Hayes Investment Fund

2003 Awards

Final Progress Report

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2003 HAYES INVESTMENT FUND AWARDS

FINAL PROGRESS REPORT

INTRODUCTION

The process of soliciting and evaluating proposals for the Hayes Investment Fund Program was consistent with previous competitive review cycles for this research support program. Forty-four preliminary proposals were received in response to the RFP issued on January 30, 2003. Owing to the wide range of science and technology disciplines represented by these proposals, a total of sixty-two external readers were engaged to review and evaluate these preliminary proposals. Each proposal was read by at least three external peer reviewers, who evaluated the proposals according to criteria that included the project's potential for national excellence, the capabilities of the project investigators, the potential for leveraging future support from federal and industrial sources, the potential to achieve the delineated research goals, the advancement of basic research and education, and meaningful collaboration among the partners.

Based upon the evaluations and rankings of the external readers, all of whom were leaders in their disciplinary areas, a total of thirty-two proposed projects were selected to move to the final proposal phase of the competition. An eight person Review Panel was engaged to evaluate and rank these projects. The members of the Panel were selected on the basis of their research expertise their experience in directing diverse research programs that spanned multiple disciplines.

The Panel members were provided with copies of the reviews from the disciplinary readers for the preliminary proposals. Each final proposal was read by all eight members of the Panel and detailed written evaluations were provided by at least three Panel members. For this evaluation the Panel was instructed to use not only the evaluation criteria employed by the readers of the preliminary proposals, but also to consider the relationship and consistency of each proposal with the goals, objectives, and existing programs of **The Third Frontier Project.** As a result of this review and evaluation, including oral presentations by a number of the finalists, a total of eight projects were recommended for funding. The Panel recommended that each of the eight proposals listed in the following table be granted a 2003 Hayes Investment Fund award. The Board of Regents at their meeting on July 17, 2003 approved the recommendations of the Panel.

Research Consortium Members	Program	HIF Award
University of Cincinnati, Wright State University,Procter & Gamble Pharmaceuticals, Air Force Research Laboratory, and Acero.	Proteomics and Protein Characterization in the Post-Genome Era	**$1,000,000**
University of Cincinnati, Case Western Reserve University, University of Dayton, Air Force Research Laboratory, First Nano, ThermoNicolet, and Procter & Gamble	Nanoscale Hybrid Materials: Novel Synthesis, Applications, and Characterization	**$800,287**
Ohio State University, Ohio University, Wright State University, NASA Glenn Research Center, Air Force Research Laboratory, Battelle, and Lake Shore Cryotronics, Inc.	Ohio Nanoscale Patterning Consortium	**$2,000,000**
Ohio State University, University of Cincinnati, Wright State University, Air Force Research Laboratory, Knolls Atomic Power Laboratory, Ford Motor Company, Alcan Technology & Management, The Timken Company, and GE Aircraft Engines.	Accelerated Maturation of Materials	**$2,000,000**
Ohio State University, University of Akron, University of Dayton, Procter & Gamble, Cleveland Clinic Foundation, Air Force Research Laboratory, Ashland Specialty Chemical Company, Applied Sciences, Inc., Owens Corning, and Honda.	Consortium for Affordable Manufacturing of Polymers at the Nanoscale	**$2,000,000**
Ohio State University, Kent State University, University of Akron, University of Cincinnati, and NexTech Materials, Ltd.	Hydrogen Production and Storage Consortium	**$1,000,000**
Ohio State University, Kent State University, Case Western Reserve University, BTG International, Inc., DuPont Circleville, AlphaMicron, Inc., and Nanofilm.	Ohio Organic Semiconductor Consortium	**$1,000,000**
University of Toledo, Ohio State University, Case Western Reserve University, Cleveland State University, Cleveland Center for Structural Biology, Cleveland Clinic Foundation, and Anatrace.	Macromolecular Crystallography Consortium	**$1,181,600**
	HIF Award Total	**$10,981,887**

SUMMARY OF RESULTS

As indicated on the table, awards totaling $10,981,887 were made to the eight research consortiums. whose members included nine of the doctoral granting research universities in the state in addition to the Cleveland Clinic Foundation, the Air Force Research Laboratory at Wright Patterson Air Force Base, the NASA Glenn Research Center, Battelle, and twenty Ohio companies. As of the winter of 2007, these Hayes Investment Fund awards have resulted in federal and industry research awards to the consortium university members totaling over $52,000,000. In addition, over 345 peered reviewed publications have been published and 71 new research collaborations have been established with other universities (27) and industry partners (44). Fourteen patents have been filed as a result of this research, with one new start-up company being formed. Finally, students using the equipment acquired under these awards for their research projects have received 33 Ph.D. degrees and 35 MS degrees. The final progress report submitted by each consortium follows this section.

Proteomics and Protein Characterization in the Post-Genomic Era

Final Research Progress Report

Partners: ***University of Cincinnati****, Wright State University, Procter & Gamble Pharmaceuticals, Air Force Research Laboratories, Acero*

Achievement of Goals and Objectives

In 2003-2004 the Genome Research Institute (GRI) competed successfully for a Hayes Award to supplement University funds to build a high quality Proteomics and Protein Characterization laboratory that would support research projects across the region. We are now approaching year three since receiving the award and thus the following highlights the lasting impact of this investment.

The primary impact from building these proteomics capabilities fall into three categories: the scope of projects supported, grant support generated, and the recruitment of quality investigators to the region. First, the GRI proteomics laboratory has provided project support to over 30 investigators across the GRI, the University System and within the Cincinnati Children's Hospital Research Foundation. In addition, the GRI Proteomics laboratory has been a primary outsourcing option for proteomics services from Procter & Gamble Pharmaceuticals and the Air Force Research Laboratories located at Wright Patterson Air Force base. Contract services for the Cincinnati branch of the EPA have also been provided over the past two years. Finally, protein characterization services have been provided for two start-up companies in the area. Thus collectively, the GRI proteomics laboratory has broad utilization across the region's research community and is positioned to continue to extend the scope of its impact.

Secondly, proteomics and biological mass spectrometry data generated in the GRI Proteomics laboratory has provided data for many researchers. Proteomics core work completed since acquisition of the Hayes funded equipment includes:

- Identification of novel targets for improved recovery from post-traumatic brain injuries (K. Strauss, UC). This project also has high interest for the Department of Defense and could serve as the basis for major new funding. Commercial applications in diagnostics and drugs would be a long term goal of such projects.
- Identification of early participants in collagen fibril assembly. (R. Wenstrup, Children's)
- Proteomic analysis of decidual diffentiation (S. Handwerger, Children's).
- Proteomic analysis of long-term effects of embryonic exposure to environmental tobacco smoke on the development of cardiac diseases (K. Seta, J. Hove, T. Penberthy, UC)
- Identification of novel targets for improved diagnosis of age-related cardiac left ventricular hypertrophy (J. Hove, T. Penberthy, UC)
- Identification of peptide hydroxylation in intermittent hypoxia (M. Czyzyk-Krzeska, UC)

- Identification of protein alterations in lung cancer (M. Anderson)
- Identification of novel biomarkers for acute lymphoblastic leukemia in human serum (N. von Neuhoff, Univ. of Hannover, Germany)
- Two-dimensional gel electrophoresis analyses for several investigators at Cincinnati Childrens Hospital and the University of Cincinnati. In a collaboration with Dr. Tim Weaver at Cincinnati Childrens Hospital the laboratory performed an in-depth characterization of surfactant protein B, a protein that has been shown to be required for normal function of newborn and adult lung.
- A series of two-dimensional gel electrophoresis experiments were performed in collaboration with Dr. Kenneth Strauss at the University of Cincinnati. Using a rat models system this project aims to identify new targets for improved recovery from traumatic brain injuries. Traumatic brain injuries have been associated with an increased long term susceptibility to neuronal diseases and stroke, and improved recovery could potentially result in a lower incidence of these diseases.
- Identification of novel biomarkers for amyotrophic lateral sclerosis in human serum for improved diagnosis and development of new treatment options. (J. Schlager, AFRL). As noted above, this project is the first of a series which GRI, AFRL and other new partners will pursue to use the Department of Defense Human Serum repository as a unique source of biological samples which can be studied to identify the medical and environmental causes of disease for warfighters and the general population. The capabilities installed at GRI and Wright State under the BRTT program have made possible their participation in these programs and can bring to Ohio major new federal funding. Additionally, these projects will be raw material for the future development of diagnostics including biosensors and therapeutic drugs.
- The proteomics laboratory continued the collaboration with Proctor&Gamble Pharmaceuticals, performing two-dimensional gel electrophoresis experiments for the obesity drug development program. These experiments have now entered the data evaluation phase. Extensive analysis of the generated two-dimensional gels will generate a list of novel biomarker candidates that can be used to identify inhibitors of a cell surface receptor implicated in the development of type 2 diabetes, a disease currently affecting more than 16 million people in the United States.
- The proteomics laboratory also continued its mass spectrometry-based quality control analyses for Girindus, Inc. Girindus is a manufacturer of synthetic oligonucleotides, which play an increasingly important role in the development of new therapies in genetic medicine.
- In addition, the proteomics laboratory started a series of two-dimensional and one-dimensional analyses for Meridian Bioscience, Inc. Meridian Bioscience is a manufacturer of diagnostic technologies for infectious and parasitic diseases based in Cincinnati, OH. The proteomics laboratory performs quality and purity analyses of recombinantly expressed proteins for the company during various steps of the purification protocol development. The highest purity and integrity of the expressed proteins are crucial for the development of new and improved kits for the diagnosis of various human diseases such as Herpes, stomach ulcer and food poisoning.

P&GP, Meridian and Girindus are all companies whose success will mean a significant increase in Ohio based biotechnology jobs.

Many new projects are now underway at GRI which take advantage of the proteomics capability partially funded by the Hayes Investment fund. An excellent example is a recently funded study of kidney cancer, specifically renal clear cell carcinoma (RCC). This highly malignant cancer is linked to the loss of activity of the von Hippel-Lindau tumor suppressor protein (pVHL), encoded by a gene located on the short arm of chromosome 3. Epidemiologically, RCC is associated with a number of factors, such as cigarette smoking, hypertension, diabetes and obesity. In particular, a role for oxidative stress, including that resulting from cigarette smoking has been proposed. The laboratory of Maria Czyzyk-Krzeska at the GRI has discovered a novel molecular and biochemical pathway regulated in response to oxidative stress. Because changes in gene expression are the fundamental molecular basis for the oncogenic process, this research proposes that changes in the expression of genes resulting from the loss of pVHL-dependent ubiquitylation of Rpb1 or loss of P1465 hydroxylation are causative for the development of renal cancer. In this application, they will seek to identify the specific gene targets regulated by hydroxylation and pVHL-dependent ubiquitylation of Rpb1, and to functionally demonstrate their relevance for renal clear cell carcinoma. The long-term goal of this work, beyond the immediate scope of this application, will be to improve both the treatment and detection of RCC . It is expected that the proteins characterized using proteomics to be useful as therapeutic targets for the development of new drugs to treat RCC, or as biomarkers to identify individuals at risk for RCC (thus improving chances for early disease detection) or to determine the best treatment for those already diagnosed.

Finally, a research community is only as good as its investigators. In today's research climate with all the expensive technologies, including proteomics, it is no longer feasible for an investigator to control all these capabilities at the level of individual labs. Thus it is necessary for even the best investigators to have access to, and collaborate with core laboratories. As a result, top investigators choose those research environments which have the best core resources available to them. The capabilities now available at GRI Proteomics laboratory have enabled the Institute to recruit and keep several internationally recognized investigators. Many of these investigators have become some of the strongest advocates for the core laboratory approach due to the successful collaborations they have developed with the Proteomics laboratory. Thus investing in the proteomics capabilities at the GRI has been instrumental in attracting some of the best investigators in the world to this region. The net impact is greater research funding for these investigators which in turn provides additional jobs in the region.

In closing, nearly 3 years have passed since the Hayes Award was made available to the University to help build proteomics capabilities. As outlined above, these capabilities have already had an impact on grant proposals and attracting top-rated faculty to the region; however, like any investment the ideal situation is for the investment to continue to grow. As the impact of these proteomics capabilities continues to reach additional investigators, I expect the impact of this investment to continue to grow as well.

2. Leveraging Results

The existence of the Genome Research Institute has significantly impacted the leveraging of Federal, industry, and private foundation funds for R and D activities in this area of research. As indicated in the table below, over $15,000,000 in new awards have been received since the development of this laboratory.

2005-2006 SPONSORED AWARDS	
Principal Investigator, award, agency	FY06 DIRECT FUNDING
Anderson - Chemoprevention of Lung Cancer (NCI)	2,666,292
Anderson - Genetic Epidemiology of Lung Cancer (NCI)	924,329
Anderson - Mechanisms of Mouse Lung Carcinogenisis (NCI)	47,389
Anderson - Wash U Sub (NCI)	80,925
Czyzyk-Krezska - ACS	21,577
Czyzyk-Krezska - NIH HL 58687Gene Experession	185,685
Czyzyk-Krzeska - NIH HL66312 Hypoxia/Apnea	206,000
Dedman - AHA	55,000
Dedman - AHA Ohio Valley (Ji)	55,000
Drew - ACS	27,273
Hove - AHA	55,000
Hove - Kidney Award	27,905
Millhorn - NIH HL 33831 Oxygen Sensing	124,887

Millhorn - NIH HL 59945 Hypoxia		152,000
Millhorn- Army Breast Cancer		108,000
Plas - NIH Young Investigator		147,650
Schmann - ManTech / Alion		110,000
Schumann - ALS Military		50,000
Schumann - Orise Fellowship (Wendy Dominic)		35,000
Seta - Smoking Award		100,000
Thomas - Novartis (Um)		55,000
Thomas - Orise Fellowship (Dann)		40,000
Thomas - Sloan Kettering		86,344
Thomas - Swiss Institute of Cell Biology		173,964
Wortman - Third Frontier Network		615,000
Davidson-Apolipoprotein A-1 (NIH)		175,000
Davidson-Apoliproprtotein Cholesterol (NIH)		175,000

Davidson-Ceramide (Pfizer	182,000
Benoit-CNSMelanocortin (NIH)	143,500
Benoit-CNS Behavior (NIH)	143,500
Herman-Stress Adaptation (NIH)	22,000
Herman-Limbic Circuits (NIH)	225,000
Herman-Glucocorticoid (NIH)	225,000
Herman-Brainstem (NIH)	225,000
Herman-Pituitary (NIH)	216,000
Kascow-Schizophrenia (NIH)	225,000
Mueller-Pituitary (NIH)	44,000
Sakai-Stress and Body Weight (NIH)	220,000
Seeley-Gut/Brain Obesity(NIH)	141,000
Seeley-Mouse Diabetes (NIH)	100,000
Seeley-CNS Adiposity (NIH)	191,000

Seeley-Energy Balance (NIH)	172,000
Stern-Angiotensin (NIH)	30,000
Stern-Hypertension (NIH)	330,000
Woods-Obesity (NIH)	150,000
Woods-Homeostasis (NIH)	272,000
Woollett-Sterol Metabolism (NIH)	158,000
Woollett-Bile (NIH)	158,000
Tso- Mouse Phenotyping (NIH)	580,000
Sun-Plasma Triglycerides (NIH)	55,000
Tso-Obesity Signals (NIH)	225,000
Tso-Obesity and Diet (NIH)	205,000
Liu-Food Intake (NIH)	165,000
Hui-Lipogenisis (NIH)	225,000
Hui-Vascular (NIH)	250,000
Hui-Apolipoprotein (NIH)	248,000
Hui-Lipolytic Enzymes (NIH)	230,000
Hui-Lipid Metabolism (NIH)	50,000
Frolov-Lipoprotein (NIH)	59,000
Granholm-Appo (NIH)	275,000
D'Allessio-Diabetes (NIH)	450,000
Anthonelli-Stress, Alcohol (NIH)	300,000
Thomas: NIH	225,000
Kozma: NIH	200,000
Drew: ACS National	150,000
Czyzyk-Krzeska: DoD	300,000
Hove:NIH	200,000
Wortman: TFN	300,000
Czyzyk-Krzeska: UC Cancer Center	40,000
Czyzyk-Krzeska: ORISE	30,000
McOsker: ORISE	100,000
Clegg: NIH	250,000
Obichi:NIH	100,000
TOTAL	$15,285,219

3. **Publications Resulting from this Award**

Since the laboratory commenced operation some 115+ papers have been published by the user community in peer-reviewed journals. This process continues unabated. Listed below are the peer-reviewed papers and abstracts published and in press.

V. Kuznetsova, J. Meller, P.O. Schnell, J.A. Nash, M.L. Ignacak Y. Sanchez, R.C. Conaway, J.W. Conaway, M. F. Czyzyk-Krzeska (2003) VHL tumor suppressor complex binds hyperphosphorylated large subunit of RNA polymerase II through a proline hydroxylation motif and targets it for ubiquitination. Proc. Natl Acad. Sci. USA 100, 2706-2711.

P. O. Schnell, M. L. Ignacak, A. L. Bauer, J. B. Striet, W. R. Paulding, M. F. Czyzyk-Krzeska (2003) Regulation of tyrosine hydroxylase promoter activity by hypoxia-inducible factors and von Hippel-Lindau tumor suppressor protein. J. Neurochem, 85, 483-491.

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M.F. Czyzyk-Krzeska and J. Meller (2004) Von Hippel-Lindau tumor suppressor complex: not only HIF's executioner. Trends in Molecular Medicine. Ternds in Molecular Medicine, 10, 146-149.

E. Gozal, Z.A. Shah, J-M. Pequignot , J. Pequignot , L. R. Sachleben , M. F. Czyzyk-Krzeska, R.C. Li , S-Z. Guo, D. Gozal. (2005) Changes in Tyrosine Hydroxylase Expression and Activity in the Rat Brain Following Long-term Intermittent or Sustained Hypoxia J. Appl. Physiology, *In press*.

A. Zakrzewska, P. O. Schnell, J. B. Striet[1,2], A.S. Hui, J. R. Robbins, M. Petrovic, L. Conforti , D. Gozal, M.G. Wathelet, M. F. Czyzyk-Krzeska (2005) Hypoxia-activated metabolic pathway stimulates phosphorylation of p300/CBP in oxygen-sensitive cells. J. Neurochem. In press

A.L. Bauer, A. S. Hui, J. B. Striet, P.O. Schnell, M.F. Czyzyk-Krzeska (2005) Regulation of HIF 1α protein translation by calcium. (submitted to Mol Cell Biol)

M.L. Ignacak, S.V. Harbaugh, A. Zakrzewska, J.B. Striet, M.F. Czyzyk-Krzeska (2005) VHL- and prolyl hydroxylation –dependent ubiquitylation of Rpb1 regulate growth of renal cancer cells. (submitted)

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Hove, J.R. (2004). In vivo biofluid dynamic imaging in the developing zebrafish. *Birth Defects Research C: Embryo Today* **72**: 277-289.

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Bartman, T and Hove J.R. (2005). Mechanical forces and signals in heart development. *Developmental Dynamics* **233**:373-381.

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Ji Y, Zhao W, Li B, Desantiago J, Picht E, Kaetzel MA, Schultz JE, Kranias EG, Bers DM, Dedman JR., Targeted inhibition of sarcoplasmic reticulum CaMKII activity results in alterations of Ca2+ homeostasis and cardiac contractility. Am J Physiol Heart Circ Physiol. 2005 Sep 2; [Epub ahead of print]

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Nanoscale Hybrid Materials: Novel Synthesis, Characterization, and Applications

Final Research Progress Report

Partners: ***University of Cincinnati****, University of Dayton, Case Western Reserve University*

1. General Objectives

The main objective of this collaboration of the University of Cincinnati, the University of Dayton, and Case Western Reserve University was to establish a Consortium to conduct research in the rapidly developing field of nanoscale hybrid materials. Nanoscale hybrid materials consist of exciting new combinations of materials in which at least one component is a "nanoscale material" that has one or more dimensions on the order of nanometers. These "nanoscale materials" are not simply scaled-down versions of their macroscopic counterparts; they exhibit profoundly different physical, chemical, and mechanical properties when compared to their macroscopic counterparts and impart important new properties to nanoscale hybrid materials. Structural composites made by reinforcing appropriate matrix materials with nanoscale particles such as carbon nanotubes, alumina, or titania are one example of a nanoscale hybrid material. Another example is active synthetic membranes that allow the passage of ions or molecules upon receipt of a triggering signal. These hybrid materials are fabricated by forming nanoscale lipid "bilayers" within the pores of a flexible, porous substrate.

The field of nanoscale hybrid materials is highly multidisciplinary, requiring expertise in such areas as materials synthesis, characterization, processing, and surface engineering. Research in this field requires expensive facilities and instruments for materials preparation and characterization. Formation of a Consortium for nanoscale hybrid materials was essential since it is not usually possible to find all of the expertise and facilities required for successful research and education programs in this field on one campus.

2. Scientific and Technological Progress

A. Synthesis of Nanoscale Materials

Professor P. T. Murray (University of Dayton) is focusing his research on the synthesis of materials systems composed of nanoparticles that are embedded in a matrix. These nanoscale hybrid materials systems are of interest because of potential applications ranging from optical and electronic to medical; however, nanoscale hybrid materials systems are also of considerable fundamental interest.

Murray used funds from the Hayes Investment Fund award to purchase a high power, excimer laser, to purchase a UV-visible spectrometer, and to construct a vacuum system in which to carry out materials synthesis. The laser and vacuum system are used to synthesize nanoscale composite systems by laser ablation of a target material while the UV-visible spectrometer is used to monitoring and control the

synthesis process. The UV-visible spectrometer has also enabled Murray to explore the photo-physics of laser ablation and to acquire a more fundamental understanding of the laser ablation process.

In the pulsed laser ablation (PLA) process, a target material is irradiated with the output of a high power, pulsed laser to produce nano-particles. The apparatus that Murray constructed eliminates nano-particle agglomeration, which has been a major problem associated with the development of nanoscale hybrid materials. This was accomplished in collaboration with Mound Laser and Photonics Center (MLPC) in Miamisburg, OH. The UD/MLPC team devised a new method of nano-particle synthesis by PLA. In this process, the target consisted of a very thin film that was deposited onto an optically transparent support. It is interesting to note that with this process, nano-particles can be formed in the absence of a background gas.

The new instruments that were installed at UD allowed Murray to establish an important collaboration with scientists in Germany. Murray received funding from the Fraunhofer Society for an exchange program that enabled him to spend four months at the Fraunhofer Institutes in Dresden and enabled a Fraunhofer scientist to work in Murray's lab at UD for six months. Murray plans to make this a long-term collaboration and is currently discussing several research projects with Fraunhofer personnel. One intriguing possibility is to use Murray's new equipment to fabricate nano-scale composites that can be used as prototype materials for qualifying nondestructive evaluation techniques.

Murray is also collaborating with F. J. Boerio (University of Cincinnati) on the synthesis of novel composites through simultaneous PLA and plasma polymerization. Plasma polymerization is used to form films of polymer matrix materials on a selected substrate while PLA is used to form nanoparticles that are incorporated into the growing polymer films. This approach to forming nanocomposites has great potential since it completely eliminates the problems related to agglomeration and dispersion of nanoparticles.

Professor Mark J. Schulz (University of Cincinnati) is also synthesizing nanoparticles but is concentrating on carbon nanotubes (CNTs). CNTs are very exciting materials and are expected to be the ultimate reinforcement material in polymer composites because of their high stiffness, high strength, and light weight. Composite materials reinforced with single wall nanotubes (SWNTs) are expected to be ten times stronger and six times lighter than steel. These materials are expected to have important applications in aircraft and spacecraft, where reductions in weight of at least 50% may be attainable. However, a number of issues need to be worked out before nanotubes can be expected to lead to new advanced composites, including the growth of nanotubes that are more than a few micrometers in length.

Schulz used funds from the Investment Fund award to acquire a sputtering system, quadrupole mass spectrometer, glove box, vacuum pump, ovens, amplifier, power supply, mixer, and other items that are being used to synthesize nanotubes and to process the nanotubes for applications. Specifically, Schulz and his co-workers have developed techniques for synthesizing highly aligned arrays of MWCNTs that are several millimeters in length. Oxidized Si wafers were used as substrates. E-beam deposition was employed to form a top Al layer, which was subsequently oxidized. Finally, a catalytic iron film of controlled thickness was deposited through a shadow mask on top of the Al_2O_3. The CNTs were grown by chemical vapor deposition (CVD)

from an H_2-C_2H_4-H_2O-Ar gas mixture at 750°C in a tubular furnace. An important aspect of this work has been the use of the quadrupole mass spectrometer (QMS) to monitor the partial pressures of all gases in the growth zone. The QMS indicates when there is a problem in the process and is used to confirm the concentrations of all gases including carbon in the reactor. The sputtering system is used to deposit gold on the ends of the nanotubes to make sensors. The glove box, ovens, mixer, and other equipment are used for preparing nanocomposites and sensors from nanotubes produced as described above.

B. Characterization of Nanoscale Hybrid Materials

Professor F. J. Boerio (University of Cincinnati) used funds from the Hayes Investment Fund award to purchase a Thermo Nicolet Nexus 870 Fourier-transform infrared spectrometer, a DI Instruments Dimension 3100 atomic force microscope, and related instrumentation. Boerio and his students then developed a new research tool that will be used to determine the structure and composition of polymeric materials on a much smaller size scale than previously possible by using the atomic force microscope to obtain infrared absorption spectra of polymeric materials. Eventually, this new instrument should provide infrared spectra of nanometer-scale regions of materials. Microscopes currently used for infrared micro-spectroscopy are limited by the "diffraction limit" to size scales on the order of micrometers and are thus not suitable for the analysis of materials at ultra-high spatial resolutions.

In the new instrument that Boerio's group is developing, infrared radiation from a Fourier-transform infrared spectrometer (FTIR) is focused onto a polymeric sample that is mounted on the stage of an atomic force microscope (AFM) and the probe of the AFM is placed in contact with the surface of the sample. When the sample absorbs infrared radiation, it undergoes thermal expansion of a few nanometers; this thermal expansion is detected by the AFM. The output signal of the AFM is returned to the FTIR system where the Fourier-transform is computed to obtain the infrared absorption spectrum of the sample. The infrared spectrum provides a great deal of information regarding the chemical composition and microscopic structure of the sample. Boerio's group has already obtained AFM/FTIR spectra of a number of polymers, including polystyrene, polycarbonate, and polypropylene. They are currently developing techniques to determine and control the spatial resolution in this powerful new technique for characterizing polymeric materials. One of their most exciting results involves determining molecular orientation in polymers on a localized level using the AFM/FTIR system and polarized infrared radiation.

Professor J. L. Koenig (Case Western Reserve University) used funds from the Investment Fund award to purchase a Jobin-Yvon LabRam 300 Raman spectrometer and confocal microscope system. Koenig and his students have developed the Raman spectrometer and microscope for the measurement of the chemical and defect structures (spectroscopy) of carbon nanotubes (CNTs) and the distribution of these structures (imaging) along the length of nanotube samples prepared in various ways. The first order Raman spectrum is very sensitive to variations in the microstructure of carbon materials. Generally, CNTs consist of an ordered graphitic structure characterized by a peak at 1570-1610 cm^{-1} in the Raman spectrum (referred to as the

G peak) and a disordered structure or lattice defects characterized by a peak at 1320–1360 cm^{-1} (referred to as the D peak).

Koenig is collaborating with Schulz on the use of Raman spectroscopy to determine the growth mechanisms of CNTs. The simplest carbon nanotube structures can be visualized as layers of graphite rolled up into seamless cylinders, with each end either open or capped with half a fullerene molecule. The points at which the rolled up graphite sheets are connected define a tube's diameter and chirality, which, in turn, governs its properties. Armchair, zigzag, and chiral tubes of various diameters have been observed. Raman spectroscopy provides information about the tube configuration, including the diameter, the number of the walls (single wall or multi-wall), and the presence of crystalline or amorphous carbon. Koenig's work is helping Schulz to devise ways to mass produce carbon nanotubes of high purity and to control the length, diameter, and chirality of the nanotubes.

Aligned CNT arrays prepared by Schulz at UC were characterized by Koenig at CWRU. Raman spectra of the aligned MWCNT arrays consisted of strong peaks at 1350 and 1586 cm^{-1} that were related to the D and G bands, respectively. The existence of the strong D peak was not fully understood. There might be several reasons for its appearance. The first is the presence of amorphous carbon on the CNT side surface of highly compacted arrays. The second is the relatively low crystallinity of the CNT arrays along with turbostratic structures formed in some carbon layers. It is also assumed that there is a large crystalline domain with very small (nanometer scale) dimensions that enhances the D peak. It seems that the strong D peak is a feature of highly dense CNT arrays. The growth time along with the concentration of the carbon precursor, and the deposition temperature is very important for reducing the D band. Any growth time above 50-60 minutes may not contribute substantially to the length of the CNT but will accumulate amorphous carbon. This explains why our Raman spectra show strong D-bands for samples grown longer than 30 minutes. Post thermal treatment in vacuum helps to decrease the intensity of the D peak. The large D peak seems to be an attribute or characteristic of highly dense CNT arrays, and may not be of too much concern. The Raman experiments currently underway will provide Raman spectra along the length of nanotubes as long as six millimeters and may allow optimization of the process conditions to grow even longer nanotubes. An invention disclosure has been filed and UC is planning to patent this growth process.

Professor Paul Rosevear (University of Cincinnati) purchased a Bruker EMX X-band microwave bridge electron paramagnetic resonance (EPR) spectrometer, including an 8 inch EPR magnet and power supply system. Rosevear and his students have used the new EPR spectrometer to develop a new method for the direct determination of the protein global fold from paramagnetic relaxation enhancements and dipolar chemical shifts. This approach has been applied to barnase, a ribonuclease secreted by *Bacillus amyloliquefaciens*. In a previous study, Rosevear's group developed a method for facile introduction of a metal binding tag at a specific location in a protein of interest. Distances, calculated from experimentally observed effects of manganese on longitudinal relaxation processes in barnase, when combined with angular information obtained from dipolar shifts, measured by substitution of both ytterbium and cobalt into the covalently attached EDTA derivative, were sufficient to calculate atomic coordinates for the secondary structural elements of

barnase. The calculated coordinates of the secondary structural elements were determined with a root mean square deviation of 3.7 Å from the 1.5 Å resolution crystal structure of barnase.

Rosevear has also investigated flexibility in the linker region (residues 75 to 82) that connects the two domains of calmodulin and is essential for target protein recognition. Comparative structural modeling of calmodulin domain orientation was employed to explore motions within the calmodulin linker region that target recognition. Analysis of relative domain orientation for calmodulin structures revealed that bending of the linker region occurs in a single plane. Hinge axes about which domain orientation occurs are located between residues 77 and 82. In addition bending of the linker region is correlated with the degree of twist about the D-helix. As a consequence of the restricted bending plane and coupling of inter-domain motions, domain orientation is coupled to the degree of bending required for target binding. This observation is consistent with a single pathway of domain reorientation, limiting the domain orientations available for target peptide interactions. The reduced range of domain orientations may provide a mechanism to minimize non-specific interactions and to compensate for the entropic penalty that occurs upon target binding. The range over which domain orientation occurs is thus severely restricted, a useful property for modeling the structure of calmodulin in calmodulin/ligand complexes on the basis of limited structural information.

C. Novel Applications of Nanoscale Hybrid Materials

Professors F. J. Boerio and J. Cuppoletti (University of Cincinnati) and their students are collaborating on the development of flexible polymer films with novel transport properties by forming bilayer lipid membranes (BLMs) within the pores of porous polymer membranes. Initially, BLMs were formed within the pores of commercially available porous polycarbonate and polyethylene terephthalate membranes. Subsequently, BLMs were also formed within the pores of specially prepared poly (l-lactic acid) membranes and within laser-drilled "pores" in plastic plates. Bilayers in 50 µm and smaller pores had resistance values greater than 40 M□ and were stable for up to 24 hr. When the protein gramicidin-D was added to the bilayers, the resistance dropped to less than one M□. It was concluded that BLMs were very effective barriers and prevented the diffusion of protons through the porous polymer membranes. However, when biological membrane proteins were added to the BLMs, they formed channels in the bilayers that permitted the flow of protons across the polymer membranes.

Proton pumps (H^+ ATPase) were also inserted into BLMs formed in the pores of polycarbonate membranes. An aqueous buffer solution at pH 7.4 was provided on the inside of the membrane and deionized water at pH 7.0 was provided on the outside. When no energy was supplied to the pumps, the pH on the outside of the lipid bilayer was stable. However, when MgATP was added on the inside of the membrane to activate the H^+ ATPase, the pH on the outside decreased about 0.5 pH units, indicating that protons were pumped across the bilayer.

The functional porous polymer films described above have many potential applications, such as polymer electrolyte membranes in fuel cells. In a simple fuel cell, hydrogen is oxidized at the anode to form protons and electrons. The protons

diffuse across a polymer electrolyte membrane (PEM) to the cathode while the electrons travel to the cathode through an external circuit where they can do work, such as drive an electric motor. Oxygen is reduced at the cathode to form water. One significant problem with fuel cells concerns the backward diffusion of protons from the cathode to the anode, thus limiting the power of the fuel cell. Boerio and Cuppoletti have been developing innovative techniques for reducing or eliminating the backward diffusion of protons across PEMs in fuel cells. Their approach is to place BLMs within the pores of porous polymer films that are used as PEMs and to place proton pumps into the BLMs. The BLMs will prevent proton diffusion in both directions across the PEMs but inclusion of proton pumps will enable protons to be pumped from the anode to the cathode. Boerio and Cuppoletti have already shown that this approach works.

Another significant problem with fuel cells concerns the maximum proton current density that flows across the PEM. If this current density is relatively low, the power that the fuel cell can deliver will be low. Boerio and Cuppoletti have been working to overcome this problem by developing innovative techniques for fabricating porous polymer membranes that have a very high area density of through pores. If BLMs with high concentrations of proton pumps can be formed in the pores of such films, then the proton current density flowing across the films can be maximized. Boerio and Cuppoletti have prepared macro-porous polymer films with uniform hexagonal arrays of pores from amorphous polycarbonate and polymethylmethacrylate using a dip-coating method. The films possessed pores that were relatively mono-disperse, occupied approximately 50% of the total surface area of the films, and had specific pore sizes that could be adjusted between 0.5-12 □m by altering the deposition rate. BLMs that were self-assembled within the pores of dip-coated films exhibited good barrier properties to the transduction of potassium ions, had a resistance of approximately 40 M□□ and were stable for as long as 24 hours. When ion channels were reconstituted into the BLMs, the resistance of the polymer membranes decreased to approximately 1 M□ and the films exhibited specificity for the transduction of monovalent cations such as potassium ions. The next step will be to insert proton pumps into the BLMs that are formed in the pores of these very porous polymer films.

Professor Mark J. Schulz (University of Cincinnati) is developing several exciting applications for long carbon nanotubes (CNTs), including biosensors, nanocomposites, and smart materials. For example, a biosensor is being developed for cancer detection. The sensor depends on the change in electrochemical impedance that occurs upon exposure to an antigen. Once this biosensor platform is developed, the sensor can be used for many medical applications.

Long CNTs may be used to develop new adhesive systems with interesting properties. The feet of a gecko, which is native to Southeast Asia, have about two million densely packed, fine hairs or "setae" on each toe. The end of each seta is further subdivided into hundreds or thousands of structures called spatulae which are about 200 nm to 500 nm wide (roughly the size of a wavelength of light). When a gecko steps on almost anything, these nano-hairs make such extremely close contact with the surface that they form intermolecular bonds, thus holding the foot in place. Walking is possible by rolling the hairs, thus releasing them sequentially from contact. It has been shown that constructing polymer surfaces with multiwalled carbon nanotube “hairs” produced nanometer-level adhesion forces 200 times higher than

those observed for gecko foot-hairs. The high attraction force of the hydrophobic carbon nanotube array may be used as a new super-strong releasable adhesive.

As-grown arrays of long CNTs are super-hydrophobic and have very high water contac angles; shorter length CNT arrays are less hydrophobic and have lower water contact angles. The hydrophobic property may be used to provide waterproof coatings on materials. For example, the leading edges of aircraft might be coated with "nanoskin" to prevent ice buildup, reduce rain erosion, and provide electrical conductivity.

CNT based skin and nano-strand fiber materials can improve the properties of the surfaces of composites and potentially replace micro-fibers with nanotube fibers. CNT arrays grown to millimeter lengths can be used to form nanoskin, and fibers that may replace conventional mcirofibers used in composites. CNT nanoskin can be strong, lightweight, absorb energy, restore part of its shape, reduce impact damage, and have electrical and thermal conductivity; it can be used to monitor the health of structures using impedance self-sensing. The nanoskin can also be tailored with different polymer and elastomeric matrices, spatial density, and size of nanotubes to be a highly-compressible energy absorber. Tiles of nanotube arrays can be formed into nanoskin for use on large structures.

3. Additional Information

A. F. James Boerio (University of Cincinnati)

Leveraging results (title, sponsoring agency, date, and amount of each external award received as a result of this Hayes award)

"Development of an Infrared Spectrometer/Scanning Probe Microscope for Materials Characterization at High Spatial Resolution," National Science Foundation, August 1, 2003, $250,055.

"Surface Properties of Graphite/Epoxy Composites: Effect of Peel Ply Materials," Boeing Commercial Airplane Company, April 15, 2006, $68,725.

"Surface Chemical Characteristics of Polyurethane Coatings," Boeing Commercial Airplane Company, April 15, 2006, $30,000.

"Factors Affecting Topcoat to Topcoat Paint Adhesion," Boeing Commercial Airplane Company, March 1, 2005, $35,000.

"Surface Properties of Epoxy Composites and Polyurethane Coatings," Boeing Commercial Airplane Company, March 1, 2005, $55,000.

"Surface Properties of Epoxy Composites and Polyurethane Coatings," Boeing Commercial Airplane Company, November 1, 2004, $30,000.

"Factors Affecting Topcoat to Topcoat Paint Adhesion," Boeing Commercial Airplane Company, November 1, 2004, $30,000.

Number of graduate students who completed thesis/dissertations under this award (number of each degree awarded, e.g. 2 M.S., 3 Ph.D., etc.)

3 M.S.

Publications resulting from this award (title, date, and journal name)

M. A. Dhoke, D. Wieczorek, F. J. Boerio, J. Cuppoletti, and D. Malinowska, "Porous Membranes for Reconstitution of Membrane Transporters and Ion Channels," Biochim. Biophys. Acta, **1716**, 117-125 (2005).

B. D. Stephens, F. J. Boerio, and J. Cuppoletti, "Dip-Coated Breath-Figure Films for Biomembrane Scaffolding," Nanotechnology, submitted for publication, 2006.

F. J. Boerio, Michael Starr, Brian Stephens, and Shaun Rostron, "Infrared Spectroscopy Using an Atomic Force Microscope," Appl. Spectrosc., submitted for publication, 2006.

Technology transfer activities (patents, licenses, start-ups, etc.)

Invention Disclosure, UC 107-051, "Infrared Spectroscopy Using an Atomic Force Microscope."

Invention Disclosure, UC 106-073, "Porous Polymer Films and Membranes by Dip Coating and Solvent Casting."

Collaborations established (new or enhancement of existing ones with other universities or industry)

Department of Chemical and Materials Engineering, University of Dayton, Dayton, OH; Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH; Boeing Commercial Airplane Co., Seattle, WA; Thermo Electron Company, Madison, WI; Procter & Gamble Co., Cincinnati, OH; Materials Directorate, Air Force Research Laboratory, Wright Patterson AF Base, OH

B. P. T. Murray (University of Dayton)

Leveraging results (title, sponsoring agency, date, and amount of each external award received as a result of this Hayes award)

"Nanoparticle Films Fabricated by Laser Ablation and Their Characterization," Fraunhofer Society, May 1, 2006, $80,000

"Laser Plasma Manufacturing of Oriented Carbon Nanotubes and Nanowires," Air Force Office of Scientific Research, July 29, 2005, $90,000

"Laser Plasma Manufacturing of Oriented Carbon Nanotubes and Nanowires," Air Force Office of Scientific Research, November 14, 2006, $750,000

Number of graduate students who completed thesis/dissertations under this award (number of each degree awarded, e.g. 2 M.S., 3 Ph.D., etc.)

None yet; 2 PhD and 1 MS student will graduate in the future

Publications resulting from this award (title, date, and journal name)

"Nanomaterials Produced by Laser Ablation Techniques: Highly Spatially Resolved Characterization of Nanostructures", B. Koehler, P. T. Murray, E.Shin, S. Lipfert, and J. Schreiber, SPIE Proc. **6175**, 61750C-1 (2006).

"Nanomaterials Produced by Laser Ablation Techniques: Synthesis and Passivation of Nanoparticles, P. T. Murray, B. Koehler, J. Kaspar, J. Schreiber, S. Lipfert, SPIE Proc. **6175**, 61750D-1(2006).

Technology transfer activities (patents, licenses, start-ups, etc.)

None

Collaborations established (new or enhancement of existing ones with other universities or industry)

Department of Chemical and Engineering, University of Cincinnati, Cincinnati, OH; Mound Laser and Photonics Center, Miamisburg, OH; Fraunhofer Insitute for Beam and Material Technologies, Dresden, Germany; Fraunhofer Institute for Nondestructive Evaluation, Dresden, Germany; Materials Directorate, Air Force Research Laboratory, Wright Patterson AF Base, OH

C. Jack L. Koenig (Case Western Reserve University)

Leveraging results (title, sponsoring agency, date, and amount of each external award received as a result of this Hayes award)

None

Number of graduate students who completed thesis/dissertations under this award (number of each degree awarded, e.g. 2 M.S., 3 Ph.D., etc.)

1 Ph.D. John Bobiak, 2005

Publications resulting from this award (title, date, and journal name)

J. P. Bobiak and J. L.Koenig "Regions of interest in FTIR imaging applications: diffusion of nicotine into Ethylene-Co-Vinyl acetate films," Journal of Controlled Release, **106**, 329-338 (2005).

Technology transfer activities (patents, licenses, start-ups, etc.)

None

Collaborations established (new or enhancement of existing ones with other universities or industry)

Sumitomo Rubber, Kobe, Japan; Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH; Department of Mechanical Engineering, University of Cincinnati, Cincinnati, OH; Department of Chemical Engineering, Case School of Engineering, Case Western Reserve University, Cleveland, OH

D. Mark J. Schulz (University of Cincinnati)

Leveraging results (title, sponsoring agency, date, and amount of each external award received as a result of this Hayes award)

"Development of Multifunctional Sensors Based on Carbon Nanotubes," KITECH, $20,000, May 1, 2006.

"Development of a Smart Nanofurnace to Synthesize Long Carbon Nanotube Arrays for Multifunctional Nanoskin and Nanocomposite Applications, ONR, $189,831, May 1, 2006.

"Synthesis of Carbon Nanotube Arrays for Multifunctional Materials," NCA&TSU/ONR, $60,000, January 1, 2006.

"Telescoping Nanotube Arrays," NSF, $270,000, September 1, 2005.

Number of graduate students who completed thesis/dissertations under this award (number of each degree awarded, e.g. 2 M.S., 3 Ph.D., etc.)

4 M.S., 2 Ph.D.

Publications resulting from this award (title, date, and journal name)

Gautam Seth, YeoHeung Yun, Vesselin N. Shanov, Adam Bange, Brian Halsall, William Heineman, Michael Behbehani, Sarah Pixley, Zhongyun Dong, Amit Bhattacharya, Alexzandra Spatholt, Mitul Dadhania, Mark J. Schulz, "Carbon Nanotube Needle and Gap Electrochemical Biosensors," in review, IEEE Transactions on Nanotechnology.

Andrew Gorton, Vesselin Shanov, Yun YeoHeung, Mark J. Schulz, Sudheer Nerella, Sergey Yarmolenko, and Yi Tu, "Substrate and Process Optimization for Synthesis of Long Multi-Wall Carbon Nanotube Arrays," in review, IEEE Transactions on Nanotechnology.

Inpil Kang, Joo Young Jung, Gyeong Rak Choi, Hyungki Park, Jong Won Lee, Kwang Joon Yoon, Yun Yeo-Heung, Vesselin Shanov, and Mark J. Schulz, "Developing of Carbon Nanotubes Composite Smart Materials," *Solid State Phenomena (2007)*, Vol. 119, pp.207-210.

Inpil Kang, Mark J. Schulz, Jong Won Lee, Gyeong Rak Choi, Joo Young Jung, Jae-Boong Choi and Sung-Ho Hwang, "A Carbon Nanotube Smart Material for Structural Health Monitoring," *Solid State Phenomena*, Vol. 120 (2007), pp. 289-296, SCI:ISSN 1012-0394, Trans Tech Publications LTD.

Inpil Kang, Gyung Rak Choi, Joo Yung Jung,Yong Hoon Chang, Yeon Sun Choi, and Mark J. Schulz, "A Carbon Nanotube Film for Power Harvesting," *Key Engineering Materials (2006),* Vols. 326-328, pp.1447-1450.

Inpil Kang, Mark J. Schulz, Jong Won Lee, Gyeong Rak Choi and Yeon-Sun Choi, "Strain Sensors Using Carbon Nanotube Composites", *Transactions of the Korean Society for Noise and Vibration Engineering ,* Vol. 16, No. 7, pp. pp.762-768, 2006.

YeoHeung Yun, Adam Bange, Vesselin N. Shanov, William R. Heineman, H. Brian Halsall, Danny K. Wong, Michael Behbehani, Sarah Pixley, Amit Bhattacharya, Zhongyun Dong, Mark J. Schulz, "A Nanotube Composite Microelectrode for Monitoring Dopamine Levels using Cyclic Voltammetry and Differential Pulse Voltammetry, submitted," Journal of Nanoengineering and Nanosystems.

YeoHeung Yun, Adam Bange, William R. Heineman, H. Brian Halsall, Vesselin N. Shanov, Zhongyun Dong, Sarah Pixley, Michael Behbehani, Abdul Jazieh, Yi Tu, Danny K.Y. Wong, Mark J. Schulz, "A Nanotube Array Immunosensor for Direct Electrochemical Detection of Antigen-Antibody Binding" accepted, Sensors & Actuators: B.

YeoHeung Yun, Adam Bange, Vesselin N. Shanov, William R. Heineman, H. Brian Halsall, Zhongyun Dong, Abdul Jazieh, Yi Tu, Danny Wong, Sarah Pixley, Michael Behbehani, Mark J. Schulz, "A Carbon Nanotube Needle Biosensor," accepted, Journal of Nanoscience & Nanotechnology.

YeoHeung Yun, Vesselin Shanov, Yi Tu, Srinivas Subramaniam, Mark J. Schulz, "The Effect of Process Parameters and Substrate Thickness on the Synthesis of Vertically Aligned Multi-Wall Carbon Nanotube Forests," submitted Mat Chem and Phy, 2/06.

YeoHeung Yun, Vesselin N. Shanov, Yi Tu, and Mark J. Schulz "Hydrophobicity, Capillarity, and Electro-wetting of Carbon Nanotube Carpets," submitted Smart Materials and Structures.

Suhasini Narasimhadevara, Mark J. Schulz, Peng He, Donglu Shi, F.J. Boerio, Vesselin Shanov, Douglas Hurd, Subrahmin Srivinas, George Kreishman, "Processing of Nanocomposites Based on Epoxy and Carbon Nanofibers," submitted 2/06, Composites Engineering, Part B.

YeoHeung Yun, Vesselin Shanov, Mark J. Schulz, Zhongyun Dong, Abdul Jazieh, William R. Heineman, H. Brian Halsall, Danny K. Y. Wong, Adam Bange, Yi Tu, Srinivas Subramaniam, High Sensitivity Carbon Nanotube Tower Electrodes, Sensors and Actuators B, accepted.

YeoHeung Yun, Vesselin Shanov, Yi Tu, Mark J. Schulz, Sergey Yarmolenko, Sudhir

Neralla, Jag Sankar, Srinivas Subramaniam, "A Multi-Wall Carbon Nanotube Tower Electrochemical Actuator," Nanoletters, vol. 6, no 4, 2006.

YeoHeung Yun, Vesselin Shanov, Yi Tu, Srinivas Subramaniam, Mark J. Schulz, *The Effect of Process Parameters and Substrate Thickness on the Synthesis of Vertically Aligned Multi-Wall Carbon Nanotube Forests*, in revision.

YeoHeung Yun, Ram Gollapudi, Vesselin Shanov, Mark J. Schulz, Zhongyun Dong, Abdul Jazieh, William Heineman, Brian Halsall, Danny Wong, Yi Tu, Srinivas Subramaniam, Carbon Nanotubes Grown on Stainless Steel to form Plate and Probe Electrodes for Chemical/Biological Sensing, accepted, Journal of Nanoscience & Nanotechnology.

Hyukjae Lee, Shankar Mall, Peng He, Donglu Shi, Suhasini Narasimhadevara, Yun Yeo-Heung, Vesselin Shanov, and Mark J. Schulz, "*Characterization of carbon nanotube/nanofiber reinforced polymer composites using an instrumented indentation technique,"* Composites B, accepted.

Inpil Kang, Mark J. Schulz, Jay H. Kim, Vesselin Shanov, Donglu Shi, "*A Carbon Nanotube Strain Sensor for Structural Health Monitoring*," Volume 15, Number 3, June 2006, Smart Materials and Structures.

Yun Yeo-Heung, Vesselin Shanov, Mark J. Schulz, Zhongyun Dong, Abdul Jazieh, Tony He, Donglu Shi, Yi Tu, Srinivas Subramaniam, "*A Versatile Carbon Nanofiber Electrochemical Biosensor,"* submitted to IEEE NanoBioScience.

Inpil Kang, Yun Yeo Heung, Jay H. Kim, Jong Won Lee, Ramanand Gollapudi, Srinivas Subramaniam, Suhasini Narasimhadevara, Douglas Hurd, Goutham R. Kirikera, Vesselin Shanov, Mark J. Schulz, Donglu Shi, J.F. Boerio, Shankar Mall, Marina Ruggles-Wren, "*Introduction to Carbon Nanotube and Nanofiber Smart Materials,"* Composites B Journal, 37, 2006.

Yeo-Heung Yun, Vesselin Shanov, Mark J Schulz, Suhasini Narasimhadevara, Srinivas Subramaniam, Douglas Hurd, and F J Boerio, "*Development of novel single-wall carbon nanotube–epoxy composite ply actuators,"* Smart Mater. Struct. 14 (2005) 1526–1532, among top twenty downloaded papers of 2005 for SMS journal.

Yun Yeo-Heung, Atul Miskin, Phil Kang, Sachin Jain, Suhasini Narasimhadevara, Douglas Hurd, Mark J. Schulz; Vesselin Shanov, Tony He, F. James Boerio, Donglu Shi, Subrahmin Srivinas; *Carbon Nanofiber Hybrid Actuators, Part I: Liquid Electrolyte-Based*, Journal of Intelligent Material Systems and Structures, 2006, vol 17, no 2, pp. 107-116.

Yun Yeo-Heung, Atul Miskin, Phil Kang, Sachin Jain, Suhasini Narasimhadevara, Douglas Hurd, Mark J. Schulz; Vesselin Shanov, Tony He, F. James Boerio, Donglu Shi, Subrahmin Srivinas; *Carbon Nanofiber Hybrid Actuators, Part II: Solid Electrolyte-Based*, Journal of Intelligent Material Systems and Structures, 2006, vol 17, no 3, pp. 191-197.

Technology transfer activities (patents, licenses, start-ups, etc.)

Invention Disclosure, UC 107-044, "Catalyst and Method for Manufacturing Carbon Nanostructured Materials."

Collaborations established (new or enhancement of existing ones with other universities or industry)

North Carolina A&T State University, Greensboro, NC; Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH

E. Paul Rosevear (University of Cincinnati)

Leveraging results (title, sponsoring agency, date, and amount of each external award received as a result of this Hayes award)

"Structural Mechanisms Modulating Contraction in Normal and Diseased Heart," NIH, April 1, 2007, $1,922,112.

Number of graduate students who completed thesis/dissertations under this award (number of each degree awarded, e.g. 2 M.S., 3 Ph.D., etc.)

None

Publications resulting from this award (title, date, and journal name)

K. J. Reszka, G. M. Denning, and B.E. Britigan, "Photosensitized oxidation and inactivation of pyocyanin, a virulence factor of Pseudomonas aeruginosa" Photochem Photobiol, **82**, 466-473, 2006.

K. J. Reszka, M. L. McCormick, G. R. Buettner, C. M. Hart, and B.E. Britigan, "Nitric Oxide Decreases the Stability of DMPO Spin Adducts" Nitric Oxide: Biology and Chemistry **15**, 133-141, 2006.

S. Sadayappan, N. Finley, J. W. Howarth, O. Raisa, R. Klevitsky, J. N. Lorenz, P. R. Rosevear, and Robbins "Conserved Acidic-N'-region of Cardiac Troponin I is Critical in Regulating Myocardial Function," submitted for publication, J. Biol. Chem. (2006).

Technology transfer activities (patents, licenses, start-ups, etc.)

None

Collaborations established (new or enhancement of existing ones with other universities or industry)

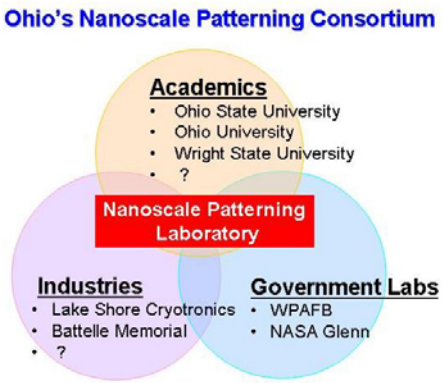
Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH

Ohio Nanoscale Patterning Consortium

Final Research Progress Report

Partners: ***The Ohio State University****, Ohio University, Wright State University, Lakeshore Crytronics, Battelle Memorial Institute, Wright-Patterson AFB, NASA Glenn*

Achievement of Goals and Objectives



The Ohio State Nanoscale Patterning Laboratory (OSU-NPL) began operations as a shared user facility as of January 9, 2006 operating under a cost center model (see http://www.ece.osu.edu/~berger/ebl.html). This was the linchpin acquisition proposed by this consortium. The world class Leica EBPG-5000 electron beam lithography (EBL) system, funded by a $2M Hayes award, and augmented by OSU costshare was accepted by Ohio State on the same day. The installation, vacuum loadlock upgrade, and acceptance tests were performed between September 2005 and January 2006. Prior to placement of the tool in the OSU site, the specifications of the electron beam system required renovations to the cleanroom facility to improve the cleanliness, temperature and humidity control, and the installation of utilities specific to the tool site. The majority of these improvements were completed in late 2005, with official certification of the room in March 2006. Table 1 shows the timeline of room renovation, tool installation, and acceptance. For long-term success of the OSU-NPL a service contract (~$156K/yr) was purchased and a staff engineer hired to meet the customer's needs and training.

It should also be highlighted here that the OSU-NPL negotiated a competitive deal with Vistec (formerly Leica) for the purchase of an EBPG-5000 system, which had been used as a loaner to a French manufacturing facility. The total cost of this Leica system was priced at only $1.85M whereas a brand new comparable system has a list price of $4.16M! A slightly used system actually is highly beneficial for EBL as the first-time users were able to establish optimal electron beam working conditions beforehand, facilitating rapid deployment at OSU.

Table 1-Leica EBPG 5000 installation and acceptance timeline

Task	Date	Comment
Leica EBPG 5000 delivered to OSU	September 2004	Placed in storage pending site improvements
Site improvement project began	May 2005	Camp Dresser and McKee Architects
Tool moved to Dreese cleanroom site	September 2005	

Ebeam engineer arrived	September 2005	
Leica field service engineers arrived, installation began	September 2005	
Loadlock upgraded	September 2005	
First beam down column, exposures begin	October 2005	
Conditional tool acceptance	December 20, 2005	Pending final images from 100kV exposures
Final tool acceptance	January 9, 2006	
Cleanroom upgrades completed	March 2006	Room certified at cleanroom Class 100
Kickoff Celebration event to publicize new system's availability to users	April 3, 2006	

OSU-NPL operates as a cost center facility and is open to universities, government labs, and industrial users both within Ohio and beyond. The facility's daily operations are currently run by Ms. Aimee Bross, Sr. Research Associate, under the direction of Professor Paul R. Berger who is the Director of both the OSU-NPL and the affiliated processing lab, Nanofabrication and Materials Processing Center (NanoMPC). The investment by the Hayes Fund in the EBL has added significantly to the nano-processing capability in the State of Ohio, as well as the entire mid-West region. The OSU NPL and NanoMPC facilities work closely with Ohio State's Nanotech West Laboratory (formerly Ohio MicroMD). These labs provide complementary techniques that have and continue to foster collaboration within and outside of Ohio State University. Table 2 shows the collaborations and users that have active projects at OSU-NPL using the Leica EBPG-5000.

As Table 2 indicates, the OSU-NPL has established more than 40 collaborations and/or users of the Leica EBPG-5000 system in the 11 months since tool acceptance. Many of these users are from Ohio, including industrial entities. Figure 2 shows the breakdown of users by NPL charges over the course of the first eleven months of the OSU NPL's existence. It should be noted that there are three stratified cost structures, common to similar multi-user facilities such as the National Nanofabrication Infrastructure Network (NNIN), available for example at Cornell. Rates are commensurate to the NNIN, partitioning rates into internal Ohio State users, academics external to Ohio State, and industry/government lab users. This is in keeping with the spirit of the OBOR's HIF with significant augmentation by OSU in equipment cost-sharing (~$260K), lab renovations (~$275K) and qualified staff support over the first 4 years (~$473K).

The feedback has been extremely positive from both industry and academic users. Dr. Mahavir Sanghavi stated "*Having access to OSU EBL facility and an expert like Aimee Bross to run it has made a great difference to Lake Shore Cryotronics. Having the facility here in Central Ohio has given us the flexibility in scheduling and getting it right first time …*" In addition, giving users access to the system has allowed them to establish and secure their own collaborations. Elvin Beach, a Ph.D. student of Prof. Patricia Morris in Materials Science & Engineering at OSU, said "*EBL has enabled us to have an ongoing collaboration with the AFRL at Wright Patterson. If not for the EBL*

preliminary result we generated this summer (and hopefully results we can duplicate in the coming month) this project with WPAFB would be done and considered unsuccessful." The addition of the EBL has resulted in collaborations that go beyond even the traditional ideas of multi-disciplinary. NPL staff has formed a relationship with Professors Kenneth Rinaldo and Amy Youngs in the Department of Art and Technology at Ohio State. Professor Rinaldo stated "*I/we in Art & Technology are extremely excited to have access to the EBL and will be looking forward to working more collaboratively with the EBL facility and staff. We feel that this facility will result in important cross disciplinary research at the nexus of Art & Science and we can foresee developing industry ties as a result.*"

To address the local needs of the Southeastern Ohio nanotechnology community, a portion of the HIF funds were also used to purchase a LEO scanning electron microscope (SEM) that was upgraded to perform rudimentary electron beam lithography on a daily basis. This system provides affordable small feature sizes, but without the ability to perform large area patterns, or multiple layer lithographies available at the OSU-NPL. This system was bought and installed at Ohio University. However, this system was later relocated to Virginia Tech in Summer 2006 with the departure of Prof. Jean Heremans. New joint opportunities are being pursued presently with Ohio University, but no definitive plans are in place yet. Currently, some researchers at OU are utilizing the services provided by the OSU-NPL (see Table 2).

Leveraging Results (title, date, sponsoring agency, and amount of external award received as a result of this Hayes award).

Numerous proposals have now been submitted based on work to be performed using the EBL system or including EBL components and we will discover the outcome of the first wave of these proposals within the next several months.

Proposals Awarded

- PI: Paul R. Berger (OSU), Patrick J. Fay (Notre Dame), Phillip E. Thompson (Naval Research Lab), Charles L. A. Cerny (AFRL/SNDX, WPAFB) and Joseph E. Van Nostrand, (AFRL/SNDX, WPAFB) titled "Highly Nonlinear MM-wave Sensors for Passive Threat Detection," under J., Volakis' The Ohio State University Connection One Center for Radio Frequency Systems, $58,164.00

Proposals Submitted/Awaiting Decision

- Professor Greg Lafyatis (OSU-Physics) submitted a proposal to the National Science Foundation's Physics Division, titled "Cold Atoms on Optical Waveguides," which leverages the OSU-NPL facility. Total request: $500,833 over 3 years.
- A multi-disciplinary proposal for the MURI program funded by the Army Research Office was submitted by The Ohio State University, Kent State University, and Rensselaer Polytechnic Institute. The PI is Professor Wu Lu from the Department of Electrical and Computer Engineering at Ohio State. The title is Integrated GaN sensors for Multivariate WMD Threat Identification and the researchers have proposed $5,033,647 for 5 years, 4/1/2007-3//31/2012. This work will use the

EBL lab for much of the fabrication work. The Co-PIs are Wu Lu (lead), Leonard Brillson, L. Jim Lee, Stephen Lee, Steven Ringel, Fred Schubert, Qi-Huo Wei

- A multi-university Wright Center of Innovation proposal for photovoltaic work proposal mentioned EBL directly, especially for its availability to support a) nanotechnology for PV and b) photomask generation for rapid prototyping. The proposal was submitted 6/21/06, with a decision expected 12/15/06, and a tentative start date Feb. 2007. The title is "Wright Center for Photovoltaics Innovation and Commercialization" (PVIC), lead by the University of Toledo with partners at Ohio State University and Bowling Green State University. Total request is $18.1M.
- Professor Wu Lu at Ohio State has submitted an NSF proposal for III-Nitride Heterojunction Field Effect Transistors for Biological Sensing, PI: Wu Lu, National Science Foundation, Funding Requested: $291,186, 4/1/2007 to 3/31/2010.
- An interdisciplinary team, lead by Malcolm Chisholm (Chemistry) with team members, Arthur J. Epstein (Physics/Chemistry), Paul R. Berger (ECE/Physics), Steven A. Ringel (ECE/Physics/MSE), Nitin P. Padture (MSE) and Terry L. Gustafson (Chemistry) titled "Novel Hybrid Organic-Inorganic Solar Conversion Systems," submitted to Basic Energy Science at the Department of Energy. Budget: $2,868,669 over 3 years.

Publications

Many of the results from work performed in the first year of the EBL have not been published yet, as the EBL work is only a small portion of the overall device or project. We expect the first installment of OSU-NPL work performed in 2006 to result in submissions and publications in early to mid 2007.

Professor Derek Hansford and a Ph.D. student in his research group, Nick Ferrell, have submitted an abstract, however, to the Materials Research Society conference for Spring 2007. They are currently awaiting a decision. The title of the work is "Micro/Nanofabrication by Spin Dewetting on a Poly(dimethylsiloxane) Mold"

Graduate Students Completing Thesis/Dissertations

Ms. Hang-Yan "Polly" Yuen at Iowa State (Material Science Engineering) has now defended her Ph.D. dissertation which included work done by OSU-NPL (see Table 2).

Technology Transfer Activity

As of yet, there have not yet been formal patent or licensing activities associated with the EBL system. However, we work with several startup companies to fabricate structures for their proprietary technology. Typically, small companies cannot afford the capital necessary for purchasing, maintaining, or operating an EBL system, but require its services. Since the OSU EBL's acceptance, many companies have either begun work that they could not have performed previously or have moved their work to OSU from other remote sites, often outside the State of Ohio. See Table 2 for examples of industrial users. We have several users who have used EBL systems located outside Ohio in the past and have now begun performing their work at OSU for either convenience, ease of use, or enhanced quality. It is also important to emphasize that the

OSU-NPL is exempt from the restrictions imposed by the NNIN about public disclosure, which make it difficult for NNIN's to handle proprietary industrial and government projects. Therefore, the needs of the State of Ohio and it constituency is better served through this OBOR supported facility.

Table 2- OSU NPL active users as of 12/15/2006.

User	Affiliation	Department	State of Ohio	# of Part i	Project Area	Level of Use
Prof. Greg Lafyatis	Academic – The Ohio State University	Physics	Yes	2	Atomic Physics /Quantum Computing	High
Prof. Chris Hammel	Academic – The Ohio State University	Physics	Yes	2	Spintronics	Low
Prof. Nitin Padture	Academic – The Ohio State University	Materials Science & Engineering	Yes	3	Heterojunction Nanowires	Mediu m
Prof. Arthur Epstein	Academic – The Ohio State University	Physics	Yes	3	Conducting Polymers /Polymer Electronic Devices	Mediu m
Prof. Paul Berger	Academic – The Ohio State University	Electrical & Computer Engineering	Yes	4	Nanoelectronics and Remote Sensing of Threats	High
Prof. Patricia Morris	Academic – The Ohio State University (collaboration with Wright Patterson Airforce Base)	Materials Science & Engineering	Yes	2	Electro-optic Modulator	Mediu m
Prof. Liwei Chen	Academic – Ohio University	Chemistry & Biochemistry	Yes	2		Low
Prof. Derek Hansford	Academic – The Ohio State University	Biomedical Engineering	Yes	2	Soft Lithographic Techniques for nano-biological applications	Low
Dr. Jingjiao Guan/Profes sor James Lee	Academic – The Ohio State University	NSEC / Chemical Engineering	Yes	2	Bio-MEMS/Sensors	Low
Prof. Wu Lu	Academic – The Ohio State University	Electrical & Computer Engineering	Yes	4	Large Bandgap Semiconductors / NEMS / Sensors	High
Dr. Robert Davis	Academic – The Ohio State University	Ohio State Nanotech West Lab	Yes	3	Nanoimprint Lithography	Mediu m
Professor	Academic – The	Physics	Yes	3	Conducting	Low

Arthur Epstein	Ohio State University				Polymers	
Prof. Steven Martin	Academic- Iowa State University	Materials Science & Engineering	**No**	1		Medium
Army Research Lab	Government		**No**	1	Sensors	High
Battelle Memorial	Industrial		Yes	2	Sensors	Medium
Prof. Stefan Zauchser	Academic – Duke University		**No**	2	Surface Plasmon Resonance	Low
Gainesville Fl. Company (name proprietary)	Industrial		**No**	2	Proprietary	Low
Lakeshore Cryotronics	Industrial		Yes	1	Proprietary	Low
Srico	Industrial		Yes	2	Proprietary	Low
Analex	Industrial		Yes	1	Proprietary	Low

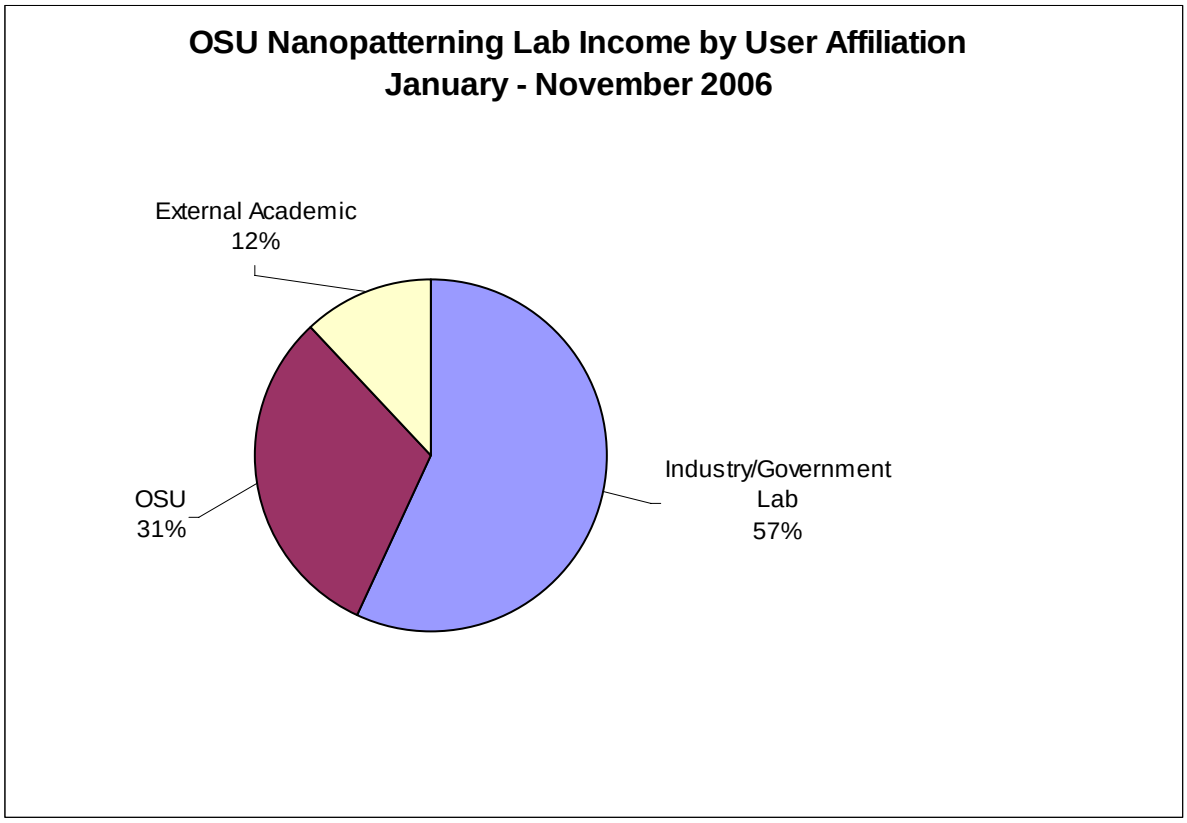


Figure 2 –OSU NPL users by affiliation. Note that the breakdown of lab costs are ~1:2:6 for OSU: external academic: industrial users. The lab is highly used by OSU users, but the fees are substantially lower resulting in lower percentage of income from OSU research.

Center for the Accelerated Maturation of Materials: An Enterprise for Visualization, Imaging, Simulation and Modeling

Partners: ***Ohio State University,*** University of Cincinnati, Wright State University, Air Force Research Laboratory, Knolls Atomic Power Laboratory, Alcan Technology & Management, Ford Motor Company, The Timken Company, GE Aircraft Engines

Summary

This document describes the significant degree by which the equipment provided the Hayes Investment Fund has enabled the Center for the Accelerated Maturation of Materials (CAMM) to make real progress towards its principal objectives. CAMM involves a multi-disciplinary and multi-institutional approach to provide for major technological advances to significant sectors of the State's and Nation's industrial base and to deliver significant advances to science and technology. The stated objectives of the center are to: provide a new approach to the development of high performance materials allowing for their accelerated maturation into components; translate this approach into a broad-based educational effort; and, effectively transfer newly developed concepts on materials development to materials-based industries through direct partnerships and through asynchronous web-based instruction and tools which will be accessible remotely.

The equipment provided under this program has enabled significant progress to be made in the collaborative research programs of the PI's. For example, there has been extended research into novel alloys with enhanced elevated temperature performance, investigations into the effect that nanoscaled microstructural features impact properties, process modeling of novel manufacturing techniques, atomistic simulations of defects in both semi-conductors and metallic systems, characterization of elemental distributions of species, and progress towards providing remote access to state-of-the-art characterization techniques. Additionally, based on equipment provided in this program, CAMM leveraged the investment and has secured funding from the Air Force and the Office of Naval Research for programs based on the technologies developed under this program. Additionally, CAMM is in a strategic position to now compete for large, long-term Center-type funding and has developed a business plan that would ultimately result in a division of a company to be established on the campus of The Ohio State University.

Technological Progress Made

Combinatorial Methodology – Hamish Fraser

The acquisition of the hot isostatic press (HIP) and the enhanced inert gas and vacuum chamber for the ETMT (*fig. 1*) has directly impacted the ability to perform combinatorial research within CAMM. After the acquisition of these two pieces of equipment, researchers within CAMM have been able to prepare and test β-stabilized Ti-based alloys with the end goal

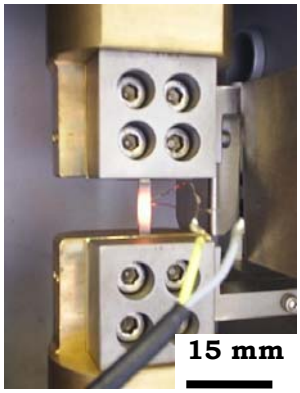


Fig. 1: Sample in ETMT for rapid investigation of creep

being an increase in the maximum operating temperature for Ti-based alloys by optimizing the balance of the two limiting properties, namely creep and oxidation resistance. The methodology is based on a combinatorial approach where a large number of different alloy compositions can be produced using an additive manufacturing route, processed using the HIP, and subsequently tested in inert gas using the inert gas and vacuum chamber of the ETMT. By increasing the operating temperature by 50°C, it is possible to improve the overall performance of engines or decrease their gross weight by replacing higher density materials such as Ni-based superalloys with lower density materials, such as new β-Ti alloys. Additionally, such materials have been identified as materials for acreage thermal protection systems (i.e., skins or subskins of high speed aircraft of re-entry vehicles). While still being investigated to determine underlying scientific mechanisms, material has been produced and tested, and data analyzed by personnel from the Wright PattersonAir Force Base and from Timet (Toronto, OH and Henderson, NV).

Advanced Characterization Techniques

The program also supported the acquisition of a state-of-the-art transmission electron microscope with the highest possible performance in the world (*see fig. 2*). Such a microscope has allowed researchers to investigate the early stages of materials microstructural evolution, as well as the role that nanoparticles and nanoscaled microstructures play on the performance of materials. This has been directly leveraged into other programs, as will be described below. Additionally, the program has supported the purchase of an electron probe microanalyzer for the direct quantification (at a level of 10's-100's of parts per million) of the distribution of elemental species in a material. Ultimately, the quantification (rather than semi-quantified methods that currently exist) of such distributions will be vitally important to both experimentalists and modelers, as they play an important role in the spatial-temporal evolution of materials.

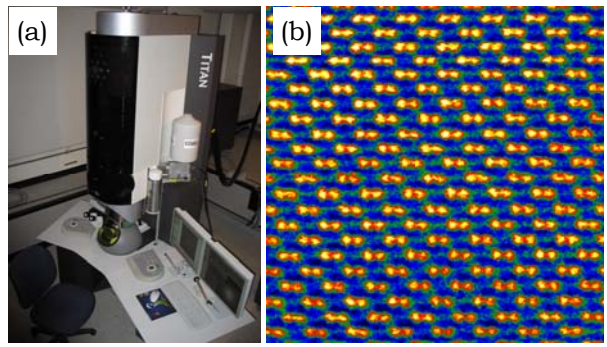


Fig. 2: (a) The Titan TEM at OSU after installation (b) False color images of Si atomic "dumbbells" showing the resolution

Remote Access and Web-based modules

An effort at providing real-time remote access to computational models and research equipment is continuing under the support of the VIM program and under the guidance of the PI. Initial work carried out under this program showed that the methodologies, while technically feasible, were not optimized. Currently, effort is underway to aid in the maturation of attractive remote-access technologies, and to also provide for web-based training modules. Work to increase the functionality of web-based storage and equipment reservations occurred during the scope of this program. An undergraduate team working with J. Wilkins established a working web portal. Currently it is not available to public but all the software exists and could be installed. Most likely it will move to Ohio Supercomputer Center (OSC) where an additional security label will be necessary to protect OSC databases.

First Principals Research – John Wilkins

Although limited funding could be provided for personnel, there is a continued strong commitment to simulation and visualization of multiscale physical processes. A team has made great progress in simulation and visualization efforts, with a recent modeling and visualization effort focused on 500 random interstitial defects in a lattice of 8000 Si atoms formed in a nanosecond (physical time) a dense atomic layer of interstitials known in the industry as the {311} defect. The most striking aspect of this work is that an order of magnitude smaller test took an order *longer* time to form a starter {311} defect. Larger trials based on disordered material produced by the modeling of irradiation doping will be used as the initial material thus removing any artificiality to the demonstration. This supports the participants' conjecture that earlier negative estimates of difficulty underestimated the acceleration of local processes in the presence of a larger driving force (e.g., defect concentrations). Work on metallic alloys is ongoing. The density functional theory can reproduce the measured phase diagram is nearly complete. Subsequently a classical potential shall be developed and tested. This will allow metallic studies similar to the silicon example above to demonstrate ability to model and visualize the formation of alloy mesoscale structure.

Simulation and Modeling at Wright State University

The WSU funds were used to establish the CAMM Materials Modeling & Simulation Laboratory located in room 018 Russ Engineering Center. The facility houses state-of-the-art computer hardware and commercial software for the simulation and modeling of advanced materials and manufacturing processes, and has seating for up to six graduate or undergraduate student researchers. The facility has leveraged other external support from both NSF and AFRL/DAGSI for basic research in two areas directly related to the accelerated maturation of materials. The first area is modeling and simulation of solidification microstructure in laser additive manufacturing, which allows rapid development and efficient fabrication of advanced materials for aerospace applications. One M.S. and one Ph.D. student have completed their degrees working in this area. The second area is simulation and modeling of dissipated energy during fatigue crack growth, which will potentially enable the rapid evaluation of prospective new materials without the need for extensive crack growth testing. One Ph.D. student completed his degree working in this area, and a second is slated to complete his M.S. in August, 2007.

Enhanced Characterization Capabilities at the University of Cincinnati

The main objective of this project was to advance the science of visualization, imaging, simulation and modeling of advanced materials. At the heart of this lies the characterization and representation of the microstructure of materials, which, in turn, requires advanced tools. The equipment purchased through this award, which is described in more detail later, included those for sample sectioning and polishing; preparation of thin foils for transmission electron microscopy (TEM); device for analysis of the compositions of phases in the TEM; and devices for electron backscatter diffraction/orientation imaging and chemical compositions of phases in the scanning electron microscope (SEM).

The above pieces of equipment and related techniques were utilized for the characterization of materials in a number of research projects, including: 1) Nanostructured alloys; 2) New, cast high temperature aluminum alloys and nanocomposites for diesel engine applications; 3) Delamination and fracture behavior of Al-Li alloys; 4) Phase transformations in titanium alloys and aluminides; 5) High temperature, multicomponent Nb-Ti-Si-X alloys; 6) Creep and microstructure of refractory Mo-Si-B alloys; 7) Advanced boiler materials for ultra supercritical coal power plants; 8) Surface-treated and cold-worked Nickel-base superalloys; 9) Laser shock peened aero engine alloys; and 10) Mixed metal oxide catalysts. Through these efforts, considerable advances were made in visualization, imaging, simulation and modeling of these materials and valuable new insight was obtained on materials phenomena pertaining to microstructure evolution, mechanical and other properties, deformation, fracture and oxidation mechanisms.

Leveraging of Results

The Center for the Accelerated Maturation of Materials (CAMM) was not only able to compete for several additional funding opportunities during the scope of the program, including a strong commitment by the Air Force Office of Scientific Research (STW-21 program) and the Office of Naval Research (ONR-D3D), but was also able to build upon the strong interaction among the PI's on this program and expand those interactions to include several other individuals. As a result of the nurturing of the multidisciplinary interactions and their expansions, CAMM has now strategically positioned itself to attract a large business to commit to establishing a commercial division on the campus of The Ohio State University. While the initial efforts to secure State (WCI) funding were unsuccessful, the team, including multiple universities, several Eminent Scholars, and committed Industrial partners, will pursue both State and Federal funding to develop a Center aimed at the Automated Characterization of Nanoparticles and Nanostructures. The commitment of the involved parties is reflected in the level of cash cost-share, and reflects a significant leveraging of this existing, successful program. Of immediate interest to this center is the characterization of the nearly 20,000 nanoparticles that have been identified (but not investigated) as potential carriers of drugs to target particular types of cancers. Additionally, proposals based on the results obtained using this equipment are currently under review. One such program is based on the early stages of particle nucleation and growth, a subject of immediate interest to both the industrial and scientific communities. Finally, based in part upon the initial investigations, CAMM was able to pursue additional state funding for the establishment of the Visualization, Instrumentation, and Modeling program, making use of the Third Frontier Network for Remote Microscopy applications.

Additionally, collaborators at partnering universities were able to leverage the funding provided by the Hayes Investment Fund for several other research opportunities. Collaborators at Wright State University were able to leverage the funds for two new programs, and also enhance the support committed to two existing programs. The total amount of funds leveraged for programs involving Wright State University was nearly $600k. Likewise, collaborators at the University of Cincinnaty leveraged funds to obtain a number of new grants pertaining to advanced materials and surface treatment of aerospace engine alloys.

Number of Students Graduated

The funding provided with this program supported the research and enabled 16 students to graduate during the scope of the program, eight with their masters and eight with their doctoral degree. Specifically, Hamish L. Fraser graduated 3 MS and 4 PhDs, Vijay Vasudevan graduated 4 MS and 2 PhDs, and Nate Klingbeil graduated 1 MS and 2 PhDs.

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Presentations

Additionally, collaborators contributed to more than 50 presentations during the scope of the program.

Technology Transfer Activities

None

Collaborations Established

As a result of this program, CAMM was able to establish an effective partnership with FEI, and are jointly pursuing the establishment of a large center to be located on the west campus of The Ohio State University aimed at the automated characterization of nanoparticles and materials. Additionally, CAMM is now in negotiations with several industries, including Timet, Timken, and Alvac, about joining CAMM as paying members. Additionally, during the scope of this program, several international collaborations were established, including formal collaborations with The Institute for Materials Research (China) and Monash University (Australia). The University of Cincinnati was able to establish collaborations with GE Infrastructure Aviation; Rolls-Royce, LSP Technologies; Cummins Inc.; Accutek Inc.; Aerospace International Materials; UES Inc.; Air Force Research Laboratory, WPAFB; Oak Ridge National Laboratory; and The Ohio State University

Equipment Acquisitions

The Ohio State University
AIP Hot Isostatic Press for Combinatorial Methodologies
Enhanced Inert Gas and Vacuum Chamber for the ETMT (Combinatorial Methodologies)
Cameca Electron Probe Microanalyzer
FEI Transmission Electron Microscope
4-PI EDS detectors and image processors (plus computers and peripherals)
Computational Tools

Wright State University
HP XW8200 Dual-Processor 64-Bit Intel Xeon Linux Workstation and Peripherals
HP NX9600 Laptop Computer and Peripherals
Apple MacBook Pro Laptop Computer and Peripherals
HP ZX6000 Dual-Processor Intel Itanium Linux Workstation and Peripherals
HP XW8000 Dual-Processor 32-Bit Intel Xeon Linux Workstation and Peripherals
Apple G5 Dual-Processor Desktop Computer and Peripherals
Apple G4 Laptop Computer and Peripherals

University of Cincinnati
The following equipment was acquired from this award:
Fischione Model 150 Dimple grinder
Fiscione Model 1010 low angle ion milling system
Fischione Model 130 Specimen Punch
Fischione Model 160 Specimen Grinder
Buehler Isomet 5000 Linear Precision Saw
Buehler Electromet-4 Polisher/Etcher
MHI Z-Series Z17 1700°C Box Furnace
Genesis XMS 2000 energy dispersive x-ray analysis (EDS) system from EDAX for the FEI CM20 TEM
Pegasus 4040 Integrated OIM 4000/Genesis 4000 EBSD/OIM and EDS system for the XL-30 ESEM from EDAX-TSL Co.

Consortium for Affordable Manufacturing of Polymers at the Nanoscale

Final Research Progress Report

Partners: ***Ohio State University,*** *University of Akron, University of Dayton, Cleveland Clinic Foundation, Air Force Research Laboratory, Ashland Specialty Chemical Company, Applied Sciences, Inc., Owens Corning, Procter & Gamble, Honda*

A. Introduction

Demand has been growing rapidly for products with nanoscale features and functions for industrial, information, biomedical, and environmental applications, presenting significant career opportunities for future generations. However, manufacturing at the nanoscale is new and largely unknown, evaluation of its economic and environmental implications also needs to be addressed. We are addressing these issues through a multi-institutional, interdisciplinary Consortium for Affordable Manufacturing of Polymers and Composites at the Nanoscale, with broad-based research, education and outreach programs, centered at The Ohio State University (OSU) with satellite facilities at The University of Akron (UA) and University of Dayton (UD). Collaborators include more than 10 companies in and outside of Ohio, Wright Patterson Air Force Laboratories (Dayton) and the Cleveland Clinic Foundation.

Our research and development efforts focus on affordable manufacturing of nanoparticle-reinforced polymer structures for applications in two specific fields: **Polymeric Nanocomposites** and **Polymer/Composite Based Biomedical Devices**. Our **objective** is to combine robust traditional manufacturing approaches with new nano-manufacturing concepts to enable commercial realization of new products and improvement of existing products. We are collaborating with industry and national labs via joint projects, NIST-ATPs, SBIRs, and other opportunities. **Our education and outreach goal** is to integrate the latest research developments into a practical student curriculum and to impart the necessary multidisciplinary skills to both graduate and undergraduate students. This includes introducing nano-manufacturing and related topics into the curriculum and arranging internships in industry and national labs.

B. Technical Progress Report

A short report follows that describes each major equipment item obtained through the award and its impact; as well as direct outcomes resulting from the new equipment including leveraged funding, publications, technology transfer, and collaborations that have resulted.

The Ohio State University

Femtosecond Laser System – David Farson – The femtosecond laser is being effectively used for a wide range of micro/nano scale machining for fabrication of various devices. Ultrashort laser pulses (with a duration of 150 fs or 150 x 10^{-15}

second) have a very high peak power, and consequently can machine materials more precisely than conventional nanosecond pulsed lasers (with typical pulse durations of 10 ns or 10 x 10^{-9} second). The femtosecond laser has been widely used to date for biomedical applications, display applications, and industrial material processing applications, such as: (1) producing very precise patterns on the mesh surfaces of electro-spun PCL fiber for tissue engineering scaffolds; (2) fabricating part of a simple DNA stretching device on PDMS (polydimethyl siloxane) by creating thousands of 2μm wells within a second; (3) combining femtosecond laser micromachining with hot embossing to develop magnetic particle separation devices with 50μm and 8μm microchannels, potentially useful for cancer diagnosis and fabrication technology at an affordable price; (4) for display fabrication by clean ablation of ITO (Indium Tin Oxide), a transparent conducting film layer which must be patterned for fabrication of LCD display electrodes; and (5) enhancing lubrication of bearing and die surfaces for industrial applications by combining the femtosecond laser with a digital micro mirror array device (DMD) for programmable maskless area ablation. To contribute to education and outreach goals, various demonstrations and workshops are regularly held for local high school and freshman college students, in which students learn the basic physics and principles of femtosecond laser micromachining. Students participate in a hands-on experience using the laser to create micro- and nano-scale features on a polymer. In addition, a lecture on femtosecond laser processing is presented as part of a nano-fabrication technology group studies course to senior- and graduate-level engineering students.

EVG 620 Precision Alignment System – L. James Lee -- The EVG 620 aligner is effectively used by many students and post-docs at OSU for research and training. Participating departments and centers include Chemical and Biomolecular Engineering, Industrial, Welding, & Systems Engineering, Electrical and Computer Engineering, Biomedical Engineering, the Biophysics program and the Nanoscale Science and Engineering Center (NSEC) for Affordable Nanoengineering of Polymeric Biomedical Devices. The EVG 620 alignment system is mainly used for photolithography, the standard microfabrication technique employed by the microelectronics industry. We also use the EVG 620 aligner for nanoimprint lithography, a relatively novel method capable for generating nanometer scale patterns with high throughput and low cost. Microcontact printing is another technique successfully used with the EVG 620 aligner. The EVG 620 aligner has excellent ability for alignment at 1 μm resolution. We also use it to align mold and substrate and for subsequent embossing performed in our EVG 520 embossing system. Microstructures have been fabricated by our EVG 620 Precision Alignment System for a variety of applications, such as biomedical devices and biosensors.

Microinjection Molding Machine – **Kurt Koelling** – We have not yet determined whether to purchase a machine that can mold accurate microscopic features on larger products, or one that can accurately mold tiny products (such as plastic lenses for cell phone cameras). In today's market it is not possible to purchase a single machine that can do both.

Hitachi S-3400 Field Emission SEM – C. H. Menq – The objective of our research is to develop efficient and robust manipulation methods for nanoparticles and biomolecules with ultra high precision, essential for characterizing nanocomposites and developing biomedical devices. The nanometer resolution imaging capability of the

Hitachi S-4300 Field Emission Scanning Electron Microscope (SEM) greatly enhances our research toward this objective. Its real-time imaging capability provides the necessary guidance and feedback that enable automated manipulation of micro/nano structures. Due to a high image resolution, the SEM has also become a core instrument in NSEC, characterizing various products ranging from biomedical sensors and micro machining tools, to nanofluidic channel molds and 3D tissue scaffolds. It helps researchers improve design and manufacturing processes. Other researchers outside the center have also benefited from this instrument, such as studying the strength and damage of thin film coatings. These activities facilitate collaborations among various departments, including mechanical engineering, electrical engineering, chemical engineering, and industrial and welding engineering. More than 20 graduate students from the engineering college have been trained to use this instrument. Moreover, many undergraduates have gained experience with the latest nanotechnology through the REU (Research Experience for Undergraduates) program.

Moore Nanotechnology 350FG Three Linear Axis – Allen Yi – Since the Nanotechnology 350 ultraprecision machine was installed in 2004, we have worked continuously on different projects. We developed the slow tool servo diamond-turning process for micro- and nanoscale machining on different materials, including common engineering metals (nickel, aluminum and copper) and polymers (e.g., Polymethylmethacrylate or PMMA). A unique capability of the 350 ultraprecision machine (compared to expensive cleanroom processes) is that it allows real 3D micro- and nanoscale features to be machined directly without a photomask, therefore providing an economic and accurate platform for small-batch micro- and nanoscale fabrication. In one experiment we demonstrated the direct manufacturing capability of the micromilling process on water-soluble polymer material for 3D microstructures. These results were published in several peer-reviewed journals as a demonstration of their academic and industrial values. As one of the primary tools for non-cleanroom nanoscale manufacturing, we have used this machine in creating mold inserts and stampers with nanoscale features for various groups from both inside and outside of OSU. The 350 ultraprecision machine provides an ideal platform for the integration with other high-precision devices (such as the femtosecond laser), and its multi-axis movements with nanometer accuracy allows fabrication of real 3D devices with high aspect ratio nanometer pores or grooves. A full-time, highly qualified research technician was hired to support the equipment. The equipment and technician together allow us to offer full capabilities for non-cleanroom 3D micromachining processes.

University of Akron

Nanocomposite Synthesis and Compounding System – William Brittain – Prof. Brittain recently left the University of Akron for a job in private industry. We have been unable to reach him for a report.

University of Dayton

X-Ray Diffraction and X-Ray Spectrometry – Khalid Lafdi – This state-of-the-art equipment is a primary way that Ohio can achieve better quality control of its manufacturing processes and assure enhanced competitiveness, especially in the area of characterizing nanocomposites. The ability to study these novel materials at

different lengths of scale is crucial for future economic competitiveness. Many research projects from military to commercial goods have already benefited from these capabilities to visualize and derive information on the size, orientation, morphology and dispersion of nanoparticles and to measure their physical properties (i.e., stiffness, strength, ability to dissipate heat and conduct electricity) and relate these properties to the manufacturing processes.

C. Measurable Outcomes from this Award

1. Leveraging results – external awards received as an outcome of this Hayes award

Title	Affiliated Faculty	Sponsor	Total Award	Duration
Nanoscale Science and Engineering Center: Affordable Nanoengineering of Polymeric Biomedical Devices	Lee	National Science Foundation	$12,900,000	5 years
Evaluating the Impacts of Nanomanufacturing via Thermodynamic and Life Cycle Analysis	Lee	Environnmental Protection Agency	$375,000	2 years
Microfluidic CD Biochips for Enzyme-Linked Immunosorbent Assays	Lee	Bioprocessing Innovative Co Inc	$42,000	3 years
Surface Texturing by Femtosecond Laser Ablation	Farson	Edison Welding Institute	$116,000	2 years
Nanoscale solid freeform fabrication process with a photo-assisted spark plasma thermal source	Farson	National Science Foundation	$350,000	3 years
Femtosecond laser ablation for LCD panel repair processes	Farson	LG Electronics	$2,500	1 year
Fabrication and Characterization of Exfoliated Graphite	Lafdi	Wright Brothers Institute, DoD	$50,000	1 year
Fabrication and Thermal Evaluation of Aligned carbon nanofibers	Lafdi	Northrop of Grumman	$40,000	5 months
Fabrication and Heat transfer study of carbon nanofluid and carbon foams	Lafdi	DoD	$40,000	5 months

Development of an Automated Visually Guided Motion Control System for Multi Scale Imaging and Manipulation of Biological and Engineered Systems	Menq	National Science Foundation	$420,000	3 years
Precision Compression Molding of Glass Optics	Yi	Fraunhofer Munich and Fraunhofer Institute of Production	56,650	2 years
Ultraprecision Diamond Micromachining for 3D Self-Assembled MEMS Devices	Yi	DARPA	$125,000	2 years
Slow tool servo diamond turning of optical components	Yi	Northrop Grumann	$147,916	2 years
		Total	**$14,665,066**	

2. Number of graduate students who completed theses/dissertations under this award

   3 M.S. and 2 Ph.D. students completed theses/dissertations
   2 M.S. and 14 Ph.D. theses/dissertations in process

3. Publications resulting from this award

Elgafy A., and Lafdi K., (2006), "Engineering solution in monitoring nanoparticle-fluid flow during nanocomposites processing" Accepted for publication by Journal of Nanoparticle Research, Ref. No. NANO273R1, April 2006.
Elgafy A., and Lafdi K., (2006), "Carbon Nanofluids flow behavior in novel composites," Journal of Microfluidic Nanofluidic, ISSN: 1613-4982 (Paper) 1613-4990, March 2006 (Available Online).
Elgafy A., Lafdi K., (2006), "Carbon nanoparticle-filled polymer flow in the fabrication of novel fiber composites," Carbon Journal, Ref. No. 3952, in Press.
D. F. Farson, H. W. Choi, S I Rokhlin, *"Electrical discharges between platinum nanoprobe tips and gold films at nanometer gap lengths"* Nanotechnology, 17(1):132-139 Jan. 2006.
D. Farson, H W Choi, C Lu, and L. James Lee *"Femtosecond bulk laser micromachining of microfluid channels in PMMA"* Journal of Laser Applications, 18 (3): 210-215 Aug. 2006

G. C. Firestone, A. Y. Yi, "Precision Compression Molding of Glass Microlenses and Microlens Arrays – An Experimental Study," *Applied Optics*, 44 (29) October 10 (2005).

L. Li, A. Y. Yi,* C. N. Huang, David Grewell, Avraham Benatar, Y. Chen, "Fabrication of Diffractive Optics by Use of Slow Tool Servo Diamond Turning Process," accepted for publication in *Optical Engineering*, April (2006).

Mesalhy O., Lafdi K., Elgafy A., (2006), "Carbon foam matrices saturated with PCM for thermal protection purposes," Carbon Journal, Ref. No. 3904, in Press.

D. G. Yao, P. Nagarajan, L. Li, A. Y. Yi, "A Strategy for Rapid Thermal Cycling of Molds in Thermoplastic Processing," in press, *ASME, Journal of Manufacturing Science and Engineering*, March (2006).

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S. Lai, X. Cao and L.J. Lee, "A Packaging Technique for Polymer Microfluidic Platforms", Analytical Chemistry, 76, 1175-1183 (2004).

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H. He, X. Cao and L.J. Lee, "Design of a Hydrogel Based Intelligent System for Controlled Drug Release", Journal of Controlled Release, 95(3), 391-402 (2004).

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Y. Yang, X. Hu, L.J. Lee and K.W. Koelling, "Investigation of Structure Evolution in Polymer Blending Using Microfabricated Samples", Polymer, 45(6), 1959-1969 (2004).

S. Wang, C. Zeng, S. Lai, Y.J. Juang, Y. Yang and L.J. Lee, "Polymeric Nanonozzle Array Fabricated by Sacrificial Template Imprinting", Advanced Materials, 17, 1182-1186 (2005).

C. Lu, Y-J. Juang, L.J. Lee, D. Grewell and A. Benatar, "Analysis of Laser/IR-Assisted Micro-embossing", Polymer Engineering & Science, 45(5), 661-668 (2005).

G. Xu, L. Yu, L.J. Lee and K.W. Koelling, "Experimental and Numerical Studies of Injection Molding with Microfeatures", Polymer Engineering & Science, 45, 866-875 (2005).

Y. Yang, L.J. Lee, and W. Lu, "Subcritical Carbon Dioxide Assisted Polymer Nanofabrication at Low Temperatures", Journal of Vacuum Science and Technology B, 23 (6), 3202 (2005).

L.J. Lee, "Polymer Nanoengineering for Biomedical Applications", Annals of Biomedical Engineering, (34)1, 75-88 (2006).

H. He, J. Guan, L.J. Lee and D. Hansford, "An Oral Delivery Device Based on Self-Folding Hydrogels", Journal of Controlled Release, 110, 339-346 (2006).

4. Technology transfer activities (patents, licenses, start-ups, etc.):

- Invention disclosure: Processing of high purity exfoliated graphite
- "Gas assisted material removal for internal channel fabrication on transparent material," Invention disclosure (OSU: #05080) with D. Farson and H. Choi
- A start-up company, BioLOC has been established by L.J. Lee and S.T. Yang with technology focus on polymer based biochips
- L.J. Lee, S.T. Yang, and S. Lai, "A CD-like Microfluidic Platform for Enzyme-Linked Immunosorbent Assay" U.S. Provisional Patent Application filed on November 8, 2004, patent pending.
- L.J Lee and S. Lai, "Gas-Assisted Resin Injection Technique for Bonding and Surface Modification of Microfluidic Devices", U.S. Provisional Patent Application No. 10/438,278 files on May 14, 2003, patent pending.
- L.J. Lee, S. Wang, Y. Xie and C. Zeng, "Polymeric Nanonozzle and Nanotip Array Cell Patch for Drug and Gene Delivery", U.S. Provisional Patent Application No. 60/728,465, filed October 20, 2005.
- L.J. Lee, and C. Lu, "Design of Superhydrophobic Valve for Plastic Microfluidic Chips" U.S. Provisional Patent Application filed on November18, 2005.
- J. Guan, L.J. Lee and D. Hansford, "Fabrication of Polymeric Micro-Devices for Drug Delivery by Surface Patterning and Self-Folding", U.S. Provisional Patent filed, 2005.

5. Collaborations established (new or enhancement of existing ones with other universities or industry)

- Texas A&M University, Nanocomposites and foams, collaboration with Dr. O. Oochoa
- Georgia technical University, Nanotribology, collaboration with Dr. Z. Yuri
- Chalmers University, Sweden, Nanorelay devices with Dr. Olin Hakan
- Czech Republic, Spine Surgery with Dr. K. Balik (Czech Academy of Sciences)
- Czech Republic, NSF grant with Dr. Z. Weiss (University of Ostrava)
- Taiwan, Chung Yuan University with Professor Shia-Chung Chen
- China, Zhengzhou University with President C.Y. Shen
- Korea, National Seoul University with Dr. Woo Lee
- France (1994), University of Bordeaux with Dr. P. Lecoustumer
- LG electronics is one of leading display manufactures in the world. We had fundamental study of ITO ablation for LCD applications.

- IMRA America is a manufacture of femtosecond laser system and the collaboration was established to study the high speed femtosecond laser application on ITO ablation.
- EWI has been sponsoring corporation-research project for texturing on biomedical and industrial applications with femtosecond laser and DMD (digital mirroring device).
- LMTB is a German based company and technical/scientific information for ITO patterning was shared. The collaborative publication is being prepared with an engineer at LMTB.
- Prof. Avi Benatar, micro and nano scale optical fabrication. The results were published in two different papers.
- Prof. Eric Marsh (Penn State) and Prof. Ryan Vallance (George Washington), micromachining research. Prof. Vallance's expertise is on micro tool fabrication and Prof. Marsh's expertise is on machine tool metrology and characterization.

6. EQUIPMENT PURCHASED TO DATE (see attached spreadsheet for summary by category)

Purchased to Date

EVG610 Precision Alignment System	OSU: Lee
Moore Nanotechnology 350FG three linear axis	OSU: Yi
Clark MXR femtosecond pulsed laser system	OSU: Farson
Hitachi S-3400 Field Emission SEM	OSU: Menq
Nanocomposite synthesis and compounding system (not confirmed)	UA: Brittain
X-Ray Diffraction and X-Ray Spectrometry	UD: Lafdi

Pending

Microinjection Molding Machine	OSU: Koelling

Hydrogen Storage Production Consortium

Final Research Progress Report

Partners: ***Ohio State University,*** *Kent State University, University of Akron, University of Cincinnati, NexTech Materials, Ltd.*

University of Akron, Steven Chuang

Goal and Objectives:

Develop better catalysts and sorbents with high activity for H_2 production, fuel cell, CO_2 capture, and photocatalysis through fundamental study of the reaction/adsorption mechanisms.

Leveraging results:

"Coal-based Fuel Cell," Ohio Coal Development Office, $160,000, 9/1/05 - 8/31/07.

"Metal Monolithic Amine-grafted Zeolites for CO2 Capture," U.S. Dept of Energy, $764,995, 2/1/07 – 1/31/10 (Pending undergo negotiation with DOE)

Number of graduate students who completed thesis/dissertations under this award:

1. R. Khatri, Dissertation, " In Situ Infrared Study of Adsorbed Species during Catalytic Oxidation and CO_2 Adsorption," 2005.
2. F. Guzmann Montanez, M.S. Thesis," Smarium-based Intermediate Temperature Solid Oxide Fuel Cells," 2005.
3. D. Miller, M. S. Thesis," In Situ Infrared Spectroscopy Study of Gold Oxidation Catalysis," Augurst, 2006.
4. J. C. Fisher II, M.S. Thesis," A Novel Fuel Cell Anode Catalyst, Perovskite LSCF: Compared in a Fuel Cell Anode and Tubular Reactor," August 2006.

Publications resulting from this award:

1. "Catalysis of Solid Oxide Fuel Cell," Steven S. C. Chuang, Catalysis: Volume 17 Series: Specialist Periodical Reports, Ed. J. J. Spivey, Vol. 18, pp 186-198, Royal Society of Chemistry, Cambridge, U.K., 2005.
2. "CO_2 Capture by Diamine-grafted SBA-15: A Combined FT-IR and MS Study," R. Khatri, S. S. C. Chuang, M. Gray, and Y. Soong, Industrial Engineering Chemistry, Res, 44, 3702-3708. 2005.
3. "Thermal and Chemical Stability of Regenerable Solid Amine Sorbent for CO_2 Capture," R. Khatri, S. S. C. Chuang, M. Gray, and Y. Soong, Energy&Fuels, 20(4), 1514-1520, 2006

4. "In situ IR-TPD Study of the Synthesis of C_3-Oxygenates from Propylene Partial Oxidation over a Rh/Al_2O_3 Catalyst," R. Singh, S.S.C. Chuang, and R. Khatri, CIENCIA, 14, 135-149, 2006.
5. "In Situ IR Study of Adsorbed Species and Photogenerated Electrons during Photocatalytc Oxidation of Ethanol on TiO2," Z. Yu and S. S. C. Chuang, J. Catal., in press.

Technology transfer activities:

Collaborations established (new or enhancement of existing ones with other universities or industry): with Kent State, OSU, and Univ. of Cincinnati.

Type and number of equipment items acquired:

Digilab Excalibur FastImageIR large sampling imagining FTIR system with a Stingray 2 Lancer FPA Detector).

1. Pfeiffer mass spectrometer (OmniStar Gas Analysis System GSD 301-O).

Kent State University, M. Jaroniec

Scientific progress report

Although porous carbons have been used for a long time in industry and everyday life as adsorbents and catalysts, the possibility to design their structure at the nanoscale level appeared in the current decade. This design has been firstly achieved by filling the ordered pores of siliceous materials (used as hard templates) with liquid-type carbon precursors such as sucrose, pitch and polymerizing compounds, followed by polymerization and stabilization if needed, high temperature pyrolysis and template dissolution. One of the main research activities of HSPC was the use of siliceous templates of well-defined rigid structures to obtain their inverse carbon replicas having accessible and uniform pores at the nanoscale level. By selecting silica templates with thin pore walls it was possible to design nanostructured carbons having pores below 1 nm, and consequently to increase their capacity for storage of hydrogen and methane. Also, this type of structures after suitable modification are promising materials for energy-related applications such as electric capacitors and supports for fuel cell catalysts. Although the "hard-templating" synthesis strategy allows us to fabricate nanostructured carbons of desired structural properties, its main limitations are high cost of the resulting carbons and difficult to scale up their processing.

Recently, we started to explore an alternative strategy for the preparation of nanostructured carbons. This strategy, which appeared in literature just a couple years ago, involves the supramolecular self-assembly of organic precursors of carbon such as phenol and formaldehyde (or related compounds) in the presence of block copolymers (used as soft template). The main concept of this process is to organize carbon precursors in the hydrophilic regions of the block copolymer template followed by polymerization of carbon precursor, decomposition (removal) of soft template, and high temperature pyrolysis (carbonization). The removal of soft template creates small pores depending on the size of the template used, whereas pyrolysis of polymerized

carbon precursors creates carbon matrix. This synthesis strategy is simple, less expensive and easy to scale up. In addition, the "soft-templating" synthesis allows us to control the morphology of the resulting nanostructured carbons, i.e., to fabricate them in the form of particles, fibers, films and monoliths.

Leveraging results

"NIRT: Novel Nanostructured Carbons from Self-Assembled Block Copolymer Precursors: From Synthesis and Characterization to Devices",
NSF, Subcontract from Carnegie-Mellon University in Pittsburgh for $112,976; 2003-2007.

"Improved Methods to Manufacture Brominated Carbon Adsorbents for Power-Plant Mercury-Emission Control" (SBIR phase II)
NSF, Subcontract from Sorbent Technologies, Inc., Twinsburg, Ohio, for $40,000, 2006.

"Periodic Mesoporous Organosilicas with Multifunctional Bridging and Surface Groups for Removal of Heavy Metal Ions",
NSF, $200,000, 2006-2008; although this project is not related to carbons, the purchase of powder X-ray diffraction system was essential for this award.

Number of graduate students who completed thesis/dissertations under this award

Two PhD graduate students: **Kamil P. Gierszal** (defense planned in 2007) and **Joanna Gorka** (one year in PhD program). Both students are involved in the design and synthesis of nanostructured carbons for gas storage, environmental and energy-related applications.

Publications resulting from this award (19)

K. P. Gierszal, M. Jaroniec: Carbons with Extremely Large Volume of Uniform Mesopores Synthesized by Carbonization of Phenolic Resin Film Formed on Colloidal Silica Template. *J. Am. Chem. Soc.* 128 (2006) 10026-10027.

Kamil P. Gierszal, Suk Bon Yoon, Jong-Sung Yu and Mietek Jaroniec: Adsorption and structural properties of mesoporous carbons obtained from mesophase pitch and resorcinol-formaldehyde carbon precursors using porous templates prepared from colloidal silica. *J. Mater. Chem.* 16 (2006) 2819-2823.

Michal Kruk1, Bruno Dufour, Ewa B. Celer, Tomasz Kowalewski, Mietek Jaroniec, Krzysztof Matyjaszewski: Well-defined Poly(ethylene oxide)-Polyacrylonitrile Diblock Copolymers as Templates for Mesoporous Silicas and Precursors for Mesoporous Carbons. *Chem. Mater.* 18 (2006) 1417-1424.

Xinqi Chen, Donald R. Cantrell, Kevin Kohlhaas, Sasha Stankovich, James A. Ibers, Mietek Jaroniec, Hongsheng Gao, Xiaodong Li, Rodney S. Ruoff: Carbide-derived nanoporous carbon and novel core-shell nanowires. *Chem. Mater.* 18 (2006) 753-758.

J. Choma, M. Jaroniec: Characterization of nanoporous carbons by using gas adsorption isotherms; in "Activated Carbon Surfaces in Environmental Remediation" (T. Bandosz, Ed.), Academic Press, Oxford, 2006, chapter 3, pp. 107-158; published in series: Interface Science and Technology, vol. 7 (2006) 107-158.

Kamil P. Gierszal, Tae-Wan Kim, Ryong Ryoo, Mietek Jaroniec: Adsorption and Structural Properties of Ordered Mesoporous Carbons Synthesized by Using Various Carbon Precursors and Ordered Siliceous p6mm and Ia3d Mesostructures as Templates. *J. Phys. Chem.* B 109 (2005) 23263-23268.

M. Kruk, B. Dufour, E.B. Celer, L. McCullough, M. Jaroniec, K. Matyjaszewski, T. Kowalewski: Carbon nanosurfaces from polyacrylonitrile grafted on the surface of porous silica. Polymer Division Preprints, American Chemical Society, Vol. 46, No. 2, 2005, pp. 173-174.

M. Kruk, B. Dufour, E.B. Celer, L. McCullough, T. Kowalewski, M. Jaroniec, K. Matyjaszewski: Atom transfer radical polymerization initiated from the surface of nanoporous silica. Polymer Division Preprints, American Chemical Society, Vol. 46, No. 2, 2005, pp. 156-157.

J. Choma, M. Jaroniec, M. Kloske: Ordered nanoporous carbonaceous materials: Synthesis, properties and applications (review in Polish). *Wiadomosci Chemiczne* 59 (2005) 305-352.

Suk Bon Yoon, Jeong Yeon Kim, Jong-Sung Yu, Kamil P. Gierszal, Mietek Jaroniec: Fabrication and Characterization of New Mesostructured Silica, HUM-1 and its Ordered Mesoporous Carbon Replica. *Ind. Eng. Chem. Res.* 44 (2005) 4316-4322.

M. Kruk, B. Dufour, E.B. Celer, T. Kowalewski, M. Jaroniec, K. Matyjaszewski: Synthesis of Mesoporous Carbons Using Ordered and Disordered Mesoporous Silica Templates and Polyacrylonitrile as Carbon Precursor. *J. Phys. Chem. B* 109 (2005) 9216-9225.

T.W. Kim, R. Ryoo, K.P. Gierszal, M. Jaroniec, L.A. Solovyov, Y. Sakamoto, O. Terasaki: Characterization of Mesoporous Carbons Synthesized with SBA-16 Silica Template. *J. Mater. Chem.* 15 (2005) 1560-1571.

S.B. Yoon, G.S. Chai, S.K. Kang, J.S. Yu, K.P. Gierszal, M. Jaroniec: Graphitized Pitch-Based Carbons with Ordered Nanopores Synthesized by Using Colloidal Crystals as Templates. *J. Am. Chem. Soc.* 127 (2005) 4188-4189.

Ch. Tang, M. Kruk, E.B. Celer, A. Laurent, M. Jaroniec, K. Matyjaszewski, T. Kowalewski: New, direct route to mesoporous carbons based on pyrolysis of block copolymers with polyacrylonitrile blocks. Preprints of Symposia, Fuel Chemistry Division, American Chemical Society, Vol. 50, No. 1, 2005, pp. 118-120.

M. Kruk, B. Dufour, E.B. Celer, T. Kowalewski, M. Jaroniec, K. Matyjaszewski: Controlled radical polymerization of polyacrylonitrile initiated from surface of nanoporous silica and synthesis of porous carbon from polyacrylonitrile graft.

Preprints of Symposia, Fuel Chemistry Division, American Chemical Society, Vol. 50, No. 1, 2005, pp. 73-75.

K. P. Gierszal, M. Jaroniec: Pitch-Based Carbons Synthesized by Using Silica Colloids and Ordered Mesoporous Silica Particles as Templates; in "Nanoporous Materials IV" (A. Sayari, M. Jaroniec, Eds.), Elsevier, Amsterdam, 2005, pp. 581-588; *Stud. Surface Sci. Catal.* 156 (2005) 581-588.

J. Choma, M. Jaroniec, E.A. Ustinov: Adsorption characterization of active carbons of well developed porosity (in Polish). *Ochrona Srodowiska* 26-4 (2004) 3-7.

K.P. Gierszal, M. Jaroniec: Novel Pitch-Based Carbons with Bimodal Distribution of Uniform Mesopores. *Chem. Commun.* 2004, 2576-2577.

Z. Li, M. Jaroniec: Mesoporous carbons synthesized by imprinting ordered and disordered porous structures of silica particles in mesophase pitch. *J. Phys. Chem. B* 108 (2004) 824-826.

Collaborations established

Academic Institutions

1. Professor **Ryong Ryoo** from **Korean Advanced Institute of Science and Technology**; collaboration in the synthesis of novel ordered nanoporous carbons obtained by using ordered mesoporous silicas as hard templates
2. Professor J**ong-Sung Yu** from **Hannam University (Korea);** collaboration in the synthesis of novel ordered nanoporous carbons obtained by using siliceous colloidal crystals as hard templates
3. Professors **Tomasz Kowalewski** and **Krzysztof Matyjaszewski** from **Carnegie Mellon University** in Pittsburgh; collaboration in the synthesis of nanostructured carbons by utilizing microphase separation of block copolymers
4. Professor **Rod Ruoff** from **Northwestern University;** collaboration in the synthesis of carbide-derived microporous carbons
5. Dr. **Sheng Dai** from **Oak Ridge National Laboratory**; collaboration in the synthesis of nanostructured carbons obtained by using block copolymers as soft templates.

Industrial collaboration

1. Collaboration with **Sorbent Technologies, Inc. (Ohio)** related to the usage of modified microporous carbons for power-plant mercury-emission control

2. Collaboration with **Iten Industries (Ohio)** on the fabrication of light-weight nanostructured materials

Type and number of equipment items acquired

1. Multi Purpose X-ray powder diffraction spectrometer (X'Pert Pro system, PANanalytical, Inc.) for structural characterization of nanoporous carbons and other nanomaterials *(one unit)*.

2. AutoChem II 2920 Chemisorption Analyzer fully automated for complex sequencing and
   experimental design of in situ experiments with virtually unlimited steps for temperature programmed desorption, temperature programmed reduction, temperature programmed oxidation and pulse chemisorption *(one unit).*

The Ohio State University, Henk Verweij

Scientific progress report

The Hayes investment funds have been used the purchase

- A gas chromatograph for a permeation porometry set-up, and a high temperature membrane separation set-up.
- A spectroscopic ellipsometer to measure thickness and composition of single and multi-layer coatings on dense and porous supports.
- An addition to a Rapid Thermal Processing system, purchased from other funds.

This equipment is successfully embedded in a bigger renovation and instrumentation programs in which a total of $2.12M funding was obtained to realize an up to date facility for synthesis and characterization of high-definition inorganic coatings, fuel cells and membranes. A major lab renovation is just completed and equipment is currently installed in the renovated rooms.
An important part of the program targets the development of thin supported porous membranes. These membranes are used in energy-efficient separation of gases and purification of water. Making these membranes thin (10 nm…1 μm) on a porous support without any connected defects provides a major challenge

Permeation porometry
The permeation porometry method makes use of the capillary condensation of a vapor phase to achieve a controlled blocking of membranes pores less than a certain radius. The simultaneous permeance of a non-condensable probe gas is measured to obtain an estimate for the membrane's remaining open porosity. This methods is now fully operational and it availability has led to a better interpretation for very thin membranes, and improved insight in the surface structure of porous membrane supports with an optically smooth surface.

Spectroscopic ellipsometry
A comprehensive selection procedure has led to the identification of the Woollam V-VASE spectroscopic ellipsometer. This instrument is now routinely used for the first fully non-destructive determination of the layer thickness and composition of thin supported membranes and coatings. The composition is interpreted in terms of porosity and the amount of adsorbed material. One graduate student did a training at Woollam to get acquainted with the non-trivial aspects of interpretation.

High-temperature gas separation
The high temperature gas separation set-up design is completed and the instrument is currently assembled. This set-up will be used for the determination of in-situ separation capabilities of high-temperature membranes. Typical applications of these membranes include hydrogen and oxygen production and CO_2 separation and sequesterization.

Addition to Rapid Thermal Processing

A small amount of budget was used to purchase a chiller for a rapid thermal processing (RTP) set-up. This set-up is currently being installed in the clean room. RTP will be used in heat treatment of inorganic coatings and membranes to reduce their manufacturing cycle time from days to minutes. We expect that this will largely improve to changes of large scale introduction.

Leveraging results

DOE Hydrogen 01/01/05-12/31/09
Zeolite Membrane Reactor for Water-Gas-Shift Reaction for Hydrogen Production
Development of economic H_2/CO_2 separation
Amount: $400K (out of $2M)
Ohio Department of Development 01/01/04-12/31/05
Third Frontier Action Fund
Cost-effective components for solid oxide fuel cells using nano-engineered materials.
Amount: $216,509 (out of $968,426)
Ohio Department of Development 04/01/05-12/31/06
Third Frontier Fuel Cell Program
High Performance, Nanostructured, Cathode-Supported Fuel Cell
Amount: $140K (out of $347K)
NSF Office of International Science & Engeneering 09/01/04-08/31/07
US Egypt Board
Synthesis of nano-crystalline sensing oxides
Amount: $30K
DOE Basic Energy Sciences
Hydrogen Fuel Initiative
Photoactive inorganic membranes for charge transport
Amount $165K (out of $660K)
DOE Hydrogen 1/01/2007-12/31/2007
Emtec Hydrogen program
Preparation of Nanoscale Tubular Membrane for Hydrogen
Amount: $50K (out of $100K)

Number of graduate students who completed thesis/dissertations under this award

4 M.S. students were graduated: P.M. Husemeann, G.T. Guickel, J.Y. Shi, and D. Yu.
2 of these students also completed their PhD: J.Y. Shi, and D. Yu

Publications resulting from this award

1. H. Wormeester N.E. Benes, G.I. Spijksma, H. Verweij, B. Poelsema, "CO_2 sorption of a ceramic separation membrane," Thin Solid Films, 455-56 747-51 (2004).
2. M.L. Mottern, G.T. Quickel, J.Y. Shi, D. Yu, and H. Verweij, "Processing and properties of homogeneous supported γ-alumina membranes"; pp. 26-29 in: Proc. 8th Int. Conf. Inorganic Membranes, July 18-22, 2004. Edited by Y.S. (Jerry) Lin, Cincinnati, OH, USA. Adams Press, Chicago, IL.

3. N.E. Benes, F.M. Zalar, and H. Verweij, "Diffusion on an ideal Langmuir lattice applied to membrane and fuel cell transport," pp. 196-99 in ibid.
4. J.Y. Shi, F.M. Zalar, and H. Verweij, "Properties and synthesis of ultra-thin SOFC structures," Proc. Annual Meeting AIChE, 7-12 November 2004.
5. K. Shqau, M.L. Mottern, D. Yu, and H. Verweij, "Effect of Aluminon Aqueous Solution Chemistry on the Homogeneity of Compacts by Colloidal Filtration of □-Al_2O_3 Dispersions," Proceedings of the American Ceramic Society Annual meeting, Baltimore, 2005.
6. J.Y. Shi and Henk Verweij, "Preparation of ZrO_2 Nanoparticles and Nanostructured Coatings Via Modified Emulsion Precipitation," Proceedings of the American Ceramic Society Annual meeting, Baltimore, 2005.
7. J.Y. Shi, and H. Verweij, "Synthesis and Purification of Oxide Nanoparticle Dispersions by Modified Emulsion Precipitation," Langmuir, 21 [12] 5570-75 (2005).
8. K. Shqau, M.L. Mottern, D. Yu, and H. Verweij, "Preparation of defect-free porous alumina membrane supports by colloidal filtration," Proceedings PCM 2005, Brugge, Belgium, October 20-21, 2005.
9. M.L. Mottern, M. Oyola, K. Shqau, D. Yu, and H. Verweij, "Permeation porometry of membrane supports and thin supported γ-alumina membranes," Proceedings PCM 2005, Brugge, Belgium, October 20-21, 2005.
10. J.Y. Shi, F.M. Zalar, and H. Verweij, "Design and synthesis of optimized SOFC structures," Proc. Annual Meeting AIChE, 30 October-4 November 2005.
11. H. Verweij, "Inorganic Membranes for Energy-Related Gas and Water Purification," Proc. TMS Meeting, San Antonio TX, 2006.
12. H. Verweij, Y.S. Lin, and J.H. Dong, "Micro-porous silica and zeolite membranes for hydrogen purification," MRS Bulletin, **31** [10] 756-64 (2006).
13. K. Shqau, M.L. Mottern, D. Yu, and Henk Verweij, "Preparation and properties of porous α-Al_2O_3 membrane supports," J. Am. Ceram. Soc., **89** [6] 1790–94 (2006).
14. M.L. Mottern, F. Tyholdt, A. Ulyashin, A.T.J. van Helvoort, H. Verweij, and R. Bredesen, "Textured ITO thin films by chemical solution deposition and rapid thermal processing," Thin Solid Films, in press.
15. J.A. Trimboli, M.L. Mottern, H. Verweij, and P.K. Dutta, "Interaction of Water with Titania: Implications for High Temperature Gas Sensing," J. Phys. Chem., **110** 5647-54 (2006).
16. J.Y. Shi and Henk Verweij, "Preparation and Characterization of Nanostructured ZrO_2 Coatings on Dense and Porous Substrates," Thin Solid Films, submitted, 2006.
17. M.L. Mottern, K. Shqau, J.Y. Shi, D. Yu, and Henk Verweij, "Thin supported inorganic membranes for energy-related gas and water purification," Int. J. Hydrogen Techn., accepted, 2006.
18. J.Y. Shi, K. Shqau, H. Verweij, R. Revur, S. Sengupta, and J.R. Schorr, "Preparation of well-defined thin YSZ and SSZ membranes with a narrow pore size distribution," proceedings ICIM9.
19. M.L. Mottern, K. Shqau, D. Yu and H. Verweij, "A closer examination of permeation porometry," proceedings ICIM9.
20. F.M. Zalar, and H. Verweij, "Finite-element solution of a thermodynamics-based solid oxide fuel cell model," proceedings ICIM9.
21. J.Y. Shi, M.L. Mottern, K. Shqau, and H. Verweij, "Nanostructured ceramic thin films and membranes by wet chemical processing methods," proceedings CIMTEC 2006.

22. M.L. Mottern, J.Y. Shi, K. Shqau, D. Yu, and H. Verweij, "Micro-structural optimization of thin supported inorganic membranes for gas and water purification, "in Membranes: Manufacturing and Applications, Norman N. Li, Anthony G. Fane, W.S. Winston Ho, and Takeshi Matsuura, eds., John Wiley & Sons, New York 2006 (accepted).

Technology transfer activities

The group, led by Henk Verweij, has provided the initial research focus, expertise and access to experimental facilities to MetaMateria Partners LLC, started in 2003. This resulted in several sponsored co-operation projects. In the mean time MetaMateria has grown to >30 people and commercializes devices methods based on inorganic materials and devices, based on colloidal deposition of high-definition colloidal dispersions.

- Contact person: Dr. J. Richard Schorr
- Address: 1275 Kinnear Rd
- City: Columbus OH 43212-1155

The group, led by Henk Verweij, currently provides startup assistance, expertise, and access to experimental facilities to Morgenix LLC, started in 2005. This company commercializes high-temperature sensor array technology for harsh environments, originally developed at Dupont. Morgenics has industrial funding for three years to achieve this goal, and has currently with some 5 employees.

- Contact person: Dr. Patricia A. Morris
- Address: 1275 Kinnear Rd
- City: Columbus OH 43212-1155

Collaborations established

A collaboration was established with Y.S. Lin of Arizona State University, J.H. Dong and P.G. Smirniotis and J.H. Dong of the University of Cincinnati for the realization of a high temperature membrane reactor for hydrogen production, starting form the water gas shift reaction.

In addition a co-operation was started with P.K. Dutta, and B. Kohler for direct photolytic splitting of water by sunlight by using photoactive inorganic membranes to conduct the charge transport.

Type and number of equipment items acquired, using the attached table with the generic category listing.

- A gas chromatograph for a permeation porometry set-up, and a high temperature membrane separation set-up.
- A spectroscopic ellipsometer to measure thickness and composition of single and multi-layer coatings on dense and porous supports.
- An addition to a Rapid Thermal Processing system, purchased from other funds.

The Ohio State University, Prabir Dutta

Scientific progress report

Molecular assemblies, which upon visible light absorption result in long-lived charge separated states are critical in the first step for solar to chemical energy conversion. However, in order to exploit the charge separation, the molecular assemblies need to be integrated into a specific membrane architecture, and methodology for doing so just does not exist. We are working on microporous zeolitic inorganic membranes with the following properties : 1) internal porosities consistent with the size of photochemical assemblies, 2) stability with respect to appropriate temperatures, pH and solvents, 3) can be chemically manipulated and 4) capable of maintaining charge balance, since they meet the requirements for making practical advances towards the goal of solar energy conversion.

There are three aspects to our overall plan: connecting molecular assemblies to zeolites, transporting charge into the zeolite with the help of suitable acceptors and then propagating the charge through the membrane. Using zeolite Y and zeolite L, we are examining the dynamics of electron/hole injection from a polypyridyl ruthenium complex tethered to the zeolite surface to bipyrdinium ion, conducting polymers and CdSe conducting wires in the zeolite. Transient spectroscopic studies are defining the efficiency of the charge injection process and the ability to move charge from the molecule into the zeolite. Focusing primarily on the bipyridinium acceptors, we are evaluating by spectroscopic studies the charge injection in the zeolite. Two possible mechanisms of charge transport involve self-exchange of electrons through the packed bipyridinium ions and involvement of the zeolite framework in assisting with the charge transport. Spectroscopic measurements are carried out with diffuse-reflectance transient absorption spectrometers with time resolutions extending from femtosecond to millisecond time scales. The ultrafast laser system consists of a sub-30 femtosecond mode-locked Ti:S oscillator pumped by a 5 W solid-state laser, two high-energy (> 2.5 mJ at 1 kHz, pulse width ~40 fs) regenerative amplifiers, and four optical parametric amplifiers that generate femtosecond pulses from UV to mid-IR wavelengths. This laser equipment supports additional setups for performing conventional transient absorption and fluorescence upconversion measurements.

The final phase of this study will involve assembly of the photosensitizer on a zeolite Y membrane and examine photochemically-assisted charge transport through the membrane. Studies will focus on synthesis and characterization of meso-defect free membranes and will be verified by state-of-the-art porosimetry. The zeolite membrane also provides the opportunity to build cascades of molecules with graded reduction potential to investigate if vectorial electron transfer within the membrane promotes the charge transport process.

Based on fundamental studies of the charge transport process, this research program is establishing guidelines for coupling photochemical molecular assemblies to inorganic membranes for spatial charge separation. The next phase of the project will involve development of catalysts for utilization of the redox species to generate chemicals.

Leveraging results

DOE Basic Energy Sciences
Hydrogen Fuel Initiative
Photoactive inorganic membranes for charge transport
Amount $660K
Duration: April 15, 2006 to March 31, 2009

Number of graduate students who completed thesis/dissertations under this award

Haoyu Zhang is finishing his PhD on this project. Jeremy White has started work on this project.

Publications resulting from this award

Zhang, Haoyu; Kim, Yanghee; Dutta, Prabir K.. Controlled release of paraquat from surface-modified zeolite Y. *Microporous and Mesoporous Materials* 88(1-3), 312-318, **2006**.

Y. Kim, A. Das, H. Zhang, P. K. Dutta, Zeolite Membrane-Based Artificial Photosynthetic Assembly for Long-Lived Charge Separation. *Journal of Physical Chemistry B , 109(15)*, 6929-6932, **2005.**

Y. Kim and P. K. Dutta, Photochemical Studies with a Zeolite Y Membrane Formed via Secondary Growth, *Research in Chemical Intermediates, 30,* 147-161, **2004**

Y. Kim and P. K. Dutta, Photochemical Processes in Zeolites: New Developments, Current Opinion in Solid State and Materials Science, 7, *483-490,* ***2003.***

Y. Kim, H. Lee, P.K. Dutta, A. Das, Zeolite-Mediated Photochemical Charge Separation Using a Surface-Entrapped Ruthenium-Polypyridyl Complex, *Inorg. Chem, 42,* 4215-4222, **2003.**

Technology transfer activities

None

Collaborations established

The current DOE grant is a collaboration with Henk Verweij and Bern Kohler.

Type and number of equipment items acquired, using the attached table with the generic category listing.

<u>OSU Center for Chemical and Biophysical Dynamics (CCBD):</u>

The CCBD provides access to state-of-the-art ultrafast spectroscopic instrumentation. Spread over 200 s. f. of optical table space are setups for performing femtosecond fluorescence upconversion, transient absorption, diffuse reflectance spectroscopy,

UV/vis pump and mid-IR probe measurements. Three independent femtosecond pump-probe setups are powered by two Coherent Legend regenerative amplifiers, which deliver 2.5 mJ, 800 nm pulses at a repetition rate of 1 kHz with pulse durations below 40 fs. Each setup has one or more optical parametric amplifiers (OPAs) that provide tunable, approximately transform-limited femtosecond pulses. Collectively, the OPAs can be tuned from approximately 240 nm in the UV to beyond 10 m in the mid-infrared. Each setup can supplement the OPA pulses by harmonics (x, 2x, and 3x) of the Ti:sapphire fundamental, and pulses derived from a white light continuum. The former have sufficient energy for use as excitation pulses, while the latter are ideal for probing either at single wavelengths or using a spectrometer/CCD detector for broadband detection.

Time-correlated single-photon counting (TCSPC) setup for time-resolved emission studies (50 ps time resolution), nanosecond IR, and picosecond Raman instrumentation is also available. Hayes funds contributed $250,000 to this $1 million center awarded by NSF.

University of Cincinnati, Peter Smirniotis

Brief Technological Description

We have developed a large number of ferrite transition metals–based catalysts for the ultra-high temperature Water Gas Shift (WGS) reaction. The temperatures of interest are ranging from 350 to 500 ^{o}C. We have identified selected catalysts, namely Fe-Ce, and Fe-Cu systems, which demonstrated superior performance at industrially relevant conditions (Steam/CO ranging from 1 to 7, GHSV=60,000 h^{-1}). Our catalysts are synthesized via a precipitation procedure from very inexpensive sources and show great promise (Khan and Smirniotis, 2006) for this reaction. This study is not only essential for the WGS reaction but for all the gasification studies of coal and/or biomass.

Our characterization studies (Khan et al., 2006) indicated that all our ferrite catalysts upon careful activation result in magnetite (Fe_3O_4) which is the responsible phase for the good catalytic performance we observed. We characterized our catalysts with Raman, XRD, XPS, TPR/TPO. The coal/biomass gasifier was build by INNOVENTOR, Inc. from St. Louis, MO. The unit can operate up to 1000 ^{o}C, up to 25 bars, and can process up to 10 coal pounds/hour or 4 biomass pounds/hour. We have tested the gasifier with selected coals aiming at optimizing the production of H_2 and CO (suppress the premature oxidation of CO to CO_2).

Leveraging Results

Title: Zeolite Membrane Reactor for Water-Gas-Shift Reaction for Hydrogen production, DoEnergy, Period of Performance: July 1, 2005 to June 30 2009, Total Award was $2,000,000 (amount that was awarded to P. Smirniotis was $400,000).

Number of Graduate Students

No graduate students have been involved in this Hayes award.

Publications

1) Ataullah M. Khan and P.G. Smirniotis, "*Ultra-High Temperature Water Gas Shift Reaction over Various Ferrite-Based Catalysts for Membrane Reactor Applications*", in preparation for submission to **Journal of Catalysis**, 2006.
2) Ataullah Khan, Sergey Mamedov and Panagiotis G. Smirniotis, "*Raman Studies on Various Ferrite-Based Shift Catalysts*", in preparation for submission to **Journal of Raman Spectroscopy**, 2006.

<u>*Conference Presentation(s):*</u>
A.M. Khan, and P.G. Smirniotis, "*Ferrite based Catalysts for Ultra-High Temperature Water Gas Shift Reaction for Membrane Reactor Applications*", paper presented at the 2006 Annual AICHE meeting in San-Francisco, November 13-17, 2006; Session: catalytic Hydrogen Generation (Paper #445c).

Technology Transfer Activities

No patent disclosures were submitted.

Collaborations Established
1) I have established a collaboration with Professor Jerry Lin (CHE dept. of Arizona State University), Professor Henk Verweij (MAT dept. of Ohio State University), and Professor Junhang Dong (CME dept. of University of Cincinnati) on the DoEnergy award presented above.
2) I have been trying to receive additional funds from DoEnergy for the project funded by this Hayes Award . The team of professors I collaborate are: Professor Prabir Dutta, (Chemistry of Ohio State University), Professor Steven Chuang (CHE dept. of University of Akron), and Professor Mietek Jaroniec (Chemistry of Kent State University).

Type and number of equipment acquired

1) Manufacture a coal/biomass gasifier. The gasifier was designed in collaboration between P. Smirniotis and INNOVENTOR, Inc. This gasifier has all the important characteristics of an industrial one but it is scaled down to a bench size (14 ft height).

2) The PI (Smirniotis) bought a MKS (model Cirrus MS99) mass spectrometer (see the second attachment) to analyze the species of the WGS reaction. This unit is the latest state-of-the-art of its kind.

Ohio Organic Semiconductor Consortium

Final Research Progress Report

Partners: ***Ohio State University,*** *Kent State University, Case Western Reserve University, BTG International, Inc., DuPont Circleville, AlphaMicron, Inc., Nanofilm*

Scientific Progress Report

The Ohio Organic Semiconductor Consortium focuses on the emerging interdisciplinary research and technology field of conductors, semiconductors, and magnets based on organic molecules and polymers (plastics). Until the 30 years ago the only metals known were metallurgical materials like iron and copper. Similarly semiconductor materials (of importance for electronics such as transistors and integrated circuits) were made from silicon (a component of beach sand) and magnets were made from 'transition metals' such as iron and 'rare earths' such as gadolinium. The Nobel Prize winning report by University of Pennsylvania researchers of creation of plastics that are conductors and semiconductors and the report 10 years later by OSU McGroddy Prize winner Professor Arthur Epstein and University of Utah collaborator Prof. Joel S. Miller that plastics also can be magnets created new opportunities for interdisciplinary education and research. New technologies such as flexible light emitting displays, sensors, biomedical devices have created new economic opportunity.

These new areas of research required new types of equipment to prepare and study these new systems. The OOSC budgets at OSU provided for the acquisition of two inert atmosphere glove box systems (Fig. 1) for the study of organic semiconductor materials and thin-film devices. A 'wet' glove box can operate at increased levels of H_2O and organic solvent in the inert atmosphere allowing for the chemical synthesis of organic semiconductors and their precursors. A second glove box system is custom designed for deposition of multilayer semiconductor devices. This latter system consists of four boxes with separately purified atmospheres, but all are interconnected for easy sample transfer from one box to another without exposure to ambient atmosphere. Each of the four boxes has a unique function: (i) Box 1 is used for the preparation of thin films of polymers through the use of a spin coater with accompanying hot plate and vacuum oven; (ii) Box 2 houses separately-purchased user-installed equipment including an atomic force microscope (AFM) used for material characterization; (iii) Box 3 contains two high-vacuum deposition systems (more details below); (iv) Box 4 provides space for a reaction chamber for the chemical vapor deposition (CVD) of organic-based magnets such as $V[TCNE]_2$. The high-vacuum deposition systems in Box 3, manufactured by BOC Edwards, consist of two separate chambers for independent deposition of small molecule/oligomer organic materials and metals/dielectrics. The organic deposition chamber has two resistive evaporation sources and two PID-controlled effusion cells designed for steady evaporation of sensitive materials. The metal/dielectric deposition chamber also has two resistive evaporation sources, but also has an RF/DC magnetron sputter gun as well as a four-pocket electron beam gun, each capable of depositing conducting, insulating and magnetic materials.

The glove box systems have allowed for the fabrication and study of various thin-film organic semiconductor devices. The new glove box based fabrication system is used to create many other plastic multilayer systems including solar cells to help address global warming, sensors to detect blood sugar levels, and plastics to participate in regenerative medicine.

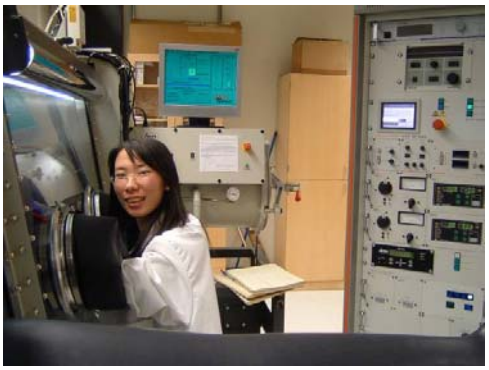

Fig. 1 Inert atmosphere glove box system.

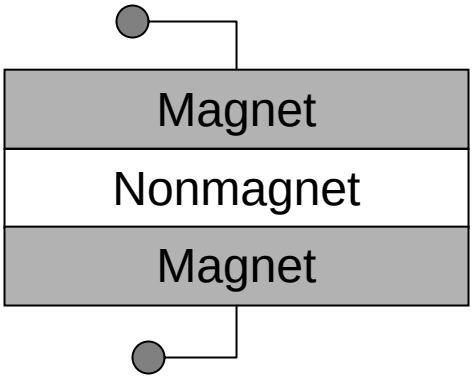

Fig. 2 Schematic of spin-valve device.

As an example of use of the glove box system spin valves, devices with two magnetic layers separated by a nonmagnetic layer (Fig. 2), have been successfully fabricated in the glove box system using both conventional metallic magnetic materials (e.g. iron) and organic-based magnetic semiconductors. Nonmagnet organic semiconductors have been successfully incorporated into the devices resulting in functional spin valves.

In addition, we have fabricated devices that show large responses to magnetic fields. This has potential application as magnetic field sensors. We have developed a model for this phenomenon that will allow the future optimization of this class of devices.

We have made devices where the properties can be manipulated by visible light and microwave radiation. This offers the opportunity for new functionality for magnetic and spintronic devices. An example of manipulation of device properties is shown in Fig. 3.

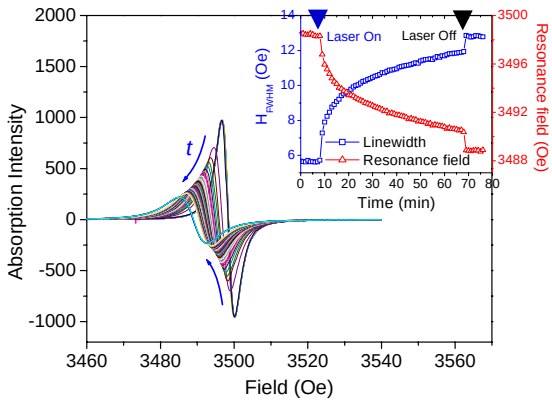

Fig. 3. Evolution of FMR spectrum under light illumination □ ~ 457.9 nm and I ~ 20 mW/cm^2, at 30 K). Inset shows the extrapolated linewidth and resonance field of the FMR spectra by Lorentzian curve.

This HIF award facilitated the purchase of a quartz tungsten halogen (QTH) lamp system filtered by a monochrometer (Fig. 4) and controlled by a personal computer running LabView long with an Oriel solar simulator for initial solar cell qualification. These are pictured to the right. Both light sources utilize a multi-mode fiber to deliver the optical beam onto samples in many configurations, including the ability to pipe light directly into, or out of, a glove box system, in the future.

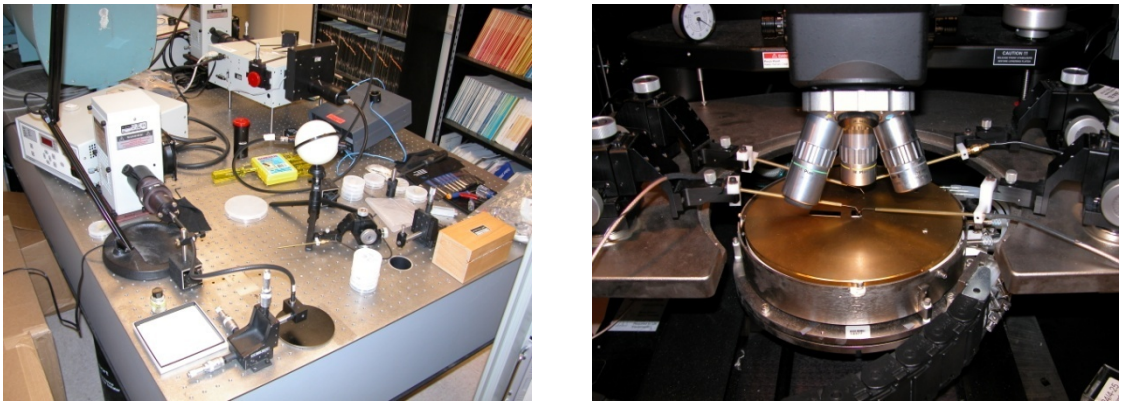

Fig. 4. quartz tungsten halogen (QTH) lamp system and device characterization system.

Other miscellaneous parts ordered under this HIF award include a specially designed shadow mask for fabrication of polymer field effect transistors, appropriate chucks for spin coating samples during the solution processing techniques, CCD camera for monitoring devices under test, a digital camera for documenting experiments and personnel involved, ultrasonic cleaner for mixing solutions and cleaning substrates, and a large area Hammamatsu photodiode for characterizing the light emission from polymer light emitting diodes.

Leveraging Results (title, sponsoring agency, date, and amount)

Title: Conducting Polymer Nanotube Composites for High Performance Supercapacitors
Sponsor: Honda R&D Co. Ltd.
Sponsor Grant No.: 10011854
Research Foundation Project Grant No.: 744416
Project Budget: $613,331
Budget Period: 3/30/03 to 3/31/06

Title: Continuation of the Program on Photoinduced Magnetism
Sponsor: Air Force Office of Scientific Research
Sponsor Grant No.: F49620-03-1-0175
Research Foundation Project Grant No.: 744492
Project Budget: $540,000
Budget Period: 3/1/03 to 2/28/06

Title: CANPBD: Conducting Polymer-based Nanofiber Networks for Affordable Biomedical Devices
Sponsor: NSF Div Engineering, Education and Centers (NSEC)
Sponsor Grant No.: EEC-0425626
Research Foundation Project Grant No.: 60006447
Project Budget: $160,000 (subproject of $12 million total)
Budget Period: 1/1/05 to 8/31/09

Title: Electron Spin Resonance Instrumentation (equipment grant)
Sponsor: Office of Naval Research
Sponsor Grant No.: N00014-05-1-0502
Research Foundation Project Grant No.: 60002276
Project Budget: $225,000
Budget Period: 05/1/05 to 2/28/07

Title: IGERT Fellowship #23 – Epstein/Adetunji and Nemzer
Sponsor: NSF Div Graduate Education and Research Development
Sponsor Grant No.: DGE0221678
Research Foundation Project Grant No.: 60004383
Project Budget: $98,000
Budget Period: 4/1/05 to 3/31/07

Title: Center for Multifunctional Polymer Nanomaterials and Devices (CMPND) (WCI Equipment grant)
Sponsor: Ohio Department of Development
Sponsor Grant No.: 26140000
Research Foundation Project Grant No.: TBD
Project Budget: $923,000 (subproject of $21 million total)
Budget Period: 6/6/05 to 6/5/08

Title: Polymer-Based Materials of Controlled Permeability and Permitivity and Application of Photoinduced Magnetism
Sponsor: Air Force Office of Scientific Research
Sponsor Grant No.: FA9550-06-1-0175
Research Foundation Project Grant No.: 60006715, 60008279
Project Budget: $540,000
Budget Period: 3/1/06 to 2/28/09

Title: Wright Center for Photovoltaics Innovation and Commercialization (PVIC)
Lead Institute: University of Toledo; partners: Ohio State Univ., Bowling Green State Univ.
Sponsor: Ohio Department of Development
Research Foundation Project Grant No.: TBD
Project Budget: $7M (subproject of $18.6M)
Budget Period: 7/1/07 to 6/30/12

Number of graduate students who completed thesis/dissertations under this award

6 PhD - Jeremy Bergeson (Physics), Nan-Rong Chiou (Chemical Engineering), Fang-Chi Hsu (Physics), Yifan Xu (Electrical Engineering), Yanyin Yang (Biomedical Engineering), Jung-Woo Yoo (Physics)

PhD underway - Chia-Yi Chen (Chemical Physics), Deniz Duman (Physics), Derek Lincoln (Chemistry), Mark Murphey (Physics), June Hyoung Park (Physics)

4 MS - Shumaila Afzal (Electrical Engineering), Louis Nemzer (Physics), Colin Shisler (Physics), James Potashnik (Physics)

Publications resulting from this award

A.J. Epstein, F.-C. Hsu, N.-R. Chiou, O. Waldmann, J.H. Park, Y. Kim, and V.N. Prigodin, *Electric-field Effect Devices Based on Doped Conducting Polymers*, **Proceedings, SPIE Conference on Organic Field Effect Transistors II,** San Diego, CA, 3-4 August 2003, Vol 5217, pp. 141-143 (2003).

A.J. Epstein, F.-C. Hsu, N.-R. Chiou, and V.N. Prigodin, *Doped Conducting Polymer-Based Field Effect Devices,* **Synthetic Metals 137**, 859-861 (2003).

Yifan Xu, Paul R. Berger, James N. Wilson and Uwe H.F. Bunz, *Photoresponsivity of Polymer Thin Film Transistors Based on PPE Derivative with Improved Hole-Injection*, **Applied Physics Letters, 85**, 4219-4221 (2004).

Y.Z. Wang, D.D. Gebler, and A.J. Epstein, *Direct and Alternating Current Light-Emitting Devices Based on Pyridine-Containing Conjugated Polymers*, **Organic Light-Emitting Devices: A Survey**, Joseph Shinar, Ed., Springer-Verlag, New York, pp. 245-263, (2004).

S.J. Etzkorn, W. Hibbs, J.S. Miller, and A.J. Epstein, *Anomalous Relaxation in a Quasi-1D Fractal Cluster Glass,* **Physical Review B 70**, 134419/1-6 (2004).

D. Haskel, Z. Islam, J. Lang, C. Kmety, G. Srajer, K. I. Pokhodnya, A.J. Epstein, and J. S. Miller, *Local Structural Order in the Disordered Vanadium Tetracyanoethylene Room Temperature Molecule-based Magnet,* **Physical Review B 70**,054422/1-9 (2004).

R. Plachy, K.I. Pokhodnya, P.C. Taylor, J. Shi, J.S. Miller, and A.J. Epstein, *Ferrimagnetic Resonance in Films of Vanadium [Tetracyanoethanide]$_x$, Grown by Chemical Vapor Deposition,* **Physical Review B 70**, 064411/1-12 (2004).

K.I. Pokhodnya, E.B. Vickers, M. Bonner, A.J. Epstein, and J.S. Miller, *Solid Solution V_xFe_{1-x} [TCNE]$_2$•zCH_2Cl_2 Room Temperature Magnet,* **Chemistry of Materials 16**, 3218-3223 (2004).

H.M. Kim, K. Kim, C.Y. Lee, J. Joo, S.J. Cho, H.S. Yoon, D.A. Pejakovic, J.W. Yoo, and A.J. Epstein, *Electrical Conductivity and Electromagnetic Interference Shielding of*

Multiwalled Carbon Nanotube Composites Containing Fe Catalyst, **Applied Physics Letters 84**, 589-591 (2004).

B.H. Kim, S.H. Hong, J. Joo, I-W. Park, A.J. Epstein, J.W. Kim, and H-J. Choi, *Electron Spin Resonance Signal of Nanocomposites of Conducting Polypyrrole with Inorganic Clay,* **Journal of Applied Physics 95**, 2697-2701 (2004).

Woo-Jun Yoon, Sung-Yong Chung, Paul R. Berger, and Sita M. Asar, *Room Temperature Negative Differential Resistance in Polymer Tunnel Diodes using a Thin Oxide Layer at the Anode and Demonstration of Threshold Logic*, **Applied Physics Letters, 87**, 203506 (2005).

R. Shima Edelstein, J.W. Yoo, N.P. Raju, J.D. Bergeson, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, *Organic-based Magnetic Thin Films by Low Temperature CVD*, **Material Research Society Symposium Proceedings 871E**, I-7.3, 1-6 (2005).

N.R. Chiou and A.J. Epstein, *Polyaniline Nanofibers Prepared by Dilute Polymerization,* **Advanced Materials 17,** 1679-1683, (2005).

N.-R. Chiou and A.J. Epstein, *A Simple Approach to Control the Growth of Polyaniline Nanofibers,* **Synthetic Metals 153**, 69-72 (2005).

M.S. Lee, H.S. Kang, H.S. Kang, J. Joo, A.J. Epstein, and J.Y. Lee, *Flexible All-Polymer Field Effect Transistors with Optical Transparency Using Electrically Conducting Polymers,* **Thin Solid Films 477,** 169-173 (2005).

A.R. Harutyunyan, T. Tokune, E. Mora, J.-W. Yoo, and A.J. Epstein, *Evolution of Catalyst Particle Size during Carbon Single Walled Nanotubes Growth and its Effect on the Tube Characteristics,* **Journal of Applied Physics 100,** 044321-1 – 044321-8 (2006).

V.N. Prigodin, J.D. Bergeson, D.M. Lincoln, and A.J. Epstein, *Anomalous Room Temperature Magnetoresistance in Organic Semiconductors*, **Synthetic Metals 156**, 757 – 761 (2006).

G. Srajer, L.H. Lewis, S.D. Bader, A.J. Epstein, C.S. Fadley, E.E. Fullerton, A. Hoffmann, J.B. Kortright, Kannan M. Krishnan, S.A. Majetich, T.S. Rahman, C.A. Ross, M.B. Salamon, I.K. Schuller, T.C. Schulthess, J.Z. Sun, *Advances in Nanomagnetism via X-ray Techniques*, **Journal of Magnetism and Magnetic Materials 307**, 1-31 (2006).

J.-W. Yoo, R.S. Edelstein, D.M. Lincoln, N. P. Raju, C. Xia, K.I. Pokhodnya, J.S. Miller, and A. J. Epstein, *Multiple Photonic Responses in Films of Organic Magnetic Semiconductor V(TCNE)2,* **Physical Review Letters 97**, 247205-1/4, (2006).

Yifan Xu, Paul R. Berger, Jai Cho and Richard B. Timmons, *Pulsed Plasma Polymerized Dichlorotetramethyldisiloxane High-k Gate Dielectrics for Polymer Field Effect Transistors*, **Journal of Applied Physics 99**, 014104 (2006).

A.R. Harutyunyan, T. Tokune, E. Mora, J.-W. Yoo, and A.J. Epstein, *Evolution of Catalyst Particle Size during Carbon Single Walled Nanotubes Growth and its Effect on the Tube Characteristics,* **Journal of Applied Physics 100,** 044321-1 – 044321-8 (2006).

F.-C. Hsu, V.N. Prigodin, and A.J. Epstein, *Electric-Field Controlled Conductance of "Metallic" Polymers in a Transistor Structure,* **Physical Review B 74,** 235219-1/6 (2006).

Technology transfer activities resulting from this award

A.J. Epstein and S. J. Etzkorn, *A Spintronic Device Having an Organic Spacer Layer and Method of Forming Same,* (provisional filing March 22, 2004, PCT WO 2006-022859 A2 published March 2, 2006).

A.J. Epstein, O. Waldmann, J.-H. Park, and N.-R. Chiou, *Multifunctional Doped Conducting Polymer-Based Field Effect Devices* (provisional filing March 25, 2004, formal filing March 25, 2005).

A.J. Epstein, N.R. Chiou, *Synthesis of Nanofibers of Polyaniline Substituted Derivatives,* (provisional filing June 28, 2004, formal filing June 28, 2005).

L. Grigorian, T. Tokune, and A.J. Epstein, *Composite Material Containing Nanotubes and an Electrically Conductive Polymer*, (provisional filing December 13, 2004).

S. Feinberg, D. Hansford, Y. Yang, and A.J. Epstein, *Electrical Stimulation of Cell and Tissue Growth with Two- and Three-Dimensionally Patterned Electrodes,* (provisional filing September 21, 2005).

N.R. Chiou, C. Lu, L.J. Lee, and A.J. Epstein, *Fabrication Methods and Applications of Aligned and Oriented Nanofibers of Polyaniline and their Derivatives,* (provisional filing April 3, 2006).

Paul R. Berger and Woo-Jun Yoon, *Demonstration of Room Temperature Negative Differential Resistance in Polymer Diodes Using a Thin Oxide Tunneling Barrier at the Anode,* (provisional filing November 3, 2005, formal filing November 3, 2006.

Collaborations established (new or existing ones with other universities or industry).

Argonne National Laboratory, George Srajer
Case Western Reserve University, Ken Singer
Honda Research Institute
Lawrence Berkeley National Laboratory, Jeff Kortright
National High Magnetic Field Laboratory
Oakridge National Laboratory
University of Dayton, Liming Dai
University of Utah, Joel S. Miller and Craig Taylor
Zyvex Performance Materials Inc., Grant Harrell

Type and number of equipment items acquired

Glove Box System (Vacuum Atmospheres) consisting of four interconnected, inert atmosphere boxes.

Atomic Force Microscope (Pacific Nanotechnology, Inc.) was installed in one of the glove boxes.

EleXsys EPR Spectrometer System (Bruker BioSpin) with cryogenic facility.

Clean Room Flooring (Rite Rug).

Quartz Tungsten Halogen Lamp

CCD Camera

Photodiode (Hammamatsu)

Ultrasonic Cleaner

Macromolecular Crystallography Consortium

Final Research Progress Report

Partners: ***University of Toledo,*** *Ohio State University, Case Western Reserve University, Cleveland State University, Cleveland Center for Structural Biology, Cleveland Clinic Foundation, Anatrace*

Introduction

With the complete sequencing of the human genome, and subsequent sequencing of the genomes of nearly 200 different species, an opportunity exists to obtain information about the structures and functions of an unprecedented number of proteins that are encoded by these genomes. Macromolecular crystallography is uniquely positioned to provide essential structural information about these complex biological systems. In recognition of this need for increased structural information on novel proteins, the National Institutes of Health has funded a number of structural biology consortia with the aim of using high-throughput methods to determine a very large number of new structures. While the number of new structures has grown dramatically through this effort, the success rate on any individual protein structure has not significantly improved, and many of the more challenging proteins have not been structurally characterized by these high throughput approaches.

Consortium Goals and Objectives

In contrast to the high throughput aims of these structural biology centers, our goal with this consortium was to apply and coordinate the expertise in crystal growth, data collection, and data analysis that was already present in a number of individual laboratories in Ohio universities to work on challenging protein structures. The macromolecular crystallography consortium was organized in 2003 for the purpose of expanding and upgrading the crystallographic capabilities in the State of Ohio through the development of a dedicated macromolecular crystallization center, and the expansion of the X-ray diffraction facilities at the University of Toledo and the Ohio State University. In addition to increasing our capacity to solve protein structures, one of the most important goals of this project was to use these facilities to support the training of students at the strong structural biology programs that exist at the consortium institutions, and also to make these state-of-the-art facilities available to the wider research community throughout the State of Ohio.

Student Training

Graduate level X-ray diffraction courses have been taught each year at the University of Toledo as part of our effort to educate the next generation of macromolecular crystallographers. The Fundamental X-ray Diffraction course (Fall semester) and the Macromolecular X-ray Diffraction course (Spring semester) were attended by an average of 10-15 students each semester. In addition, hands-on training and access to the robotics and diffractometer have been provided to all of the students who are involved in X-ray diffraction research projects.

Research Collaborations and Facilities Access

The Instrumentation Center at the University of Toledo is now being directed by Dr. Kristin Kirchbaum, an expert in small molecule X-ray diffraction. Upon receipt of the Hayes grant the Center was fortunate to attract Dr. Leif Hanson from Oak Ridge National Laboratories as a Senior Staff Scientist. Dr. Hanson is responsible for the operation of the macromolecular X-ray diffraction and robotics facilities and for the training of users of this equipment.

The impact of these new robotics and X-ray diffraction facilities have extended beyond the individual institutions. For example, over a dozen research collaborations have been initiated in which investigators at other Midwestern colleges and universities have worked with scientists at the University of Toledo to crystallize and structurally characterize proteins that are the focus of their individual research programs. Some recent collaborations with scientists at Ohio institutions include:

Dr. Paul Edmiston	College of Wooster, Department of Chemistry
Dr. Douglas Leaman	University of Toledo, Department of Biology
Dr. Michael Ogawa	Bowling Green State University, Dept. of Chemistry
Dr. Constance Schall	University of Toledo, Dept. of Chemical Engineering
Dr. William Scovell	Bowling Green State University, Dept. of Chemistry
Dr. Mark Snider	College of Wooster, Department of Biology
Dr. Jeffrey Smiley	Youngstown State University, Dept. of Chemistry

Growth of Macromolecular Cystallography in Ohio

Now that the Macromolecular Crystallography Consortium has been established to include the University of Toledo, Ohio State University, and the Cleveland Structural Biology Group, we are looking to expand membership in the consortium within the State of Ohio. The University of Cincinnati, recognizing the research opportunities in this field, has recently hired two new faculty members to establish research programs in the area of macromolecular structural studies. The Ohio Macromolecular Crystallography Conference was held in Cincinnati in October 2006 to highlight the growth and commitment by the University of Cincinnati in this area. Planning is now underway for the fall 2007 conference to be held at the University of Toledo.

We will continue our outreach efforts to attract researchers from the Midwest to take advantage of the excellent crystallography facilities that have been developed within the Ohio consortium. An expansion of our computer networking capabilities is under consideration to allow remote access for off-site users to both the crystallization robotics and the X-ray diffractometers. When established this will allow scientists to ship new protein samples and protein crystals to the consortium facilities for structural studies, and to play a role in the planning and implementation of these studies.

Leveraging Results

The Hayes award provided the instrumentation infrastructure which has supported research leading to a number of external grant awards:

Max Funk (PI), University of Toledo, Purification and Crystallization of 12-Lipoxygenases, National Institutes of Health, 2003-2005, $99,864.

Timothy Mueser (PI), University of Toledo, CAREER Award: Structural Analysis of Branched DNA Recognition, National Science Foundation, 2004-2009, $660,000.

Ronald E. Viola (PI), University of Toledo, Probing the Enzymatic Basis of Canavan Disease, National Institutes of Health, 2005-2010, $1,165,500.

Leif Hanson (PI), University of Toledo, Solvent Structure and Function in Macromolecules, National Science Foundation, 2005-2009, $883,918.

Dehua Pei (PI), Charles Bell (co-PI), Ohio State University, Mechanisms of Inhibition of S-Ribosylhomocysteinase, National Institutes of Health, 2005-2010, $1,002,548.

Michael Chan (PI), Ohio State University, L-Pyrrolysine chemical and structural biology, National Institutes of Health, 2005-2009, $1,022,000.

There are also a number of research proposals submitted by consortium members in the area of macromolecular crystallography that are being considered for funding by several agencies.

Graduate Student Theses/Dissertations

Five M.S. theses completed on research related to this award:
Anne B. Senger**,** M.S., Department of Chemistry, University of Toledo, December 2004.
Aude E. Izaac, M.S., Department of Chemistry, University of Toledo, May 2005.
L. Golovko, M.S., Department of Chemistry, University of Toledo, December 2006.
Aurelein Genet, M.S., Department of Chemistry, University of Toledo, December 2006.
Johanna Rapp, M.S., Department of Chemistry, University of Toledo, December 2006.

Five Ph.D. dissertations completed on research related to this award:
Stephen J. Tomanicek, Ph.D., Department of Chemistry, University of Toledo, May 2005.
C. Faehnle, Ph.D., Department of Chemistry, University of Toledo, August 2006.
J. Le Coq, Ph.D., Department of Chemistry, University of Toledo, December 2006.
Clara Isaza Ph.D., Department of Biophysics, Ohio State University, June 2005.
Rinku Jain, Ph.D, Department of Biophysics, Ohio State University, June 2006.

Publications supported by the instrumentation obtained from this award

J. Blanco, R. A. Moore, C. R. Faehnle, D. M. Coe, and R. E. Viola, The Role of Substrate Binding Groups in the Mechanism of Aspartate-β-semialdehyde Dehydrogenase, *Acta Crystallographica* **D60**, 1388-1395 (2004).

E. Cama, S. Pethe, J.-L. Boucher, S. Han, F. A. Emig, D. E. Ash, R. E. Viola, D. Mansuy, and D. W. Christianson, Inhibitor Coordination Interactions in the Binuclear Manganese Cluster of Arginase, *Biochemistry* **43**, 8987-8999 (2004).

J. Blanco, R. A. Moore, C. R. Faehnle, and R. E. Viola, Critical Catalytic Functional Groups in the Mechanism of Aspartate-β-semialdehyde Dehydrogenase, *Acta Crystallographica* **D60**, 1808-1815 (2004).

C. R. Faehnle, J. Blanco, and R. E. Viola, Structural Basis for Discrimination Between Oxyanion Substrates or Inhibitors in Aspartate-β-semialdehyde Dehydrogenase, *Acta Crystallographica* **D60**, 2320-2324 (2004).

A. Vahedi-Faridi, P-A. Brault, P. Shah, Y-W. Kim, W.R. Dunham, and M.O. Funk, Interaction Between Non-Heme Iron of Lipoxygenases and Cumene Hydroperoxide:

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Technology Transfer Activities

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Collaborations Established

Dr. Max Funk (University of Toledo) has entered into agreement with Biomide Inc. to conduct co-crystallization studies of 12-lipoxygenases with synthetic inhibitors.

Dr. Ronald Viola (University of Toledo) has established a research collaboration with Pfizer Pharmaceuticals to study the structures of enzymes involved in the metabolism of prodrugs.

Major Equipment Items Acquired

University of Toledo
Rigaku High Brilliance FR-E X-ray Diffractometer with Saturn 92 CCD and R-Axis Image Plate detectors
Cartesian Honeybee 963 Crystallization Robot
Rhombix Vision Digital Imaging System
Brandel Automatic Plate Sealer

Ohio State University
R-Axis IV++ Image Plate Detector
X-Stream Cryogenic System