and to fund three to five additional seed projects were funded using the project budget. The project funds also allowed the purchase and repair of sophisticated research equipment that will support continued research in these areas for many years to come. Project funds also supported faculty, graduate students, and undergraduate students, contributing to the development of a technically sophisticated work force in the region and the State. Descriptions of the technical accomplishments for each funded project are provided in the following pages.

# Project Descriptions

## 1. Enzyme Immobilization for Large Scale Reactors to Reduce Cellulosic Ethanol Cost

*James D. Palmer* – Virgil Orr Professor, Associate Professor, Director of Chemical and Industrial Engineering, Program Chair for Chemical Engineering, Ph.D. Engineering, and Engineering Management of Technology
*Yuri Lvov* – Professor, Tolbert Pipes Endowed Chair on Micro and Nanosystems
*Hisham Hegab* – Hogan Family Professor, Associate Professor, Director of Computer Science, Electrical Engineering, Electrical Engineering Technology, and Nanosystems Engineering
*L. Dale Snow* – Waggoner Professor, Program Chair and Professor of Chemistry

**Project Objectives:**

Biofuels are an important part of the solution for sustainable transportation fuel and energy production for the future. Unfortunately, the country's appetite for fuel cannot be satisfied with traditional sugar crops such as sugar cane or corn. Emerging technologies are allowing cellulosic biomass (wood, grass, stalks, etc.) to also be converted into ethanol. Cellulosic ethanol does not compete with food production and it has the potential to decrease greenhouse gas (GHG) emissions by 86% versus current fossil fuels (current techniques for corn ethanol only reduce greenhouse gases by 19%). Because of these advantages, the federal government has made cellulosic ethanol a high priority. The Energy Independence and Security Act of 2007 (EISA) requires a minimum production of at least 16 billion gallons of cellulosic ethanol by 2022. Indeed, the Obama administration has signaled an ambitious commitment of achieving 2 billion gallons of cellulosic ethanol by 2013. Louisiana is well positioned to become a national contributor in cellulosic ethanol, with an excellent growing season, a strong pulp/paper industry, and one of the nation's first cellulosic ethanol demonstration plants.

Dr. Palmer in Chemical Engineering at Louisiana Tech University is collaborating with Drs. Lvov and Snow in Chemistry and Dr. Hegab in Mechanical Engineering to capitalize on these advantages by applying nanotechnology to improve the cellulosic ethanol processes. In many of these processes, expensive enzymes are used to convert the cellulose to sugars. The nanotechnology processes developed at Louisiana Tech University can immobilize these enzymes and therefore significantly reduce the overall costs of the process. Estimates of savings range from approximately $32 million at each cellulosic ethanol plant, to $7.5 billion total if the 16 billion gallons of cellulosic ethanol is achieved. This process has the advantage of being easy to apply in a large-scale commercial environment and can immobilize a wide variety or mixture of enzymes for production.

Two primary objectives with any immobilization technique are to demonstrate reusability and catalytic activity (both reuse of the immobilized enzyme and reuse of the polymer substrate). The scale-up of the layering-by-layering process has been a focus this past year as some interesting challenges in the surface chemistry have become evident. Catalytic activity of cellulase is highly dependent upon how the feed material is pretreated to enhance digestion. Therefore, efforts this year have been performed this year to characterize our process on a few of the more prevalent pretreatment methods.

**Narrative:**

Presentations/Publications:

This has been a productive year with a number of notable accomplishments. There have been a number of activities that have raised the visibility of Louisiana Tech – the first being the Energy Systems Conference on November 5, 2009. Dr. Palmer helped organize this event and presented on the cellulase immobilization project in the afternoon session. Leading up to the event, a short press release was submitted to various news organizations (written by Dr. Palmer and provided to Tech's marketing department). Within 24 hours, the story was picked up by over 13 news outlets nationally and internationally, including R&D Magazine (audience 72,549 with a news ad value of $2166), ScienceDaily (audience of 40,795), and PhysOrg.com (audience of 17,000).

**From the recognition achieved through this press release, Dr. Palmer was invited by Elain Mulcahy (Editor) to write a Feature Article in Nano Magazine**. This article has been submitted and will appear in Issue 16, February 2010 (ISSN 1757-2517, ION Publishing Ltd). The title is: Cleaner, cheaper fuels Are Enzymes the Key?.

In addition, the Senior Editors of Biofuels have invited Dr. Palmer to contribute an editorial article related to Nanotechnology for biofuel process improvement". The deadline for submission is August 2, 2010.

Students Supported:

Qi Xing – female international PhD student working under Dr. Lvov – Graduated Fall 2009.

Dezhi Zhang – male international PhD student working under Dr. Palmer – started Spring 2009.

Joe Nealy – male US PhD student – switched to MS ETM – under Dr. Palmer – started Summer 2009.

Bam Aryal – male international MS CMEN student working under Dr. Palmer – started Fall 2009.

Bibek Uprety – male international undergraduate CMEN student working under Dr. Palmer – started Winter 2008/09.

Valessa Sprately – female US undergraduate CMEN student working under Dr. Palmer – started Fall 2009.

As described in the abstract above, there were a number of issues that were investigated this year to facilitate commercialization of this process. A number of pretreatment strategies were investigated to determine their impact on the availability of the cellulose substrate. Two of the commercially available cellulase enzymes were compared directly to determine which would be the best candidate (Novozyme and Genecor). The reusability of the beads surprisingly was an issue as is the reuse of the beads (the lower pH conditions optimum for the hydrolysis is likely the cause – current efforts are underway to determine if light cross-linking can prevent the dissolution of layers in reaction solution).
The various pre-treatments tested thus-far have not had any dramatic impact on the reactivity of the cellulose, likely because of the already processed nature of the Sigma Cell 20 being utilized.

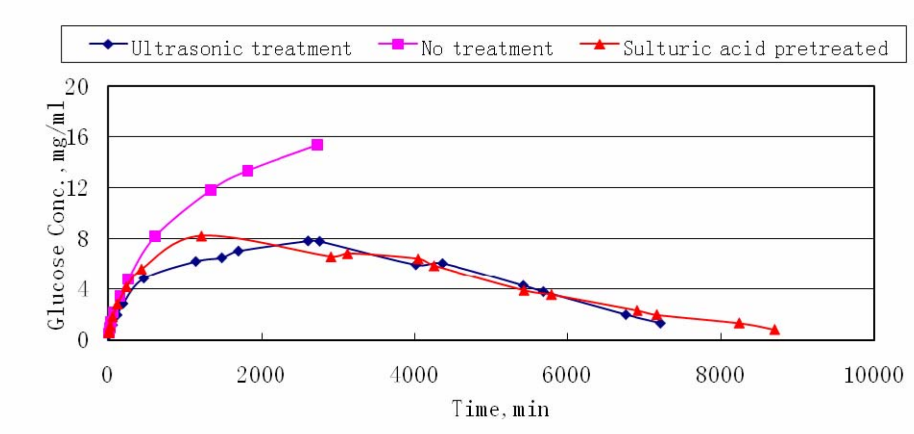

Figure 1 – Sulfuric Acid and Ultrasonic Treatments versus Control (note higher activity of control)

Interestingly, the ultrasonic treatment did not increase the activity even though the mean particle size was reduced from 20 to 3 microns within 20 minutes of exposure.

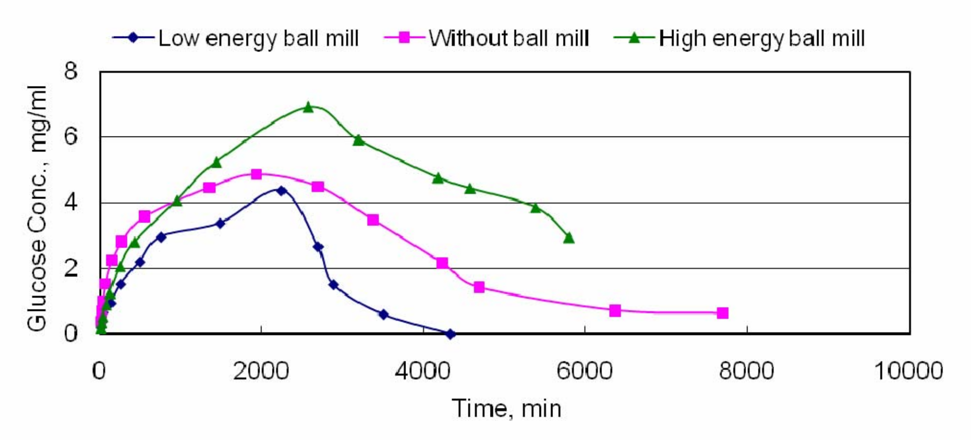

Figure 2 – Control versus Low and High Energy Ball Milling (note highest activity of high energy ball mill but not economically viable)

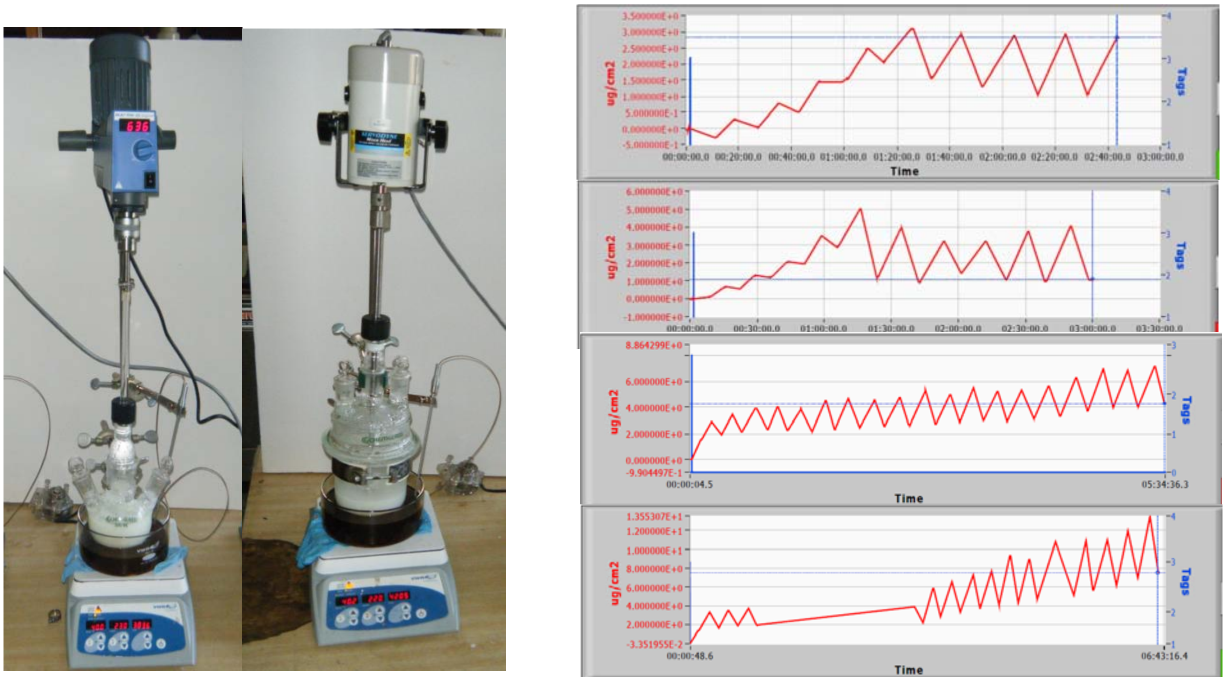

Figure 3 – Reactor testing systems (6 systems obtained for parallel studies); QCM results of various pH conditions for layering.

A number of QCM studies have been performed to determine the optimum conditions for deposition. A tris-buffer solution with a pH of 9.22 for PEI and the enzyme, and 7 for PSS was determined to be the optimum. Reactivity studies of 5 layers of cellulase and 3 layers of cellulase were compared (see Figure 4 below). There was nearly a linear dependence of enzyme layers on performance (more layers will be tested to determine the optimum). These results have been observed previously with smaller molecule substrates (urea and organophosphorous agents), however are surprising and encouraging for the LbL process. This suggests that the LbL may have a higher theoretical surface activity than single monolayers due accessibility to several layers for polymers such as cellulose.

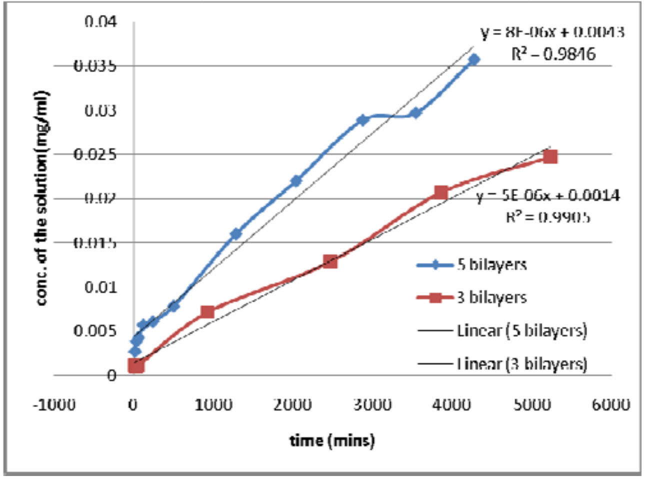

Figure 4 – Comparison of 3 and 5 layers of Cellulase Immobilized

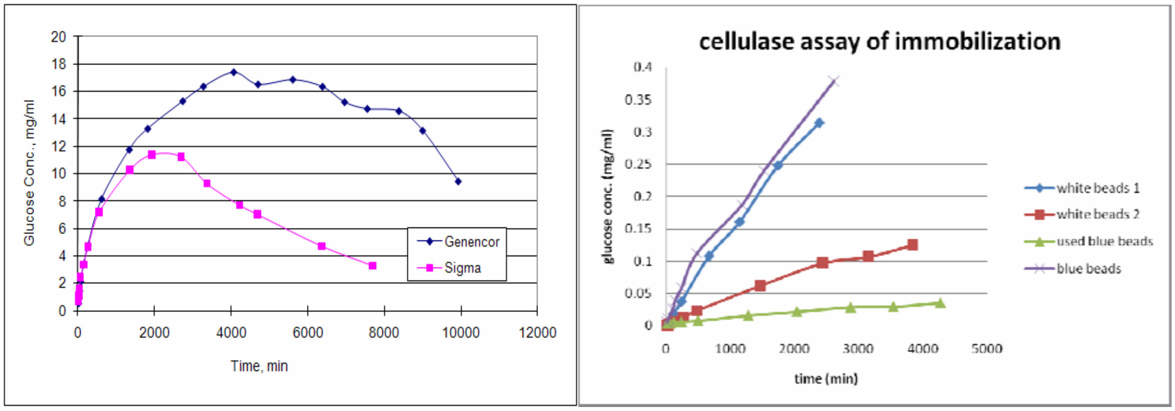

Figure 5 – A. Genecor versus Sigma (Novozyme 188) Free Enzyme Performance - left; Immobilized Substrate reuse – right

From figure 5 above it is clear that Genecor enzyme is superior to the Novozyme 188 (Sigma). This result correlates with what other researchers reported at the AIChE 2009 Fall National Conference (Novozyme appears to be superior only for a small fraction of cellulose types so most researchers us a mixture of primarily Genecor with approximately 10 or 20% Novozyme 188).

The reuse of the beads in the right column of Figure 5 is of concern. Dr. Palmer has extensive experience using LbL films for urease and organophosphorase in continuous flow reactors. The layers appeared to be very stable in the flow reactors, suggesting that the low pH desired for the cellulase reaction along with physical agitation maybe stripping the LbL layers. A variety of cross-linking methods are currently being studied to bind the layers after they have been deposited via LbL. EDC and NHS are the two cross-linkers currently being utilized (concentrations an order of magnitude lower than those suggested in the literature are being used). There was a significant impact on the activity of the enzyme (reduction by an order of magnitude), therefore further reductions in EDC/NHS concentrations and other cross-linkers are being investigated (particularly, cross-linkers that will bond the amine groups in the PEI together without impacting the cellulase).

## Public Purpose Served:

This project is highly aligned with two of the Department of Energy's strategic goals, specifically Energy Security, and Scientific Discovery and Innovation. This project serves the need of Energy Security by focusing on a critical barrier for commercialization of the cellulosic ethanol process (specifically, the reducing cost of the enzyme per gallon of ethanol produced by allowing the enzyme to be reused multiple times). Scientific Discovery and Innovation are paramount to the success of this project. Innovative nanotechnology is being applied to solve the challenge of an enzyme immobilization technique that is suitable for scale-up to a manufacturing environment.

## 2. Nanowire Catalyst for Fischer Tropsch Synthesis

*Dr. Chester Wilson*, Assistant Professor, Louisiana Tech University
*John McDonald*, Research Engineer, Louisiana Tech University

**Project Objectives:**
Determine the viability of nanowire catalyst for Fischer-Tropsch Synthesis. To accomplish this goal we constructed a laboratory catalyst evaluation reactor and constructed our own catalyst manufacturing process along with necessary procedures.

**Publications and presentations resulting from the project:**
Publications on this topic were limited due to the patent application mentioned below. However, there was one conference presentation by Josh Brown at "Transducers 2009."

**Intellectual property resulting from the project:**
As a result of this funding, a patent application was submitted for nanowire catalyst on Fischer-Tropsch and other processes.

**Number of students supported:**
Six students were supported with the funds from this grant.

**Degrees earned by students participating in the project:**
Two B.S. CHEMN
One B.S. Nanosystems Engineering
Two Ph.D. Engineering (expected)

**Narrative:**
As a result of this project the investigators are have further developed a new catalyst technology, nanowire catalyst. Nanowire catalyst have the capability to replace many applications of traditional catalysts on porous supports and the knowledge gained from these investigations will be used to design a fundamentally new reaction process for Fischer-Tropsch conversion of syngas to higher hydrocarbons. We are currently using this catalyst in our laboratory scale reaction process to produce diesel from cylinder derived syngas. These investigations will enable us to more effectively design and scale up this process to the next design level of pilot/commercial scale, and will also aid in future applications of this technology in diverse areas. Another area currently under development is a catalyst for carbon dioxide reforming of methane to produce syngas. It is our belief that this catalyst, along with our online plasma decoking process, can make dry reforming a commercially viable and environmentally important process. These two processes, F-T synthesis and Dry reforming, will enable us to construct a facility capable of converting our large and domestic natural gas resources into liquid fuels in an economical and environmentally responsible manner. A third area of research we are currently developing as a result of this project is to use this technology as a cathode catalyst for secondary lithium air battery technology. A model developed for one of these processes could easily be adapted for other processes and aid in their development as well. Future plans include a catalyst for reforming of diesel to produce hydrogen for fuel cell use and automotive catalytic converter technology. The following pages provide some

background information and detail why we are focusing much of our resources on development of this catalyst technology.

The investigators at Louisiana Tech have developed a new catalyst synthesis technique that does bust the paradigm. This catalyst system, as a result of being fundamentally different, offers many benefits over existing technology. These include greatly improved mass transfer, greatly improved heat transfer, easier decoking, and an almost 100% dispersion factor which reduces the total catalyst inventory required. Further, the catalyst can be custom designed at the nanoscale to meet other needs such as a maximum heat flux through a tube wall requirement or promotion of one reaction over another.

We believe this is the next generation of catalyst and it will advance many applications of catalyst usage over the next 10 -15 years. We believe it will impact the chemical industry in a way that “Nano-Science” has impacted other industries.

## Applications to Fischer-Tropsch Synthesis

The stoichiometry for the Fischer Tropsch synthesis is provided below:

$$CO + 2H_2 \Leftrightarrow CH_2 + H_2O$$

Generally the objective of this process is to produce long chain molecules in the range of C10 to C20 depending on markets and design. For this to occur two things generally must be maintained: first, both carbon monoxide and hydrogen must be at the active particle site in appropriate concentrations and the growing hydrocarbon molecule must stay chemisorbed to the active particle site. Two aspects of current commercial catalyst work to discourage chain growth and increase the distribution of products in F-T synthesis: pore diffusion limitations and heat transfer limitations.

Pore Diffusion - Hydrogen, by virtue of its small size has little trouble diffusing through the pores of a support. Carbon monoxide by contrast is much larger and diffuses at a much lower rate than hydrogen. Consequently, the hydrogen to carbon monoxide ratio varies with the length of pore diffusion required to reach an active site and inversely with the diameter of the pore. If insufficient CO is available at the active site, then the growing hydrocarbon molecule will likely react with hydrogen and terminate the chain growth. As there is little control over where the catalyst particles are placed within the support, this introduces great variation in the carbon number product distribution.

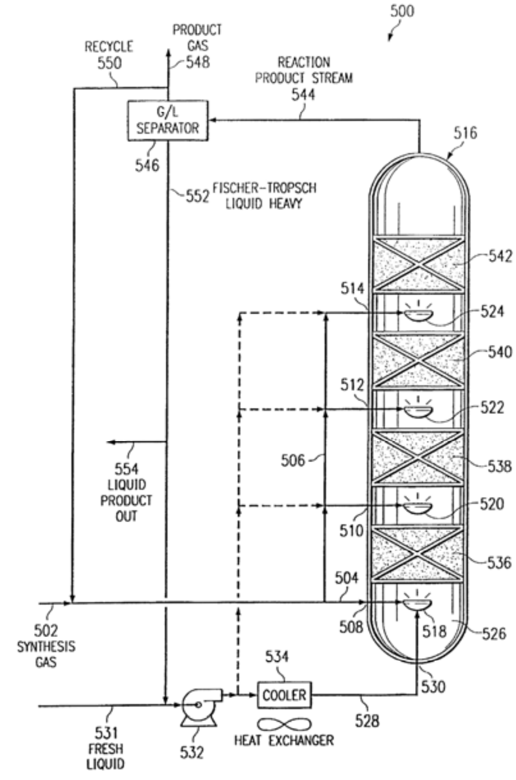

Figure 1: Sasol Advanced Fixed Bed Reactor.

Heat transfer follows a path analogous to mass transfer. Typically catalyst supports are ceramic and do not conduct heat well. For the highly exothermic F-T synthesis this can lead to hot spots at the active site that may lead to desorption of the growing hydrocarbon. Readsorption is unlikely and thus can lead to formation of light hydrocarbons.

Pictured at right is a staged fixed bed reactor patented by Sasol Petroleum. This reactor has multiple inlets for reactants and cooling in between stages to remove the heat of reaction. Multiple inlets provide a more even concentration of reactants throughout the length of the reactor, however it does not mitigate differences in the pore diffusion rates of CO and $H_2$ and a broad distribution of products is expected. The staged process provides a good method of removing the high heat of reaction; an ideal case of this design would be to make the stages infinitely small to minimize an increase in temperature. However, in actual design this must be balanced against fabrication costs and the design does not change the inherent poor conduction of the ceramic support. Thus as the catalyst particle temperature rises, the process tends to produce undesirable $C_{5-}$ products.

## **Nanowire Catalyst for Fischer-Tropsch Synthesis**

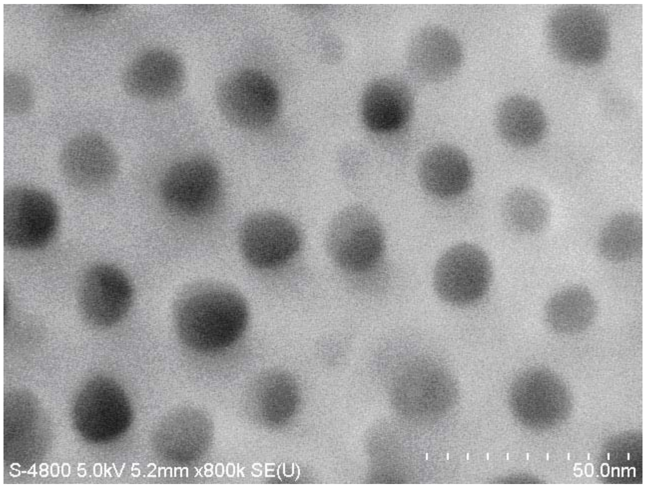

Figure 2: Anodic Aluminum Oxide (AAO) Template

Louisiana Tech University is developing a fundamentally new catalyst technology based on nanowires. These nanowires have been produced from many different metallic species, and have been produced in a variety of lengths and diameters. Our nanowires are produced by deposition of catalytic materials into the voids of an ordered anodic aluminum oxide (AAO) thin films (see figure 2). Unlike most producers of nanowires that rely on purchased AAO films that are applicable to research uses only, we grow all AAO films directly on the surface of our ultimate catalyst support material. For low temperature reactions, this is normally produced on solid aluminum supports. For higher temperature reactions, thin films of aluminum are deposited upon other substrate materials such as titanium and then anodized to produce the nano-template. One common method for deposition of the catalytic material is electrodeposition through the AAO film. This method has been used extensively in our research to produce cobalt nanowires for a Fischer Tropsch Process (see Figure 3).

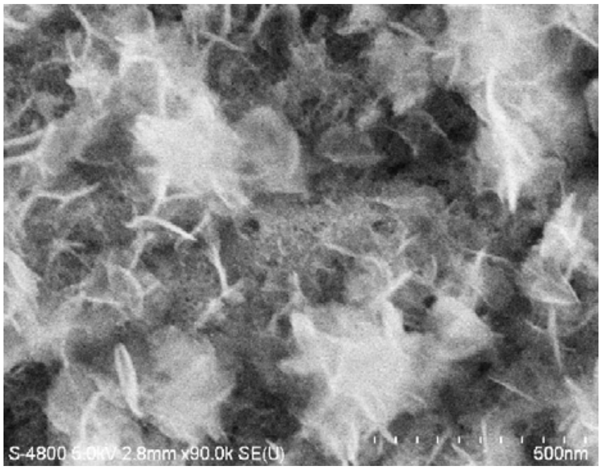

Figure 3: Nanowire Catalyst

Our current investigations are being

conducted on a first generation reactor that enables us to evaluate the catalyst real-time during experimentation. The process has capabilities for control of reactant flows, reactor temperature, pre-heater temperature, and reactor pressure. The temperature control scheme utilizes a cascade operation to promote accurate observation to the operating temperature. Also included in the system is a National Instruments SCXI 1100 data capturing system and an SRI dual-column chromatograph for online process analysis.

All control instruments, pressure, temperature, flow and the chromatograph can communicate to the data capture system to log process data. This enables the investigators to more effectively link cause and effect during future investigations. The basic reactor and associated controls began commissioning in May 2009. The design rate for this reactor is 1 liter per day of commercial diesel product.

Figure 4: Test Reactor for Catalyst Evaluation

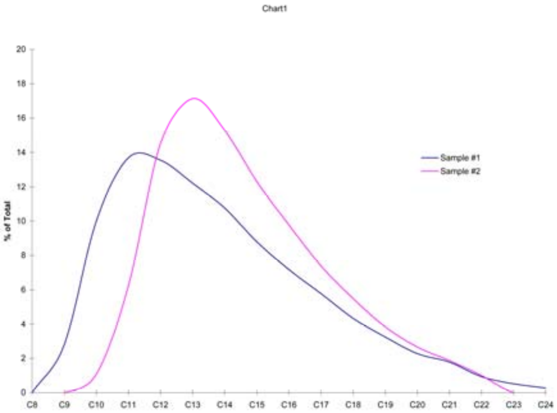

Figure 5: Carbon Number Distribution of Two Samples

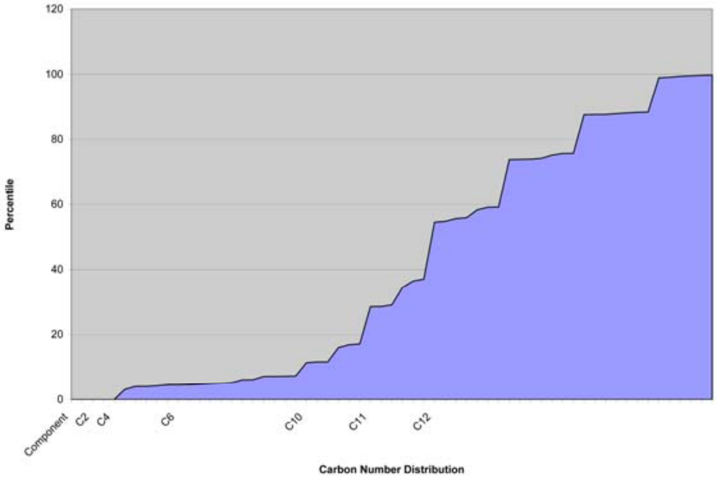

Figure 6: Carbon Number Distribution Based on Online Chromatograph with Reactor Conditions at 30 C and 25 psig

Based on our results to date, nanowire catalysts appear to offer many advantages over traditional catalyst technologies. Among these advantages are elimination of pore diffusion resistance and higher specific activity as compared to traditional catalyst. These differences are manifested in two very important ways. First, the carbon number distribution of products is greatly reduced due to an elimination of the differences in pore diffusion experienced by carbon monoxide and hydrogen. Based on results verified by an independent testing laboratory this catalyst system produced a liquid product with approximately 96% in the diesel range. This could significantly reduce downstream processing in future plant designs if nanowire catalyst were used. The Second major benefit of nanowire catalyst is a much higher catalyst activity at lower reaction temperatures. Our most recent work has explored this capability and found that by operating at very low temperature and pressure, 30 C and 25 psig, we were able to produce a product almost devoid of light ends (sub C5) as determined by online chromatographic analysis. This is attributed to the favorability of producing light ends at higher temperatures. Utilizing traditional porous catalyst support technology, temperature control is one of the most difficult challenges and lack of tight control leads to both a broad distribution of products and deactivation through sintering. Our results thus far indicate that high activity at low temperatures may improve both conversion and reduce chain termination resulting from high catalyst particle temperature.

## Commercial Potential

Nanowire catalysts have the capability to replace many applications of traditional heterogeneous catalysts. Further research developments will enable Lousiana Tech to construct a facility capable of converting the nation's large domestic natural gas resources into liquid fuels in an economical and environmentally responsible manner which would result in a sizeable commercial potential. This is especially true for the case of production of liquid fuels from natural gas as petroleum is approximately three times the cost of natural gas on an equivalent energy basis. To this end, we must fully develop and synthesize nanowire catalysts and incorporate them into processes which deliver products that would be desired by the commercial marketplace. Additionally, our nanowire catalyst technology is being developed as a cathode catalyst for secondary lithium air batteries. Louisiana Tech will also soon begin to develop this technology as a catalyst for reforming of diesel to produce hydrogen for fuel cell use, and in automotive catalytic converter technology.

Without doing an exhaustive market analysis, it is obvious that the market for synthetic liquid fuels is large, in part, due to the fact that synthetic liquid fuels are very low sulfur and have the potential to upgrade high-sulfur fuels. These factors alone indicate that the market is sizable, and that there will be substantial pressure to produce and deliver our product.

## Public Purpose Served

This project supports the Department of Energy's overarching mission to advance the national, economic, and energy security of the United States by developing new catalyst systems that will enable utilization of domestic natural gas supplies to produce liquid motor fuels. This will reduce fuel costs, reduce greenhouse gas emissions, and stimulate economic growth while reducing the nation's dependence on foreign oil.

## 3. Biofuels from Algae: A Multidisciplinary Proposal

*Dr. Lynn Walker*, Professor, College of Applied and Natural Sciences
*Dr. James Palmer*, Professor, College of Engineering and Science
*Dr. Jon Pratt*, Professor, College of Business

**Project Objectives:**

1. Discovery and characterization of microbial lytic agents to improve harvesting efficiency for large-scale processing of biomass from algae and/or cyanobacteria.

2. Development of a model for a cost-effective process for isolation and concentration of lipids from aqueous cellular lysates of algae/cyanobacteria.

3. Estimation of technical and economic feasibility for using microbial agents to improve the efficiency of production, harvest, and processing of algal biomass.

**Narrative:**

The on-going research is directed to development of improved harvesting efficiency that is based on the use of microbial lytic agents to release cellular metabolites that can be used to make biodiesel and/or ethanol.

Algae/cyanobacteria have been proposed potential sources of biofuels. Many algae/cyanobacteria exhibit rapid growth rates, thus they are capable of producing large quantities of biomass. This biomass contains lipid-rich fractions that can be processed into biodiesel, as well as carbohydrates, proteins, and other nutrients that can be used for the production of ethanol. Current technology uses various chemical and mechanical extraction methods to disrupt the cells and release the cellular contents. These processes are relatively expensive and present some of the primary economic obstacles to commercial development of algae as biofuels. The multidisciplinary project includes faculty and students from the colleges of Business, Applied and Natural Sciences, and Engineering and Science.

Specific progress:

Selected algal/cyanobacterial species were isolated locally or purchased from culture collections. Included in this group were various species of *Chlorella*, *Ankistrodesmus*, *Botryococcus*, *Anabaena*, *Oscillatoria*, and *Spirulina*. These cultures were used as target hosts to isolate lytic and flocculating microbial agents.

*Lysobacter* sp., a naturally occurring bacterium that lyses several species of cyanobacteria, was used to develop a model for processing biomass of *Anabaena* sp. (Dr. James Palmer and Associates). This model was used to estimate harvesting efficiency and to develop a general working model to estimate technical and economic feasibility for processing biomass of other species (Dr. Jon Pratt and Associates).

Related research indicates that a naturally occurring fungus can be an effective flocculating agent for a number of algal/cyanobacterial species. In these studies, the fungus was effective for harvest of algal/cyanobacterial biomass from aqueous suspensions.

**Publications and Presentations:**

Presentation:
H. L. Walker. 2009. Carbon Sequestration with Algae. Louisiana Tech University Energy Systems Conference, November 5, 2009.

**Intellectual Property:**
Walker, H. L. Lysing Microorganisms for Biofuel Production. U.S. Patent Application: 12/269,496, filed November 12, 2008.

**Number of Students Supported:**
One student, U.S. Citizen
B.S. Degree, Environmental Science, May 2009

In addition, the research supported class projects in College of Engineering and Science and the College of Business.

**Public Purpose Served:**
The research contributed to the development of environmentally friendly technology for using algae and cyanobacteria as potential sources of renewable biofuels. The research contributed to development of improved methods for production and harvest of biomass through the use of naturally occurring microbial agents. These results assisted DOE in its strategic goals related to energy security, scientific discovery, and environmental responsibility.

## 4. Thermoelectric Nano-coolers for Cryogenic Tissue Cooling

*Despina Davis, PhD*, Assistant Professor of Chemical Engineering
*Mangilal Agarwal, PhD,* Research Engineer
*Mark DeCoster, PhD*, Assistant Professor of Biomedical Engineering
*June Feng, PhD,* Assistant Professor of Biomedical Engineering

### OBJECTIVE

Conventional cryogenic cooling using liquid $N_2$ is expensive to preserve cells and tissues hence, only simple living organisms are revived. Thermoelectric phenomenon involves conversion between electrical and thermal energies, which could be used in cryobiology to monitor and control temperature at cellular level. Thermoelectric (TE) materials can generate electricity from temperature difference and can act as cooling devices when a voltage drop is applied. $Bi_xTe_y$ is the most efficient thermoelectric material for room temperature operation [1]. Hence the thermoelectric cooler (TEC) was fabricated with $Bi_xTe_y$ nanowires to provide localized cooling and to improve the scope to study about systems like proteins, cells, tissues and organisms. This device could permit fine adjustment of cooling rate which is not presently available. The impact of such accurate cooling of biological materials would be realized in the minimization of cellular damage involved in cryopreservation to maintain sample viability and multipotentiality in long-term storage. It would enable scientists to accurately control temperature of individual cells and also represent a significant advance in our ability to study biological systems with carefully delineated temperature regimes.

## DESCRIPTION

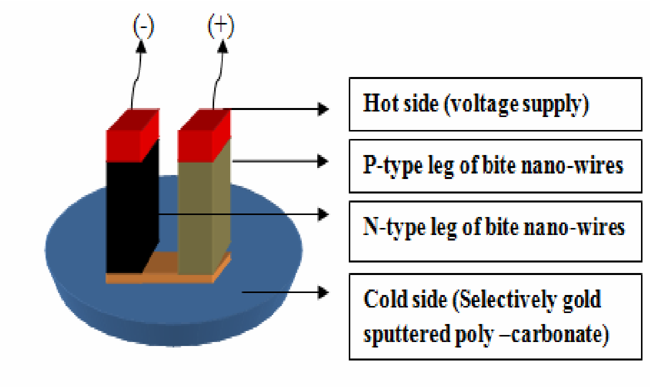

Figure 1 : An overall schematic of thermoelectric cooler.

Thermoelectric materials can generate temperature difference from electricity and vice versa. With the emergence of regenerative medicine, many researchers have turned to tissue for derived stem cells. As freshly collected tissue is not always readily available, it is important to have improved cryopreservation methods to reproducibly maintain cell viability and multipotentiality in long-term storage. The thermoelectric phenomenon provides a way to locally control temperature of individual living cells. Thermoelectric cooler can be fabricated by electrodepositing semiconductor elements like n & p type $Bi_xTe_y$ and connecting them thermally in parallel and electrically in series, as shown in Figure 1. The performance of these thermoelectric cooling materials is estimated based on a dimensionless figure of merit quantity ZT (ZT=$S^2\sigma T/\kappa$, where Z, T, $S$, $\sigma$, $\kappa$ are thermoelectric figure of merit, absolute temperature, Seebeck coefficient or thermoelectric power, electrical conductivity and thermal conductivity respectively). Temperature difference is created by the diffusion of electrons from n type (higher concentration) to p type (lower concentration). Nano structured materials when compared to thin films are alleged to have enhanced thermo electric properties like high Seebeck coefficient, smaller thermal & electrical resistance. In a reputable theoretical study Hicks and Dresselhaus [2] from MIT predicted a major increase in the figure of merit of nanostructured thermoelectric materials. For a nanowire of 0.5 nm diameter they estimated a figure of merit of 14, which would be 28 times larger than the bulk $Bi_2Te_3$ figure of merit of 0.5. Figure 2 shows the SEM images of nano wires of different dimensions on polycarbonate membrane. On the other hand research on cellular response of adult stem cells with freezing stress has been reported [2, 3, and 4], however, using micro thermoelectric cooler for cryobiology has not been investigated intensively. Devireddy *et al.* reported the feasibility of this type of device for local cooling of biological tissue using a Finite Element Analysis mathematical model [5].

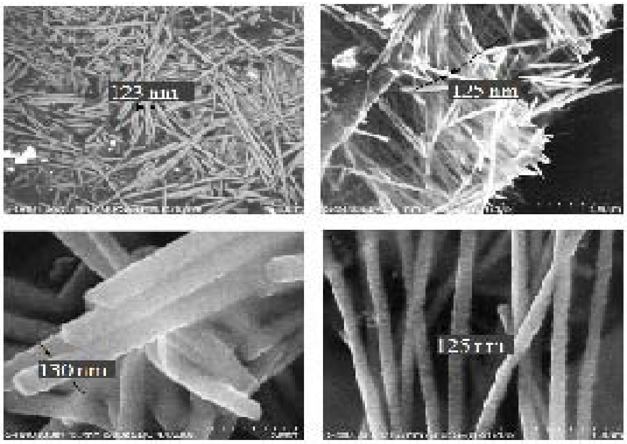

Figure 2: SEM images of nano wires in PC-membrane

## EXPERIMENTAL AND RESULTS

The thermoelectric device will have a TEC sandwiched between two PDMS (Poly di methyl siloxane) substrates with the bottom PDMS substrate having a photolithographically fabricated channel, to flow brain cells in a controlled geometry, as shown in Figure 3. The fabrication of TEC starts with selectively sputtering gold on the polycarbonate or alumina template to form a conductive layer for electrodeposition [6]. Electro deposition is carried out in an electrolyte consisting of SCE Reference Electrode, Pt Anode, and polycarbonate or alumina membrane in cathode as shown in Figure 4. Using mask made on silicon wafer by dry etching n and p-type $Bi_xTe_y$ nanowires were selectively deposited from electrolytes: the 20/20 containing 20 mM $Bi_2O_3$ and 20 mM $TeO_2$, 20/10 containing 20 mM $Bi_2O_3$ and 10 mM $TeO_2$ . The as deposited n and p-type $Bi_xTe_y$ nanowires were connected in series parallel arrangement by sputtering gold [7] as shown in Figure 5. Measurements show that n-type and p-type $Bi_xTe_y$ nanowires exhibit high Seebeck coefficients of -318.7 µV/K and 117 µV/K for depositions at -20 mV and -250 mV, respectively. Figure 6 shows the set up used for measuring seebeck coefficient, 7 and 8 shows the performance of Seebeck coefficient with respect to temperature at different potentials and electrolytes. More experimental results about cryopreservation of brain cells will be presented.

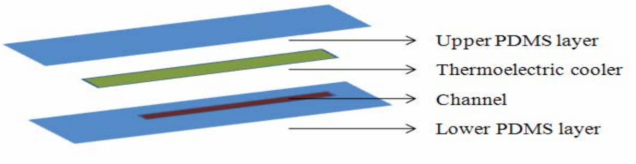

Figure 3 : An overall schematic of thermoelectric cooler.

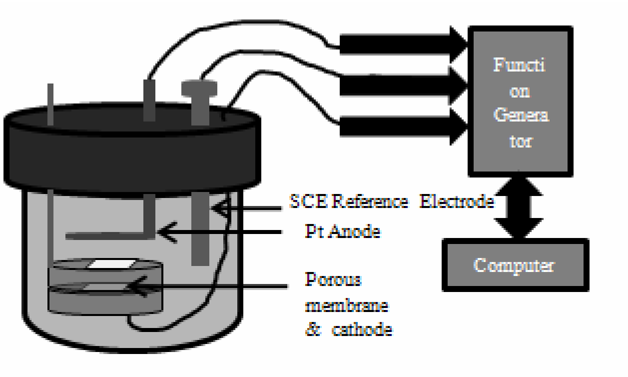

Figure 4: Experimental setup for electrodeposition

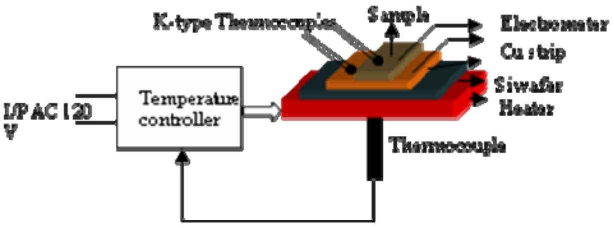

Figure 5: Seebeck measurement setup

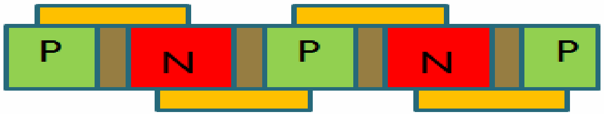

Figure 6: Schematic of N and P-type $Bi_xTe_y$ connected electrically in series and thermally in parallel

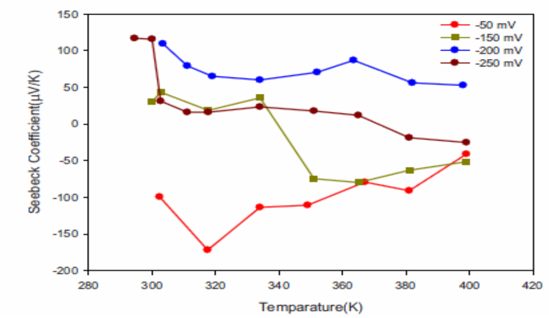

Figure 7: Seebeck coefficient as a function of temperature from 20/20 electrolyte.

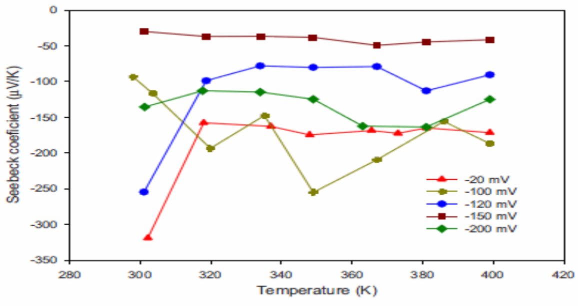

Figure 8: Seebeck coefficient as a function of temperature from 20/20 electrolyte $^2$.

## PUBLICATIONS AND PRESENTATIONS

- R. Mannam, M. Agarwal, A. Roy, V. Singh, K. Varahramyan, and D. Davis "Electrodeposition and Thermoelectric Characterization of Bismuth Telluride Nanowires" *Journal of the Electrochemical Society,* vol. 156, pp. B871-B875, 2009.
- R. Mannam, D. Davis, "Thermoelectric properties of BiTe/BiSbTe super lattice nanostructures" MRS conference- San Francisco, (April, 2010).
- K.Ananthathmakula, A.Kola, T.John, B.Mathew, M.DeCoster, H.Hegab, D.Davis, "Brain Cells Preservation by Thermoelectric Cooling" 217th ECS Meeting- Vancouver, Canada: Abstract# 796 (April 2010).
- R.Masvekar, J.McNamara, X.Du, A.Kunjumon, D.Green, S.Dua, D. Davis, & M. DeCoster. "Glial Cell Interfaces: Using Micro- and Nano-patterning for Brain Tumor Studies" American Soc. Cell Biology/ RIKEN joint meeting: "Building the Body Plan: How Cell Adhesion, Signaling, and Cytoskeletal Regulation Shape Morphogenesis.", Kyoto Japan, September 23, 2009.

## STUDENTS PARTICIPATING IN THE PROJECT

| STUDENTS | ADVISOR | DEGREES EARNED |
|---|---|---|
| Kalyan Chakravarthi Ananthathmakula | Dr. Despina Davis | Masters in Electrical Engineering |
| Avinash Kola | Dr. Despina Davis | Masters in Chemical Engineering |
| Raja Sekhar Mannam | Dr. Despina Davis | PhD in Electrical Engineering |
| Tom John | Dr. Hegab Hisham E | PhD in Micro/Nanosystems Eng |
| Bobby Mathew | Dr. Hegab Hisham E | PhD in Micro/Nanosystems Eng |
| Ramya Bellamkonda | Dr. Despina Davis | Masters in Electrical Engineering |
| Bryan Cox | Dr. Despina Davis | Masters in Electrical Engineering. |
| Chitra Jeyasankar | Dr. Mark DeCoster | Masters in Biomedical Engineering |
| Davis Richard | Dr. Mark DeCoster | Masters in Biology |

## NUMBER OF STUDENTS SUPPORTED

| STUDENTS | DEGREES EARNED |
|---|---|
| Kalyan Chakravarthi Ananthathmakula | Masters in Electrical Engineering |
| Ramya Bellamkonda | Masters in Electrical Engineering |
| Bryan Cox | Masters in Electrical Engineering. |
| Chitra Jeyasankar | Masters in Biomedical Engineering |
| Davis Richard | Masters in Biology |
| Prajon Shakya | Masters in Electrical Engineering |
| Silky Abbott | Masters in Chemical Engineering |
| Varsha Bhatia | Masters in Chemical Engineering |

## TIME LINE DISCUSSION

The below table explains the research done and future plan in different quarters

**Gantt chart**

| | Quarters | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Research tasks** | Summer 2009 | | | Fall 2009 | | | Winter 2010 | | | Spring 2010 | | |
| Literature search and ordering of materials | X | | | | | | | | | | | |
| Electro deposition & characterization of $Bi_xTe_y$ | | X | X | X | | | | | | | | |
| Fabrication of device using PDMS | | | | X | X | X | | | | | | |
| Designing mask & fabrication of thermoelectric cooler | | | | | | | X | X | X | X | | |
| Experimental & Analyzing results | | | | | | | | | | X | X | X |

## PUBLIC PURPOSE SERVED

This research project supported the Department of Energy's in the fields of science and technology, energy sources and efficiency, national security, safety and health. It developed rudiments for novel & enhanced energy technologies for alleviating the ecological impacts of alternative energy use. Projects of Department of energy in Louisiana Tech involve objectives of improving quality of life through innovations in science and technology. The research data and analysis provided by the project will be helpful for DOE to explore the amazingly diverse natural capabilities found in microbes and solve operation challenges in energy production and environmental cleanup.

## REFERENCES

1. B. Y. Yoo, C. K. Huang, J. R. Lim, J. Herman, M. A. Ryan, J. P. Fleurial, N.V. Myung, *Electrochimica Acta*. **50**, 4371 (2005).
2. L.D. Hicks and M.S. Dresselhaus, *Phys. Rev. B*, **47**, 12727 (1993).
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5. D. Rowe, in *CRC Handbook of Thermoelectronics*, CRC Press: London 1995.
6. D. M. Davis, D. Pinisetty, A. Prabhakar, M. Moldovan, D. P. Young, R. Devireddy, M. C. Murphy, E. J. Podlaha, *ECS Transactions*. **6**, 253 (2007).
7. W. Wang, F. Jia, Q. Huang, J. Zhang, *Microelectronic Engineering*. **77**, 223 (2009).

## 5. A piezoelectric photovoltaic micropower generation (PPVMG) chip

*Long Que*, *PhD*, Assistant Professor of Electrical Engineering (PI)
*Chad O'Neal, PhD*, Assistant Professor of Mechanical Engineering (co-PI)

**Project Objectives:** A novel piezoelectric photovoltaic micropower generation (PPVMG) chip is proposed and developed to harvest solar (light) energy. This chip is based on the bending of the carbon nanotube thin film upon illumination of light to deform the piezoelectric plate (PZT), therefore electric potential across the PZT will be generated. We anticipate that the PPVMG chip can have significant impact on the self-operation of microsensors, microsystem and nanosystems and VLSI circuits, and can dramatically change the power supply of wireless sensors for pervasive networks as well.

**Narrative:** The PPVMG chip is a microelectromechical system (MEMS) based device designed to harvest solar energy (Fig. 1). It can generate a high open circuit voltage suitable for voltage rectification and for powering low power VLSI circuits. We envision that several arrayed PPVMG devices could generate power on the order of 10 μW within an area of approximately 1 $mm^2$. It can be used for the operation of the low power VLSI circuits. It is particularly suitable and attractive for the operation of the wireless microsensors. Typically, digital VLSI technology requires an "on" voltage of approximately 3V or more. In order to accomplish such a high voltage, the piezoelectric energy harvesting method is most useful among all exiting methods, especially with the $d_{33}$ piezoelectric mode. The PPVMG chip can fulfill this kind of requirement.

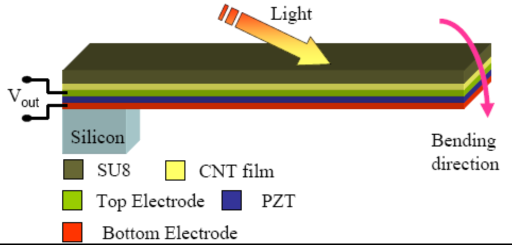


Fig. 1 Sketch of a $d_{31}$ mode-PPVMG chip

The basic principle of the PPVMG chip is based on the optical actuation of carbon nanotubes film (CNF). CNF responds to the light and will bend accordingly. As shown in Fig. 1, when the light illuminates on a piezoelectric (PZT)-cantilever coated with CNF, the cantilever bends, thereby deforming the PZT layer, resulting in the generation of electrical power. This approach might improve the conversion efficiency of current silver-based photovoltaic technology dramatically.

**Publications and presentations resulting from the project:**

1. Z. Gong, V. Kotipalli, C. O'Neal, L. Que, "A piezoelectric photovoltaic micropower generation (PPVMG) chip", Invited presentation at *Lockheed Martin Special Symposium, NSTI-Nanotech 2009*, Houston, TX, 2009
2. V. Kotipalli, Z. Gong, and L. Que, “A multiple energies harvester enabled by carbon nanotube films,” submitted to *Hilton Head Workshop 2010: A Solid-State Sensors, Actuators and Microsystems Workshop*
3. Joshua Ypya, V. Kotipalli, T. Zhang, Z. Gong and L. Que, “Thermal and optical characterization of carbon nanotube films,” submitted to *Materials Science & Technology 2010 Conference & Exhibition, Houston, TX*
4. Several ***Journal*** papers will be submitted based on this project in the following months

**Intellectual property resulting from the project:**

One patent application, entitled “A MEMS multiple-energy harvester chip”, is *in progress*

**Number of students supported:**

Four students have been supported partly by this funding, including two undergraduate students (Mr. Joshua Ypya and Mr. James Haywood) to do research in PI’s lab, who are US citizens. Mr. Joshua Ypya will continue to do research related to this topic this summer at PI’s lab and will be funded partly by DOD and NSF grants.

**Degrees earned by students participating in the project:**

One student (Mr. Venu Kotipalli) will earn a Master’s degree based on this project this Summer. Two additional students are working on the *continuation and expanded topics* of this proposed project and will earn Master’s degrees or Ph. D. degrees.

**Public Purpose Served:**

The proposed research project will support the Department of Energy's overarching mission to advance the national, economic, and energy security of the United States; and to promote scientific and technological innovation in support of that mission; In particular, this project will assist DOE in its strategic goals of providing Energy Security and promoting America's energy security through reliable, clean, and affordable energy.

# 6. Thermoelectric DNA Sequencer

*Eric Guilbeau, PhD*, Professor of Biomedical Engineering

## PROJECT OBJECTIVES

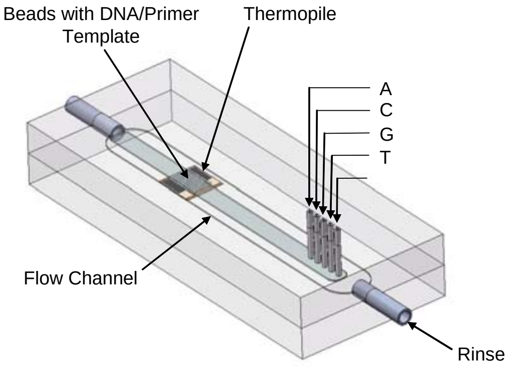
The research we proposed to accomplish in this project sought to answer the **question**, “Is it possible to sequence DNA by measuring the heat that is released when DNA polymerase inserts a deoxyribonucleoside triphosphate into a growing DNA strand?” **The long-term goal** of the research is to develop a rapid, simple-to-use, accurate, and relatively inexpensive thermoelectric method for sequencing DNA to allow DNA detection for personalized medicine in outpatient lab settings. **The specific hypothesis** *was that thin-film thermopiles have the sensitivity, dynamic response and common mode thermal signal rejection capability needed to measure the heat generated when DNA polymerase correctly inserts a deoxyribonucleoside triphosphate into DNA.* DOE funds were to be used to allow us to design and fabricate the thermoelectric DNA sequencing system (Specific Aim 1) and to allow us to obtain preliminary data that would be used in proposals seeking additional funding that would allow us to sequence single-strand DNA using the thermoelectric method (Specific Aim 2).

## NARRATIVE SUMMARY

Major accomplishments made with DOE funds include the following:

1. Conceptual design of a micro-fluidic, DNA sequencing device
2. Development of a mathematical simulation of the conceptual design that was used to optimize sequencing device performance
3. Fabrication of a prototype microfluidic sequencing device
4. Successful use of the prototype device to experimentally measure the heat of incorporation of a dCTP into template DNA.

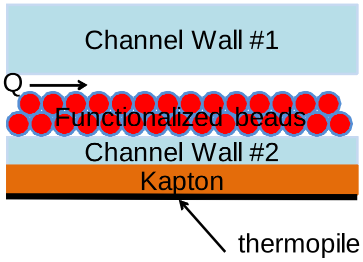
### Conceptual Device Design

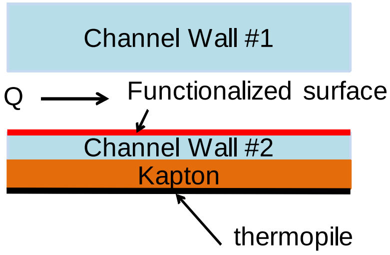


The figure to the right shows the conceptual device design. In the device, single-strand DNA of unknown sequence hybridized to an appropriate complimentary primer serves as a template for the production of a complementary nucleic acid polymer by a polymerase enzyme. The DNA template/primer is attached to a support (e.g. microfluidic device channel wall or to paramagnetic beads) to form a DNA template/primer/support complex. This complex is exposed to a laminar flow stream containing buffer, DNA polymerase, pyrophosphatase, and one of the four deoxyribonucleoside triphosphates (dATP, dCTP, dGTP , and dTTP). If the nucleoside is complementary to the next base in the DNA template, polymerization occurs lengthening the complementary polymer and releasing thermal energy. In homopolymeric regions (e.g. A,A,A,…), the amount of thermal energy released (–9.8 to –16.0 kcal/mol/base pair is proportional to the number of nucleotides incorporated. The released thermal energy increases the temperature of the DNA template/primer/support complex causing a transfer of thermal energy from the complex to the fluid flowing over the complex. A thin-film thermopile detects the temperature difference between the portion of the laminar flow stream that is in close proximity or in contact with the DNA template/primer/support complex and the portion of the laminar flow stream that is not in close proximity or in contact with the double-strand DNA template/primer/support complex. If the introduced dNTP is not complimentary to the next unpaired base, no change in temperature (emf) is measured. The nucleotide that was added to the complementary strand of the template/primer hybrid is identified by correlating the thermopile emf change (detected temperature difference) with the nucleotide that was introduced into the laminar flow stream. Once the incorporated nucleotide is known, its complementary nucleotide in the single strand template DNA molecule being sequenced is identified. By repeatedly introducing dNTPs sequentially, the entire unknown sequence of the DNA molecule (template) is determined. The amount of heat produced following the incorporation of a nucleotide may be amplified by including pyrophosphatase to hydrolyze the released pyrophosphate. The additional heat release is between -8.38 kcal/mol and -12.2 kJ/mol.

### Mathematical Simulation Results

Both a reaction zone that contains DNA template/primer complex immobilized to the surface of beads (Model #1), and a reaction zone of DNA template/primer complex immobilized to the surface of channel wall #2 (Model #2) were simulated as shown in the figures below.





Assumptions included, plug flow reactor, negligible axial conduction or diffusion, constant mass flow and physical properties, adiabatic operation, either pseudohomogenous reaction (beads Model #1) or homogeneous reaction (Model #2), the Dahlberg kinetic mechanism for DNA polymerase (KF polymerase), and the Baykov kinetic mechanism for pyrophosphate hydrolysis.

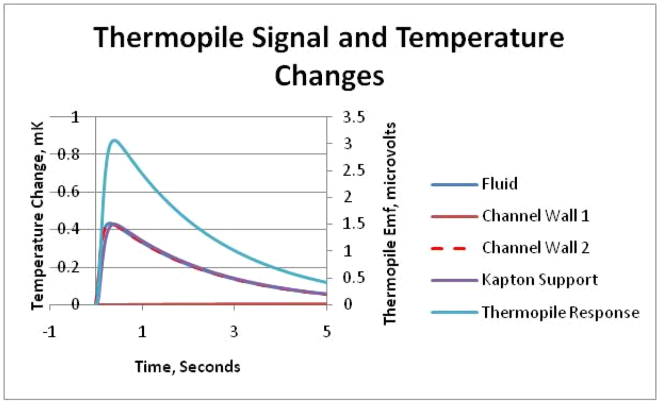
| **Model Parameter** | **Model # 1 Bead Reaction Zone** | **Model #2, Channel Wall Reaction Zone** |
|---|---|---|
| *Channel Wall 1 Material* | *Polycarbonate* | *Polycarbonate* |
| *Channel Wall 2 Material* | *Glass Coverslip* | *Streptavidin Coated Glass Coverslip (XENOPORE)* |
| *Thermopile Support Material* | *Polyimide (Kapton)* | *Polyimide (Kapton)* |
| *Channel Wall 1 thickness* | *0.5 inch* | *0.5 inch* |
| *Channel Wall 2 thickness* | *125 micron* | *125 micron* |
| *Thermopile Support thickness* | *75 micron* | *75 micron* |
| *Number of Thermopiles* | *1* | *1* |
| *Volume Rate of Flow* | *100 µL/min* | *100 µL/min* |
| *Channel Width* | *12 mm* | *12 mm* |
| *Channel Length* | *60 mm* | *60 mm* |
| *Channel Height* | *25 µm* | *25 µm* |
| *Functionalized Channel Width* | *4 mm* | *4 mm* |
| *Functionalized Channel Length* | *4 mm* | *4 mm* |
| *Channel Wall 2 DNA Reaction Site Density* | - | *1.1 x $10^{11}$ sites/$\text{mm}^2$* |
| *Beads* | *M-280 Dyna Beads (Invitrogen,)* | *None* |
| *Bead Diameter* | *2.8 µm* | - |
| *Bead DNA Reaction Site Density* | *200 pmol/mg* | - |
| *Number of Beads* | *1.288 x $10^7$* | - |
| *Bead Packing Density* | *0.74* | - |
| *Molecules of DNA* | *41.44 pmol* | *11.7 pmol* |
| *Concentration of DNA* | *104 pmol/µL* | *29.2 pmol/µL* |
| *Inlet Polymerase Concentration* | *114 pmol/µL* | *32.2 pmol/µL* |
| *Inlet dNTP Concentrations* | *114 pmol/µL* | *32.2 pmol/µL* |
| *Inlet Pyrophosphatase Concentration* | *60 µM* | *60 µM* |
| *Inlet pyrophosphate Concentration* | *0 µM* | *0 µM* |
| *Inlet Phosphate Concentration* | *0 µM* | *0 µM* |
| *Inlet phosphate reaction intermediate concentrations* | *0 µM* | *0 µM* |

The models predict the dynamic concentration change for each of the 17 reactants, reaction intermediates, and products in the KF polymerase reaction and the hydrolysis of pyrophosphate, and the dynamic temperature change of the fluid in the reaction zone, the two walls of the microfluidic channel, and the Kapton® thermopile support film in contact with the thermopile. The models were solved using Mathcad's® Radau numerical integration method for stiff systems. The thermopile response was computed by multiplying the theoretical thermopile sensitivity and the wall temperature change, assuming a 60 junction antimony/bismuth thermopile with a theoretical sensitivity of 7.14 µV $\text{mK}^{-1}$.

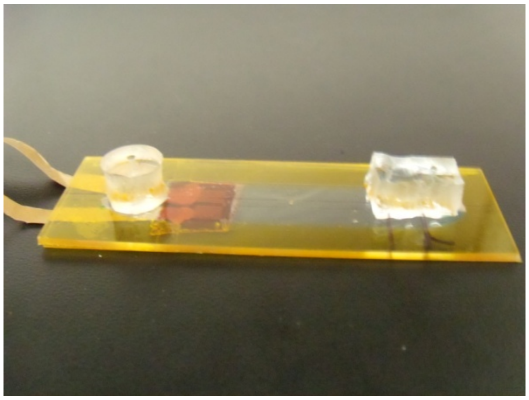
**Table 1. Kinetic Constants**

| ***Klenow Polymerase*** | | ***Pyrophosphatase*** | |
|---|---|---|---|
| *Constant* | *Value* | *Constant* | *Value* |
| $k_1^{DNA}$ | 1.2 x $10^7$ $M^{-1}$ $s^{-1}$ | $k_1$ | 3.8 x $10^8$ $M^{-1}$ $s^{-1}$ |
| $k_{-1}^{DNA}$ | 0.06 $s^{-1}$ | $k_2$ | 4100 $s^{-1}$ |
| $k_1^{DNTP}$ | 1 x $10^7$ $M^{-1}$ $s^{-1}$ | $k_A$ | 2200 $s^{-1}$ |
| $k_{-1}^{DNTP}$ | 50 $s^{-1}$ | $k_B$ | 34 $s^{-1}$ |
| $K_3$ | 50 $s^{-1}$ | $k_3$ | 1400 $s^{-1}$ |
| $k_{-3}$ | 3 $s^{-1}$ | $k_4$ | 350 $s^{-1}$ |
| $k_4$ | 150 $s^{-1}$ | $k_5$ | 800 $s^{-1}$ |
| $k_{-4}$ | 37.5 $s^{-1}$ | $k_6$ | 3 x $10^5$ $M^{-1}$ $s^{-1}$ |
| $k_{-5}$ | 15 $s^{-1}$ | $k_7$ | 3300 $s^{-1}$ |
| $k_5$ | 15 $s^{-1}$ | | |
| $K_{PPi}$ | 1150 $s^{-1}$ | | |
| $k_{-PPi}$ | 5 x $10^6$ $M^{-1}$ $s^{-1}$ | | |

The simulation predicted that the temperature difference detected by the thermopile (Kapton® temperature below the DNA reaction zone – Kapton® temperature below the rinse solution) depends on the geometry of the microfluidic device, the physical properties of the device, the rate of flow through the device, the concentration of reactants and enzymes, and the kinetics and thermodynamics of DNA polymerization and pyrophosphate hydrolysis. Using the parameters included in the tables above, Model #1 and Model #2 predict thermopile support temperature increases of 0.4 m°C and 0.11 m°C following base insertion resulting in a maximum thermopile voltage change of 2.8 µV and 0.81 µV, respectively. The maximum thermopile output signal is reached in 0.35 seconds and 0.34 seconds, respectively and returns to baseline after 5 seconds as shown in the figure to the left.

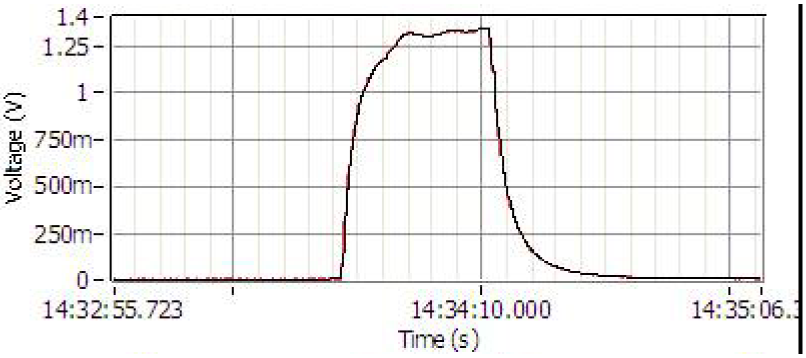


### Fabrication of Prototype Sequencing Device



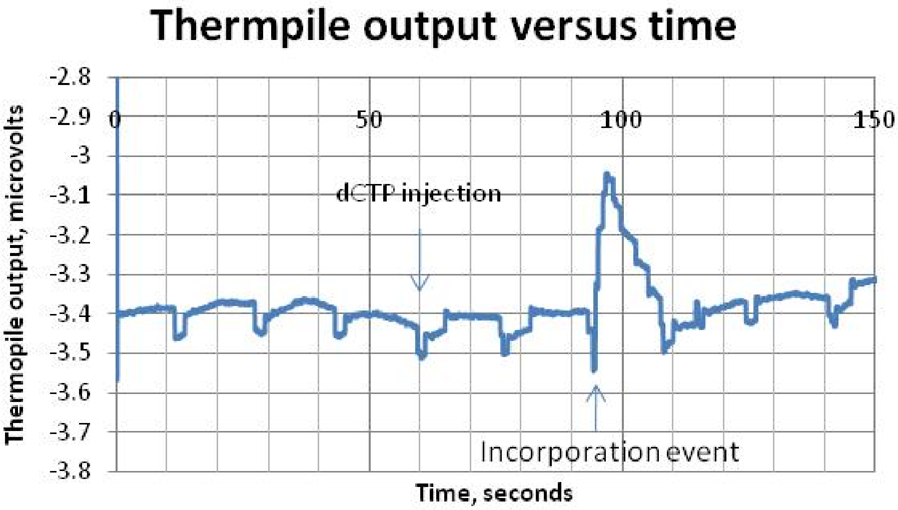
We constructed a prototype microfluidic device as shown in the figure on the right consisting of a single, straight, laminar flow channel with two inlets and one outlet. A thin-film thermopile antimony/bismuth thermopile with 60 junctions was integrated within the microfluidic device, in proximity to a reaction zone containing immobilized single-strand DNA template/primer complex. The devices was fabricated using a polymer/glass laminating technique. The DNA template was immobilized directly onto the glass surface using standard biotin-streptavidin chemistry. The figure below shows a typical prototype device. The immobilzed DNA template included the following oligonucleotide and primer. Oligonucleotide Sequence:
*TTAACCGGTACGAACGCCTGGTATCTTTATAGTCCATC*
Primer Sequence: 3-TTGCGGACCATAGAAATATCAGG-5’-biotin

The figure to the below shows the rapid response of the thermopile to a burst of laser light incident upon the measuring junctions but not the reference junctions.



### Experimental measurement of heat of dCTP incorporation

Following prototype fabrication, buffer was introduced into one of the inlets until a steady baseline thermopile output signal was obtained. A mixture of buffer, dCTP, and Klenow polymerase was then allowed to flow into the second inlet. Stealth flow of the second stream restricted the flow of the dCTPs to the center of the flow channel over which DNA template was immobilized and over the measuring junctions of the thermopile but not over the reference thermopile junctions. dCTPs were incorporated into the DNA template as predicted and the measuring junctions of the thermopile registered the small change in temperature resulting from the heat of the incorporation reaction as shown in the following figure.



The incorporation event caused a thermopile output change of approximate 0.35 microvolts, slightly less than the 0.81 microvolts predicted by the mathematical model. It is important to note, however, that the mathematical simulation included the additional heat associated with the conversion of pyrophosphate to inorganic phosphate which does not occur in the experiment because pyrophosphatase was not included in the dCTP mixture. The duration of the response was approximately, 14 second, a longer time period than the five seconds period predicted by the mathematical simulation. This is likely because the mathematical model assumed a flow rate of 100 microliters/minute compared to the 50 microliter/minute flow rate used in the experiment. The shape of the incorporation event corresponds closely to that predicted by the mathematical simulation.

We believe these results prove our hypothesis that *thin-film thermopiles have the sensitivity, dynamic response and common mode thermal signal rejection capability needed to measure the heat generated when DNA polymerase correctly inserts a deoxyribonucleoside triphosphate into DNA.*

We are now performing experiments to replicate these results and to optimize the performance of the sequencing device.

**Publications and presentations resulting from the project**

***Poster Presentations:***

"Feasibility of Thermoelectric DNA Sequencing", Eric J. Guilbeau, Presented at the 2009 Annual Fall Meeting of the BMES, Pittsburgh, PA, October 7-10, 2009.

***Abstracts:***

Guilbeau, E. J., "Feasibility of Thermoelectric DNA Sequencing", Abstract, 2009 Annual Fall Meeting of the BMES, Pittsburgh, PA, October 7-10, 2009.

***Referred Journal Papers:***

Guilbeau, E.J., "Thermoelectric Method for DNA Sequencing: A Mathematical Feasibility Study." J. Mol. Cell. Bioengr. (Status: rejected but being revised for re-submission).

Guilbeau, E.J. and Nestorova, G., "Thermoelectric measurement of nucleotide incorporation without control of ambient temperature." Sensors and Actuators (in preparation).

Guilbeau, E.J. and Nestorova, G., Experimental Demonstration of the Feasibility of Thermoelectric DNA sequencing." J. Mol. and Cell Bioengr. (planned for the future)

### Number of Students supported on the Project

Women = 1
US Citizens: 0
Permanent Residents = 0
Under-represented minorities = 0
Foreign students = 3
Total students supported = 4

### Degrees earned by students participating on the project

None to date

### Public Service Served

This research project assisted the DOE in its strategic goal of providing scientific discovery and innovation that will strengthen U.S. scientific discovery, economic competitiveness and improve the quality of life through innovations in science and technology. More specifically, scientists can now identify the genetic mechanisms of different diseases and future DNA sequence analysis will lead to new cures that arise from a better understanding of how genetic variation leads to disease. Translating genomic information into human health benefits through personalized medicine will require future de novo sequencing and re-sequencing of known genomes in search of the sequence variations that cause disease or affect the effectiveness of treatment for disease. New sequencing methods like the one proposed in this project are needed because existing DNA sequencing methods often provide more information than is needed for some applications, suffer from limited read length, have inadequate accuracy, or they are too expensive for widespread use.

## 7. Energy sustainability through novel organic solar cells

*Sandra Zivanovic, PhD*, Associate Professor of Electrical Engineering

### Project Objectives:

- Synthesis and characterization of the novel organic nanostructured aromatic diimides (nanobelts self-assembled from 3,4,9,10 –perylene tetracarboxylicacid diimide (PTCDI) or naphthalenetetracarboxylicacid diimide (NPDI) without side chains)
- Investigation of their potential applications for photovoltaic cells

### Narrative:

**Synthesis and characterization of the novel organic nanostructured aromatic diimides**

Perylene bisimide or 3,4,9,10 - perylene tetracarboxylicacid diimide (PTCDI) is a violet-colored dye. The chemical structure of the PTCDI and naphthalene diimide (NPDI) molecule is given in Figure 1.

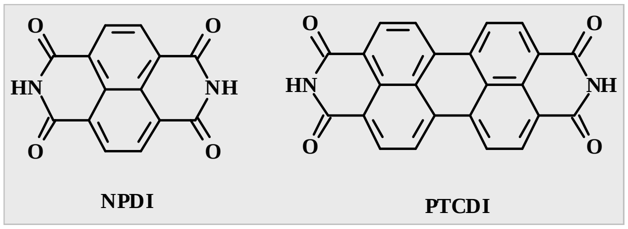


Figure1. NPDI and PTCDI chemical structure.

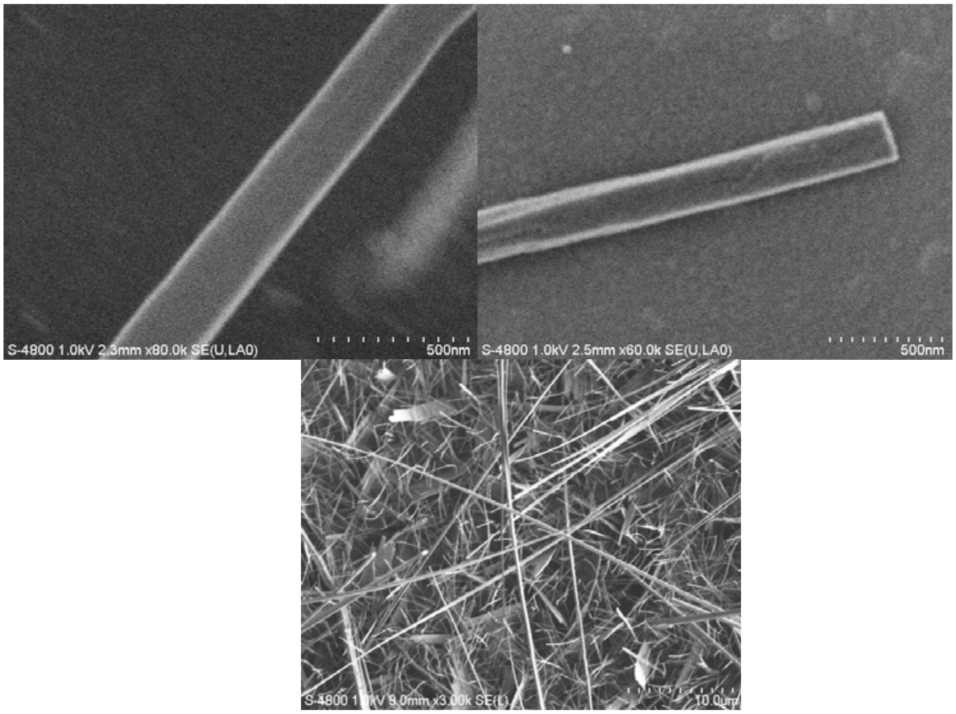


Figure 2. The SEM pictures of self-assembled PTCDI and NPDI nanowires.

The PTCDI and the NPDI have very low stability in most solvents. We obtained micrometer-long nanobelts and nanowire structures from evaporation of PTCDI and NPDI. The nanostructures are pictured under scanning electron microscope (SEM) and are shown in Figure 2. This is a new strategy to assemble organic molecules into nanostructures, is especially valuable for those having very low solubility in solvents. In our experiments, the samples were placed in a quartz tube and heated in a bench-top furnace. The 5 mg of PTCDI or NPDI power was placed in a quartz tube. The powder was heated in a vacuum or $N_2$ to 500°C for one hour. The tube was allowed to cool to room temperature. The PTCDI or NPDI vapors self-assembled on a glass substrate inside of the tube as they cooled down (Figure 2).

We electrically tested and theoretically modeled the single PTCDI nanobelt between two metal contacts. Fig 3 shows the experimental results and equivalent circuit for mathematical simulation.

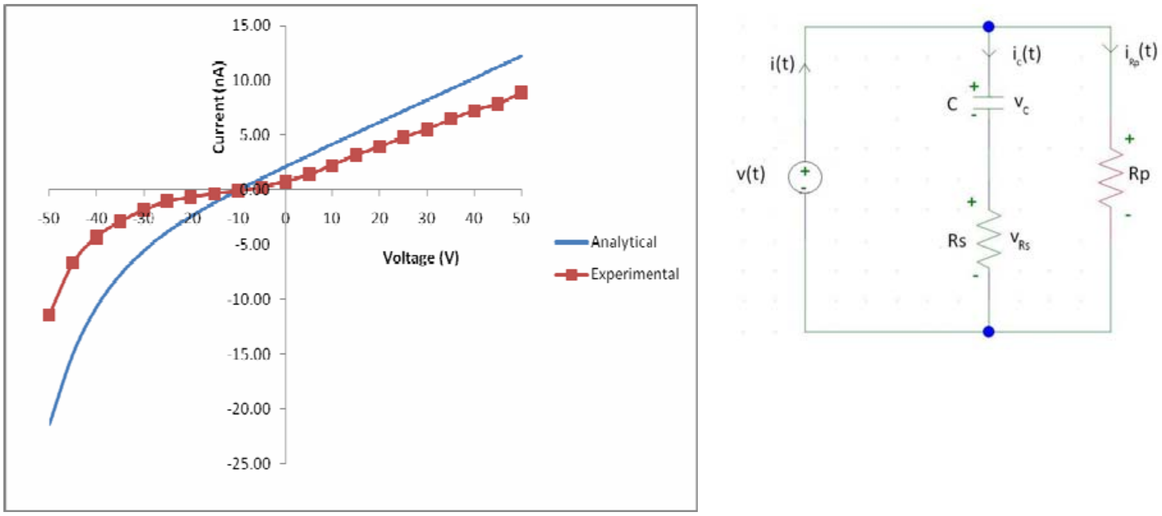


Figure 3. (a) Comparison between the I-V curve obtained analytically (by simulating the equivalent electrical circuit) and the I-V curve obtained experimentally. (b) Equivalent electrical circuit used to model the I-V curve of PTCDI nanowire.

The final equation of the model is:

$$i_c(t) = \left(\frac{-50}{R_s} - 7.4\right) e^{-\frac{(v+50)}{7.4\,pF}} + 2.24 \times 10^{-18}. \qquad (3.10)$$

### Investigation of their potential applications for photovoltaic cells

We investigated the possibility of doping sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate] (PTEBS) with the PTCDI nanobelts through ultraviolet photoelectron spectroscopy (UPS) measurements. For our experiment, PTEBS was tuned to absorb maximum light in the range of 450nm to 550nm which corresponds to the maximum solar irradiance of the Earth's atmosphere. Nanobelts of PTCDI were synthesized by gas phase self assembly process. Doping PTEBS with PTCDI or NPDI nanobelts/nanowires causes a shift in the Fermi level of the composite material with respect to the vacuum level as observed in the photoemission spectrum (see Fig. 4). The peaks corresponding to the sigma bonds shift towards the vacuum level with higher concentrations of the dopant. With increased PTCDI doping, PTCDI does not act much like an electron donor, but more like an electron acceptor. Since UPS data confirms that PTCDI nanobelts dope the PTEBS, this composite might be a promising material for optoelectronic application.

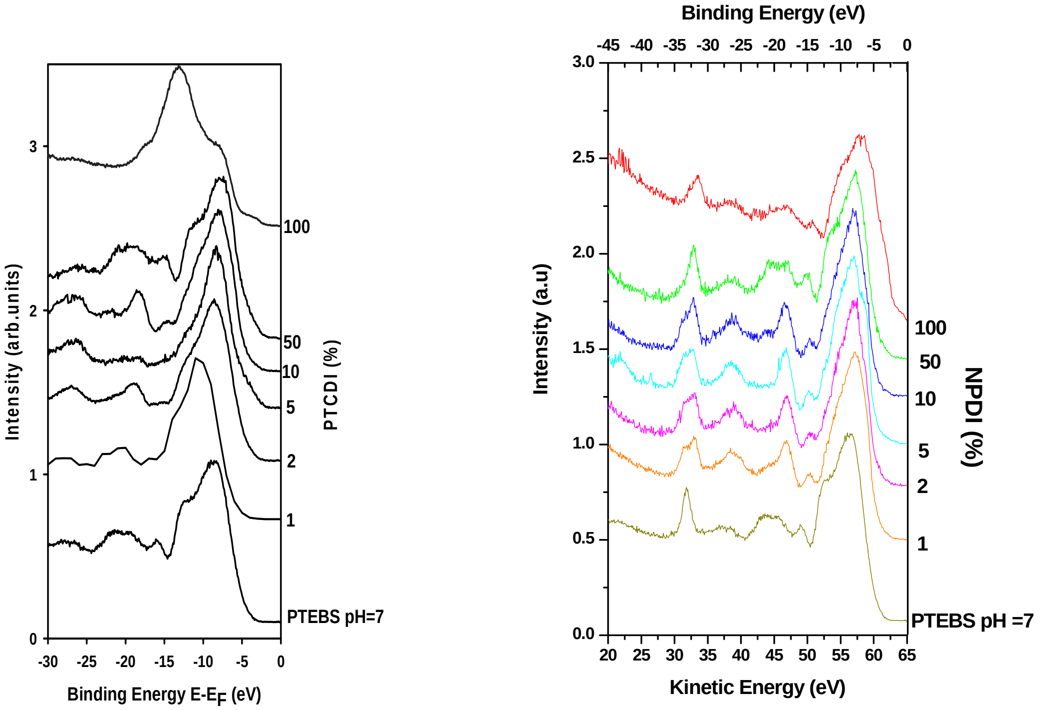


Figure 4. Photo emission spectra of PTEBS compared with increasing concentration of PTCDI dopant and NPDI dopant, respectively.

The UV-Vis spectra of the PTEBS and the PTCDI nanowires dropcasted on quartz are shown in Figure 5. It is indicative that PTEBS polymer acts as a semiconductor with the energy bandgap while the PTCDI nanobelts do not show distinct semiconductor nature and energy bandgap since they absorb light over a broad range of wavelength without distinct peak characteristic for semiconductor materials. The nanobelts show more conductor nature.

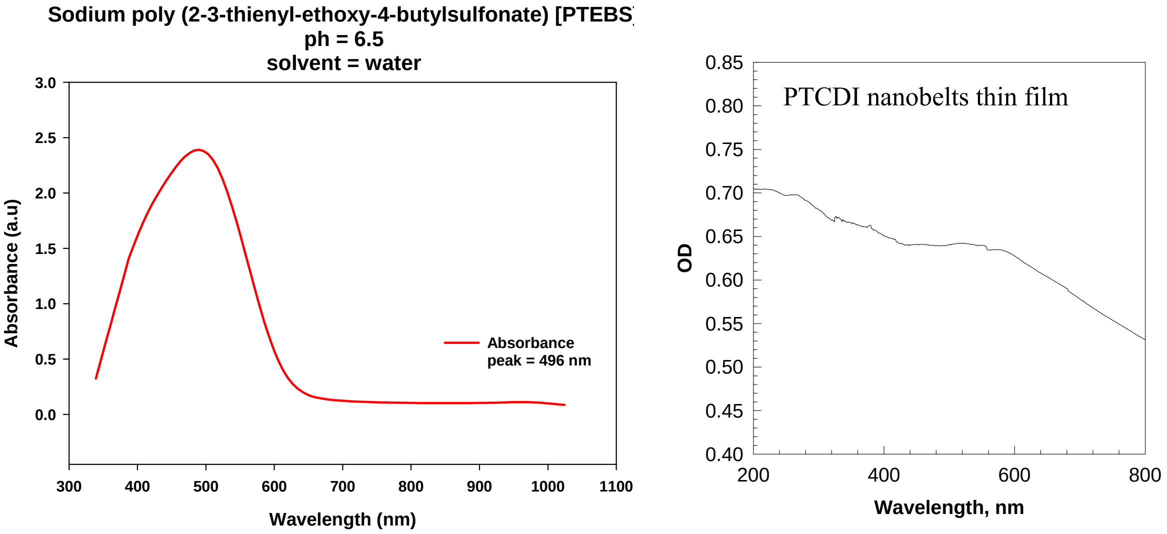


Figure 5. Optical density of the PTEBS and the PTCDI nanobelts thin film.

Photovoltaic capabilities of the PTEBS doped with the PTCDI nanobelts are investigated. Figure 6 shows I-V characteristic of a ITO/PEDOT:PSS/PTEBS-PTCDI blend/Al diode in dark and under light. Although the PTCDI nanobelts increase the reverse current for negative bias voltages, the nanobelts did not improve the solar cell characteristics as we hoped to see. One of the reasons is that diffusion length in polymers is ~20nm while the nanobelts have only one lateral dimension in that range. The other dimension is more about 300-500nm , which is large for the PTCDI nanobelts to serve as centers for exciton separation into a free charge carriers ( electron and hole).

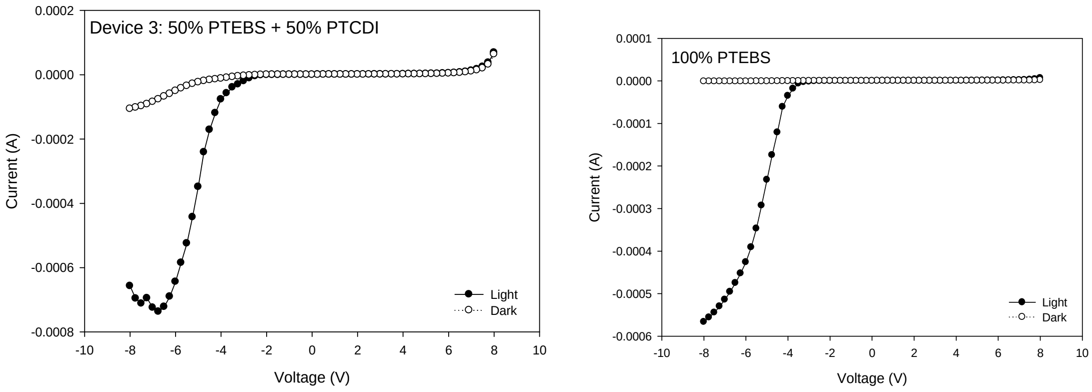


Figure 6. Current-voltage characteristic for reverse and forward bias in dark and under light. Doping with the PTCDI increases the reverse current.

## PTCDI nanobelts fro chemical sensing application

Volatile organic compounds have a charge transfer interaction with electron accepting compounds. This phenomenon can cause changes in conductivity within the organic compound giving rise to its potential application in sensors. A better surface to volume ratio gives increase in performance in sensors showing that PTCDI nanobelts would be more beneficial than PTCDI thin film. PTCDI forms nanowires and nanobelts by self-assembly process. The possible use of PTCDI nanobelts in chemical sensors is investigated based on the conductivity change in the nanobelts due to the interaction with different compounds. As the degree of conductivity change varies with each compound, these nanobelts could be used for selective detection of a particular compound.

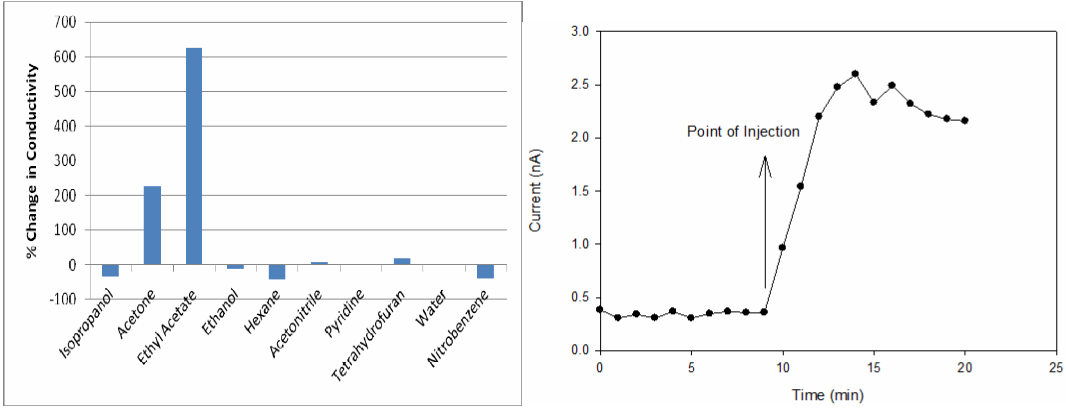


Figure 7. (a) The percent change in conductivity of PTCDI nanobelts upon exposure to individual chemical. (b) Electrical current change obtained for the exposure to ethyl acetate. A drastic increase of 625% in current was observed after exposure and was found to stabilize after some time.

The self-assembly process results in formation of a thin film of PTCDI over the glass substrate. This PTCDI nanobelt film is attached to two probes of Keithley instrument. Voltage is passed through this film of nanobelts and current is monitored. It is ensured that a stable current is obtained from the film before it is exposed to any chemical. The environment is then saturated with a particular chemical and current is monitored at regular time intervals.

**Conclusion:** We synthesized the novel nanobelts and nanowires from the PTCDI and without side chains and thoroughly investigated its electrical and optical properties. Although we did not see significant benefit of the PTCDI nanobelts to dope the polymer of the active layer of the solar cell, we discovered some other interesting properties of this novel material. The PTCDI nanobelts without side chains are new organic conductive nanostructures and have potential for chemical sensing.

## Publications and presentations resulting from the project:

### Conference Presentations and Peer Reviewed Conference Proceedings:

1. Zivanovic Selmic, S. R., Koorie, M., Pinto, L., Materials Research Society (MRS) Fall 2009 Meeting, "Ultraraviolet photoelectron spectroscopy of pure sodium poly[2-(3-thienyl)-ethoxy-4-butylsulfonate] (PTEBS) and doped with perylene tetracarboxylicdiimide (PTCDI) nanobelts," MRS, Boston. (November 30, 2009). Manuscript for Conference Proceedings is submitted and is currently under review.
2. Leon Rohan Pinto, Jovana Petrovic, Petar Matavulj, David Keith Chambers, and Sandra Zivanovic Selmic, "Photovoltaic device based poly(2-methoxy-5-(2,9-ethyl-hexyloxy)-1,4-phenylene vinylene) polymer," American Solar Energy Society (ASES) National Solar Conference "Solar 2009", Buffalo, NY, May 11-16, 2009. Status: Extended abstract accepted for conference poster presentation; Manuscript for the conference proceeding is in preparation and is due March 6, 2009.
3. Sandra Zivanovic Selmic, Leon Rohan Pinto, Jovana Petrovic, Petar Matavulj, David Keith Chambers, Difei Qi , "Experimental and Theoretical Investigation of Photosensitive ITO/PEDOT:PSS/MEH-PPV/Al Detector," in *Active Polymers*, edited by A. Lendlein, V. Prasad Shastri, K. Gall (Mater. Res. Soc. Symp. Proc. Volume 1190**,** Warrendale, PA, 2009), 1190-NN11-01, pp. 1-6.

### Peer Reviewed Journal Paper:

1. Mark A. Koorie, Yashdeep Khopkar, Leon Rohan Pinto, Haifeng Ji, Sandra Zivanovic Selmic, " Electrical and optical characteristics of conducting PTCDI nanobelts". Status: Preparation of manuscript for journal submission is in preparation. Manuscript will be submitted during spring quarter.
2. Joseph P. Cannon, Steven D. Bearden, Fauzia M. Khatkhatay, Joseph Cook, Sandra Zivanovic Selmic, Scott A. Gold, " Confinement-induced enhancement of hole mobility in MEH-PPV," *Synthetic Metals*, vol. 159, no. 17-18, pp. 1786-1791, September 2009.
3. David Keith Chambers, Brijesh Raut, Difei Qi, Chad B. O'Neal and Sandra Zivanovic Selmic,"The effect of helium plasma etching on polymer-based optoelectronic devices ," *Thin Solid Films,* vol. 517, pp. 5743-5746, May 29, 2009.
4. Petrovic, J., Zivanovic Selmic, S. R., Matavulj, P., Pinto, L. (2009). Field Induced Singlet Exciton Dissociation and Exciton-Exciton Annihilation in MEH-PPV Films Studied by

Photocurrent Spectra. *Acta Physica Polonica A, 116*(4), 595-597.
http://przyrbwn.icm.edu.pl/APP/PDF/116/a116z445.pdf

**Number of graduate students supported**: 5 (Mark Koorie, Leon Pinto, Yashdeep Khopkar, Anil Thapa, and Swetha Chopperla)
1 US citizen, 4 international students
1 woman(international), 4 men

**Degrees earned by students participating in the project**:
Two MS degrees earned (Leon Pinto “Conjugated polymer based photodetectors and photovoltaics: an experimental investigation and ultraviolet photoelectron spectroscopy” and Yashdeep Khopkar “Characterization and application of perylene tetra carboxylic diimide nanobelts synthesized by gas phase self assembly”)

**Public Purpose Served**
This research project supported the Department of Energy's mission to advance the national, economic, and energy security of the United States; and to promote scientific and technological innovation. In particular, this project at Louisiana Tech assisted the DOE in its strategic goals of promoting America’s energy security through reliable, clean, and affordable energy, and scientific discovery and innovation and improving quality of life through innovations in science and technology.

## 8. Template Wetting of $NaAlH_4$ Complex Metal Hydrides and Evaluation by Ultra Small Angle X-ray Scattering (USAXS) Studies

*Tabbetha A. Dobbins*,* Principal Investigator & Associate Professor
*Scott Gold*, Assistant Professor
*Daniela Mainardi*, Associate Professor
*Shathabish NaraseGowda*, Ph.D. Candidate

**Project Objectives:**

Doped and undoped $NaAlH_4$ were also nano-confined within porous alumina membranes and tested for effects of nano-confinement. Ultra Small Angle X-Ray Scattering (USAXS) technique has been explored to study morphological changes that occur in the hydrides during various stages of template wetting. USAXS also proved to be a factual tool to identify confined and un-confined $NaAlH_4$ in the alumina templates, since it is virtually impossible to obtain such information with techniques like SEM or $N_2$ BET alone.

**Narrative:**

INTRODUCTION

Complex metal hydrides are undoubtedly the most promising materials for hydrogen storage. Many light metal complex hydrides such as $NaAlH_4$ and $LiBH_4$ have been studied as candidate hydrogen storage materials for many years [1-4]. $NaAlH_4$, among these has been an archetype for complex metal hydrides and the most widely researched material in this category so far. However, not many researchers have quantitatively studied the changes in morphological features of these materials during desorption. Many underlying challenges in developing reversible complex metal hydrides, such as hysteresis or choosing the right catalysts and mill times can adequately be addressed by examining their morphology. To study complicated morphologies, small angle scattering of light and x-rays is an invaluable tool since it covers almost seven orders of magnitude on the length scale [5]. Measuring x-ray scattering at small angles can yield information on large electronic inhomogeneities of the size of colloidal particles. The ultra small angle x-ray scattering finds use when there is a need to extend the length scales to micron or sub micron levels while small angle x-ray scattering is limited to the nanometer scale [6]. $NaAlH_4$ is comprised of colloidal particles with extremely complex surface fractal pore morphology and USAXS technique is well suited for such materials [7]. The present work is intended to present some unique applications of ultra small angle x-ray scattering technique that addresses some of the unanswered problems in development of reversible complex metal hydrides. Catalysis, hysteresis, optimum process parameters (eg. mill time), nanostructuring strategies and characterization for complex metal hydrides are some of the primitive questions that need further/alternative investigation.

Nanostructuring of complex metal hydrides has gained tremendous interest lately due to the many advantages it offers in comparison to the bulk materials. $NaAlH_4$ [8,9] and $LiBH_4$ [10,11] have been confined in a variety of materials with a wide range of pore sizes such as porous silica, carbon scaffolds, MOFs etc. One of the key roles of a nano-scaffold is to prevent the particles from agglomerating due to sintering [14]. The particle size obtained from small angle scattering analysis can be used to decide the pore size that will effectively curb any sintering effects for that material. Various nanostructuring techniques, such as melt infiltration and solution infiltration, are adopted to load the nano-scaffolds with the hydrides but it has been a challenge to actually identify material confined within the pores from those resting on the surface. Techniques used to date for this purpose are based on measuring the changes in weight and specific surface area [12-15]. One of the recent articles showed the use of small angle neutron scattering to assess the loading of activated carbon by $Mg(BH_4)_2$ by showing a decrease in specific surface area [16]. An attempt has been made in this paper to identify the confined material based on the shape they acquire due to confinement.

Small angle scattering yields information on colloidal attributes such as specific surface area, radius of gyration, and fractal features. Specific surface area is an important parameter for all desorbing systems and increasing the surface area enhances the catalytic activity as well as increases the desorption rates [17]. Thus, specific surface area, as a parameter, can be used to assess the efficacy of any treatment aimed at enhancing desorption properties. Dobbins et al, for the first time, showed that the most effective mill times and the most effective catalyst for $NaAlH_4$ can be singled out by tracking the surface area changes via power law slopes from USAXS experiments [18]. In this paper, the adeptness of each treatment performed on $NaAlH_4$ is illustrated by virtue of specific surface area changes. $NaAlH_4$ is understood to undergo densification during sintering due to agglomeration and fusing of the primary particles [19]. This actually leads to a loss in total surface area due to agglomeration of two or more particles, which affects the hydrogen uptake capacity of the material in subsequent cycles.

## EXPERIMENTAL PROCEDURE

### Sample Preparation

Commercially available sodium aluminum hydride ($NaAlH_4$) hydrogen-storage grade (Sigma-Aldrich®) and titanium (III) chloride ($TiCl_3$) hydrogen storage grade (Sigma-Aldrich®) were used in the preparation of all samples. Both chemicals were stored and handled, at all times, in a glove box under a controlled dry $N_2$ environment. $NaAlH_4$ was milled with 4mol% $TiCl_3$ in tungsten carbide vials using a Certiprep SPEX 8000M high energy ball mill, for 5 minutes. Undoped (neat) $NaAlH_4$ was also milled for 5 minutes to compare with the catalyzed sample as well as the unmilled sample. For nanostructuring the $NaAlH_4$, porous alumina membranes (Whatman® Anodisc™) of 13mm diameter and 200nm pore size were used. $NaAlH_4$ was inserted into the pore wells of the alumina membranes by the template wetting technique (discussed in the next section) using tetrahydrofuran (THF) as a precursor. For the USAXS experiment, small amounts of each sample was packed between two layers of kapton film and the edges further sealed with kapton tape to avoid any exposure to air. An empty bilayer of kapton film was also made to account for the scattering from the kapton layers alone, which was later subtracted from all samples during the final USAXS data analysis.

### Template Wetting

Template wetting is one of the many wet impregnation techniques that is based on forming thin uniform precursor films using a low surface energy organic solvent on substrates with high surface energy [17]. Template wetting has been widely regarded as a simple and easy way to fabricate polymer nanotubes and nanowires. The procedure to fabricate functionalized nanotubes has been lucidly described in one of the earliest articles on this technique, authored by Steinhart et al [18]. The same principles were applied, but the intention was to fill the pore completely with $NaAlH_4$ and not just wet the walls to form nanotubes. Tetrahydrofuran (THF) was used as the wetting agent to form a dilute precursor solution containing $NaAlH_4$. For the present study, 50mg of a 5 minute milled sample of $NaAlH_4$ was dissolved completely in 1ml of THF. A more concentrated solution would clog the pores and form a layer on the surface, and a more dilute solution would end up just wetting the pore walls, both of which are not desired. The alumina templates were pre-treated to remove impurities by dipping in ethanol and acetone for 2 hours each and later heating to 200 deg C for a period of 6 hours using an autoclave oven. Later the templates were let to cool down to room temperature and set up on a flat Teflon plate and the $NaAlH_4$ – THF precursor was dropped on to the template using a micro-pipette.

### Ultra-Small Angle X-Ray Scattering (USAXS)

USAXS data were collected at sector 32ID, Advanced Photon Source, Argonne National Lab (IL) using incident photon energy of 16.9KeV. The beam size employed for these experiments was 0.3mm x 0.3 mm. Powder samples were on the order of 0.2mm thick and the template samples were around 0.1mm in thickness, including the two layers of kapton tape. Data reduction and analysis were made using IGOR PRO 6.05 version. The macros Indra2 (developed by Ilavsky) was used to desmear the slit-smeared USAXS data and Irena2 to analyze and fit the data [19, 20]. The scattering intensity was fit by the unified model (eq. 1), developed by Beaucage. The unified model serves as a great tool to fit multiple Guinier regions and power law regions without introducing any additional parameters than those used for local fits [21].

$$I(Q) = G\exp\left(-\frac{Q^2R_G^2}{3}\right) + B\left\{\frac{\left[erf\left(\frac{QR_G}{\sqrt{6}}\right)\right]^3}{Q}\right\}^P \qquad (1)$$

The unified model fit yields the power law slope (p) and the radius of gyration ($R_g$) for each structural level present.

## RESULTS AND DISCUSSION

One major change made for the data analysis of nanostructured $NaAlH_4$ was that the empty template packed in Kapton was treated as the 'blank' sample. Here 'blank' refers to the background material that contains the actual sample (just a bilayer of kapton tape in case of powder samples) whose scattering needs to be subtracted to evaluate the scattering from the sample. This modified correction of the USAXS data for nanostructured samples revealed that the primary particles on the porous template had absolute power law slope values less than 3 indicating mass fractal morphology. The template wetting technique involved dissolution of the $NaAlH_4$ particles in the volatile THF solution and re-crystallizing $NaAlH_4$ back by letting THF evaporate. The $NaAlH_4$ re-crystallizes into tightly packed particles (negligible internal porosity), thus possessing significant material (mass) within a shape acquired by the terrain of the template. This explains the mass fractal morphology detected by USAXS. The data was collected from six different positions on the template containing $NaAlH_4$. Some positions revealed slopes of $p = -1.41$ [Fig 1] indicating rod like particles and other positions revealed slopes of $p = -2.72$ [Fig 2] indicating flat disc like particles. It can be fairly inferred that the particles acquire the shape of an elongated rod due to their confinement inside the pore well. The particles that do not enter the pore wells are either due to clogging of the pores or those that rest on top of the pore wall. Recalling the principle of template wetting technique, the solution is expected to form a uniform precursor film on the substrate, which implies that the particles re-crystallize evenly on the surface of the substrate to form plate (or disc) like shapes. These can be accounted for the exponents that indicate disc like particles.

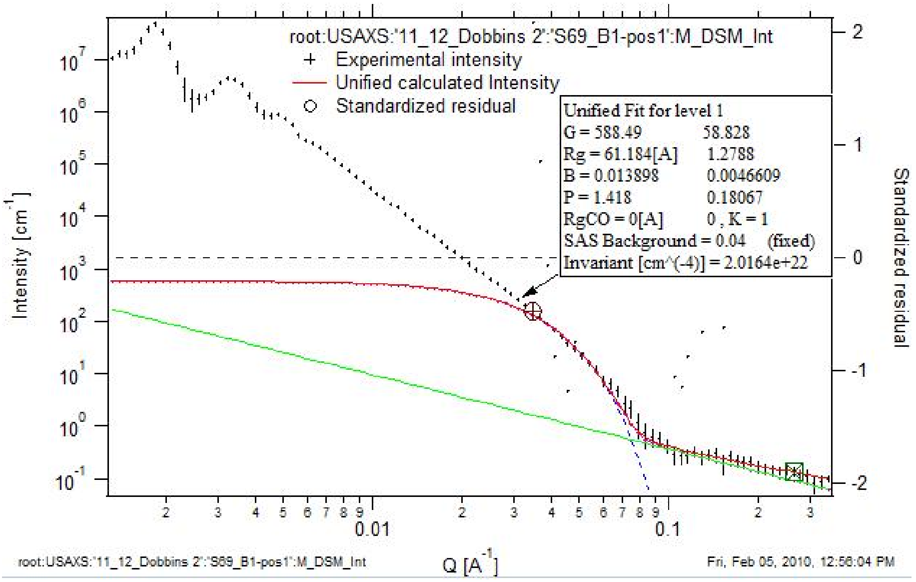


Fig 1. Unified fit for $NaAlH_4$ confined within the pores of the alumina template

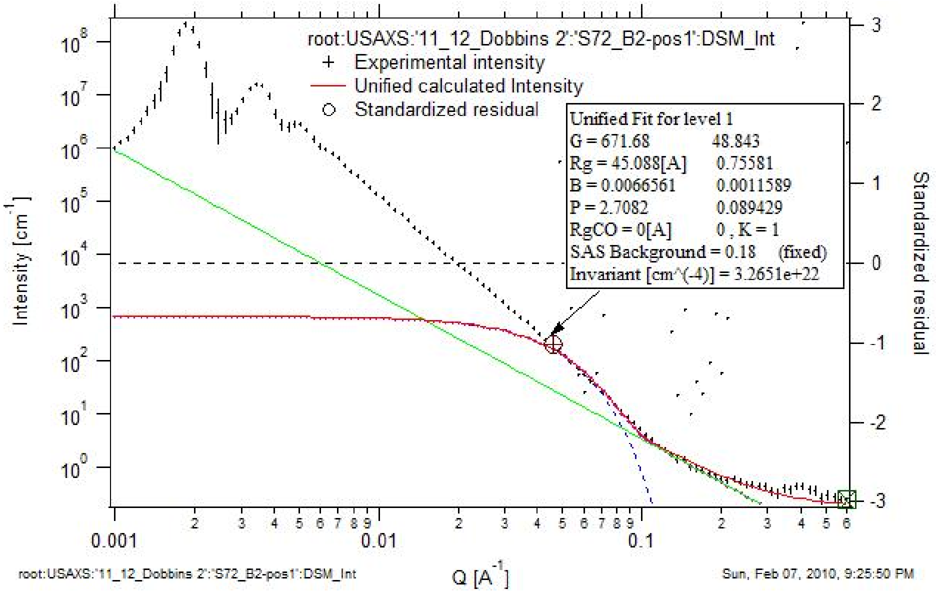


Fig. 2. Unified fit for $NaAlH_4$ on the surface of the alumina template

## CONCLUSION

Template wetting combined with ultrasmall-angle x-ray scattering was used to accurately identify confined and unconfined $NaAlH_4$ based on particle shapes. This research program was able to involve North Louisiana in the alternative energy related and nanotechnology research. As well, this work allowed students and faculty performing research in North Louisiana to share in research at a central facility (the Advanced Photon Source at Argonne National Laboratory). Similar research will be continued at our home synchrotron facility, the Center for Advanced Microstructures and Devices (CAMD) located in Baton Rouge, LA. In addition to performing research on hydrogen storage materials—the principal investigators participated in two outreach projects: (1) providing fuel cell vehicle experiment kits and training to students and teachers at the Louisiana School for Mathematics Sciences and Arts in Natchitoches, LA (photographed below) and supporting the AIChE student chapter at Louisiana Tech University in their participation in the regional conferences' fuel cell vehicle competition. Both of these projects greatly benefitted the community.

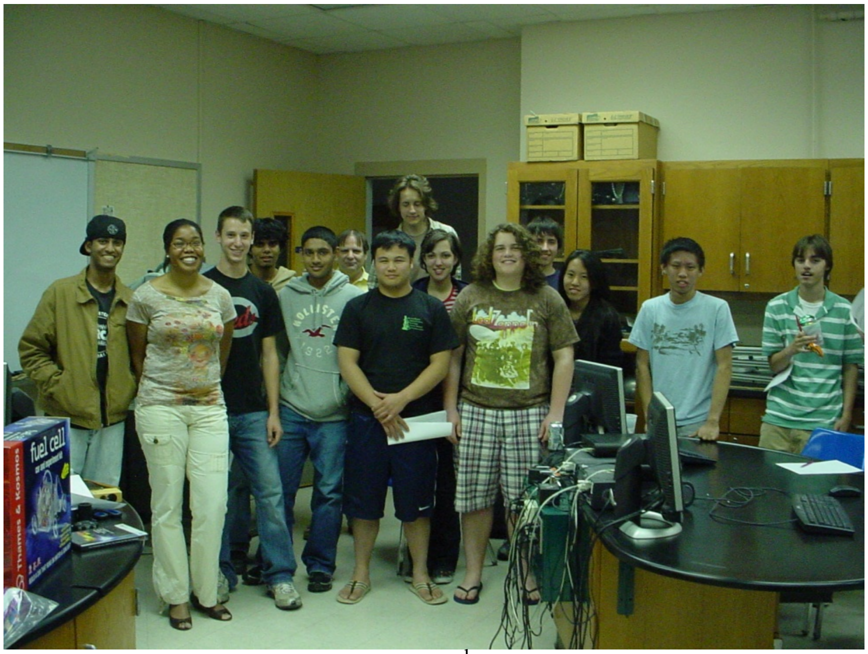


Fig. 3. Photograph of Tabbetha Dobbins (2nd from left) with students at the LSMSA. Two visits were made: (1) to discuss hydrogen using 'The Hydrogen Age' movie and (2) to construct Thames and Kosmos Fuel Cell Vehicle kits which were deployed to the school.

Publications and presentations resulting from the project (please also mention those being prepared for submission in the near-future):
Manuscripts submitted to :

- American Ceramics Society Materials Challenges in Energy 2010 Proceedings

Number of students supported: Provide a total number but please break out the numbers of US citizens/permanent residents, women, and under-represented minorities.

- 2 Ph.D. students (permanent residents)
- 1 undergraduate student researcher (underrepresented minority/woman, U.S. citizen)

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## 9. Energy Systems Conference

*Stan Napper, PhD*, Dean and Professor of Biomedical Engineering

On November 5, 2009, a one day conference titled "Building Energy Systems for Tomorrow" was held at the Louisiana Tech Technology Transfer Center in Shreveport, attended by more than 100 attendees including the local media and the general public. The stated purpose of the conference was "to inform the public about Louisiana-based research and technology to meet future energy needs and to facilitate interdisciplinary research in energy systems." After a welcome by the Vice-President for Research & Development of Louisiana Tech University and remarks by the Dean of the College of Engineering & Science, the technical program comprised of two sessions. The morning session was made up of industry leaders discussing the future prospects of nuclear energy, alternate fuels, and natural gas. The afternoon session consisted of Louisiana Tech faculty presenting research supported by the Department of Energy through various grants including this Congressional Directive.

**Morning Session:**

1. Charles Turk, Leader, R&D and University Partnerships, Entergy Nuclear, “Research & Investments in Nuclear Energy”
2. Dan Shapiro, President, Shaw Capital Investments, “Investments in Alternate Energy Sources for the Future”
3. Kim Mitchell, Community Renewal International, “Community Renewal and Green Building Requirements”
4. Hilton Nicholson, President, Sixnet, “Cellular Innovations for the Smart Grid”
5. Mike McDaniel, Louisiana State University Center for Energy Studies, “Louisiana’s Bioenergy Future”
6. Kevin McCotter, Director, Corporate Development in Louisiana, Cheasapeake “Natural Gas: America’s Energy Future”
7. Nick Akins, Exec. VP, American Electric Power Co., “Transformation to the Energy Resource Mix of the Future”

**Afternoon Session:**

8. Chester Wilson, Louisiana Tech University, “Conversion of Natural Gas and $CO_2$ to Diesel”
9. H. Lynn Walker, Louisiana Tech University, “Carbon Sequestration with Algae”
10. Erez Allouche, Louisiana Tech University, “Geopolymer Concrete for Green Construction Materials”
11. Henry Cardenas, Louisiana Tech University, “Electrokinetic Hardening of Concrete Structures”
12. Chester Wilson, Louisiana Tech University, “Radiation Detectors for Real-Time Core Monitoring”
13. Lee Sawyer, Louisiana Tech University, “Nuclear and Particle Physics”
14. James Palmer, Louisiana Tech University, “Large-Scale Reactors to Reduce Cellulosic Ethanol Costs”
15. Upali Siriwardane, Louisiana Tech University, “Heterogeneous Catalysts for Biodiesel Production”
16. Dentcho Genov and Sandra Selmic, Louisiana Tech University, “Enhanced Solar Cells”
17. Scott Gold, Louisiana Tech University, “Nanotechnology for Energy Storage”
18. Tabbetha Dobbins, Louisiana Tech University, “Hydride Storage Materials for Fuel Cells”
19. Daniela Mainardi, Louisiana Tech University, “Fuel Cell Modeling”
20. Erez Allouche, Louisiana Tech University, “Energy from Waste and Storm Water Conveyance”
21. Leland Weiss, Louisiana Tech University, “Advanced Energy Recovery Using Micro/Nano Devices”
22. Ville Kaajakari, Louisiana Tech University, “Autonomous Green Power Generation and Storage”