ORNL/PPA-2009/1

Laboratory Directed Research and Development Program

FY 2008 Annual Report

ORNL/PPA-2009/1

Oak Ridge National Laboratory

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM

FY 2008 ANNUAL REPORT

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INTRODUCTION

The Oak Ridge National Laboratory (ORNL) Laboratory Directed Research and Development (LDRD) Program reports its status to the U.S. Department of Energy (DOE) in March of each year. The program operates under the authority of DOE Order 413.2B, “Laboratory Directed Research and Development” (April 19, 2006), which establishes DOE’s requirements for the program while providing the Laboratory Director broad flexibility for program implementation. LDRD funds are obtained through a charge to all Laboratory programs.

This report includes summaries all ORNL LDRD research activities supported during FY 2008. The associated *FY 2008 ORNL LDRD Self-Assessment* (ORNL/PPA-2008/2) provides financial data and an internal evaluation of the program’s management process.

ORNL is a DOE multiprogram science, technology, and energy laboratory with distinctive capabilities in materials science and engineering, neutron science and technology, energy production and end-use technologies, biological and environmental science, and scientific computing. With these capabilities ORNL conducts basic and applied research and development (R&D) to support DOE’s overarching mission to advance the national, economic, and energy security of the United States and promote scientific and technological innovation in support of that mission. As a national resource, the Laboratory also applies its capabilities and skills to specific needs of other federal agencies and customers through the DOE Work for Others (WFO) program. Information about the Laboratory and its programs is available on the Internet at <http:// www.ornl.gov/>.

LDRD is a relatively small but vital DOE program that allows ORNL, as well as other DOE laboratories, to select a limited number of R&D projects for the purpose of

- maintaining the scientific and technical vitality of the Laboratory,
- enhancing the Laboratory’s ability to address future DOE missions,
- fostering creativity and stimulating exploration of forefront science and technology,
- serving as a proving ground for new research, and
- supporting high-risk, potentially high-value R&D.

Through LDRD the Laboratory is able to improve its distinctive capabilities and enhance its ability to conduct cutting-edge R&D for its DOE and WFO sponsors.

To meet the LDRD objectives and fulfill the particular needs of the Laboratory, ORNL has established a program with two components: the Director’s R&D Fund and the Seed Money Fund. As outlined in Table 1, these two funds are complementary. The Director’s R&D Fund develops new capabilities in support of the Laboratory initiatives, while the Seed Money Fund is open to all innovative ideas that have the potential for enhancing the Laboratory’s core scientific and technical competencies. Provision for multiple routes of access to ORNL LDRD funds maximizes the likelihood that novel ideas with scientific and technological merit will be recognized and supported.

Table 1. ORNL LDRD Program

	Director's R&D Fund	Seed Money Fund
Purpose	Address research priorities of the Laboratory initiatives	Enhance Laboratory's core scientific and technical disciplines
Reviewers	Initiative Review Committees (IRCs) composed of senior technical managers and subject matter experts	Proposal Review Committee (PRC) composed of scientific and technical staff representing the research divisions assisted by 2–3 technical reviewers for each proposal
Review process	Preliminary and full proposal review, including a presentation to the IRC, and an annual review of progress	Full proposal review including a presentation to the PRC; review of progress if funding is awarded in two phases
Review cycle	Annual	Monthly
Project budget	Typically ~$600,000	<$175,000
Project duration	24–36 months	12–18 months
LDRD outlay	~80% of program	~20% of program

Director's R&D Fund

The Director's R&D Fund is the strategic component of the ORNL LDRD program and the key tool for addressing the R&D needs of the Laboratory initiatives. The initiatives, which are the focus of the Laboratory Agenda, are the critical areas on which the Laboratory must concentrate if it is to be prepared to meet future DOE and national requirements for science and technology.

The success of an initiative depends to a large extent on the Laboratory's ability to identify and nurture cutting-edge science and technology on which enduring capabilities can be built. To do this, ORNL uses the resources of the Director's R&D Fund to encourage the research staff to submit ideas aimed at addressing initiative-specific research goals. Each spring, the Deputy Director for Science and Technology issues a call for proposals. The call emphasizes specific research priorities selected by management as being critical to accomplishing the Laboratory's initiatives.

The initiatives and research priority areas for FY 2008 were as follows:

- *Advanced Energy Systems.* Transportation technologies including innovative vehicle power systems, new concepts for transferring energy to vehicles, and new approaches for reducing road congestion; nanotechnology for energy applications such new bulk materials and nanoscale electronics; buildings technology; and transformational energy technologies including, for example, novel approaches for improving the efficiency of heat exchangers, new spent-fuel reprocessing concepts, and carbon capture
- *Advanced Materials.* New materials for catalysts and extreme environments; design and control of buried interfaces that could result in novel materials for thermoelectrics, solid-state lighting, and solar conversion; new approaches for controlling molecular processes and molecular characterization at the nanoscale; and multifunctional materials
- *National Security.* Sensors and detectors for chemical, biological, and nuclear threats; mobile power sources; computational science for homeland security; and materials research for security applications

- *Neutron Sciences.* Novel applications of neutron scattering; neutron scattering in extreme environments; neutron physics; novel instrumentation concepts; scientific challenges of power upgrades for spallation neutron sources; and biological applications of neutron scattering
- *Systems Biology for Energy, Water, and Carbon Cycles.* Bioenergy including biomass to liquid fuels; detection and simulation of ecosystem response such as new tools to explore biological systems at multiple levels of spatial and temporal resolution; new approaches to understanding linkages between biology and ecosystems to energy and carbon cycles; and tools to measure health interactions with energy and carbon cycles
- *Ultrascale Computing.* Computer science and mathematics (e.g., scalable, fault tolerant system software, improved capabilities for storing and using large data sets, new algorithms); science and engineering applications (e.g., scalable application software, predictive capabilities for energy and earth systems, atomic- and molecular-scale models to solve grand challenges in biology, chemistry, physics, and materials); knowledge management (computing hardware and architectures for data analysis and decision making for homeland and national security); and cyber security and network assurance

To select the best and most strategic of the submitted ideas, the Deputy Director establishes a committee for each initiative to review the new proposals and associated ongoing projects. The committees are staffed by senior technical managers and subject matter experts, including external members.

Proposals to the Director's R&D Fund undergo two rounds of review. In the first round, the committees evaluate preliminary proposals and select the most promising for development into full proposals. In the second round, the committees review the new proposals and ongoing projects that are requesting second- or third-year funding. After the reviews are completed, the committees provide funding recommendations to the Deputy Director for Science and Technology, who develops an overall funding strategy and presents it for approval to the Leadership Team, ORNL's executive committee headed by the Laboratory Director. All projects selected for funding must also receive concurrence from DOE.

In FY 2008, $24.2 million was allocated to the Director's R&D Fund to support 88 projects, 40 of which were new starts (Table 2). About 90% of the fund's annual allocation is awarded to projects at the beginning of the fiscal year. The remainder, about 10%, is held in reserve primarily to support research projects of new R&D staff members being recruited to address strategic Laboratory needs. The levels of investment in each initiative are summarized in Fig. 1.

Table 2. ORNL LDRD by fund

	Director's R&D Fund	Seed Money Fund
Costs	$24.205 million	$4.489 million
Number of projects	88	64
Number of new starts	40	41
Continuing (second year of funding)	48	23
Average total project budget (1–3 years)	$612,411	$142,754
Average project duration	24 months	16 months

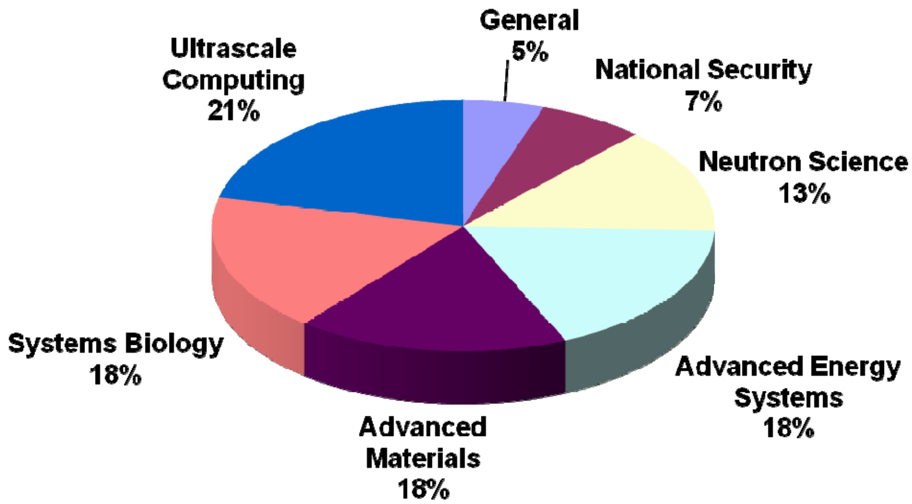

Fig. 1. Level of Director's R&D Fund investment in the Laboratory initiatives for FY 2008.

Seed Money Fund

The Seed Money Fund complements the Director's R&D Fund by providing a source of funds for innovative ideas that have the potential of enhancing the Laboratory's core scientific and technical competencies. It also provides a path for funding new approaches that fall within the distinctive capabilities of ORNL but outside the more focused research priorities of the major Laboratory initiatives. Successful Seed Money Fund projects are expected to generate new DOE programmatic or WFO sponsorship at the Laboratory.

Proposals for Seed Money Fund support are accepted directly from the Laboratory's scientific and technical staff (with management concurrence) at any time of the year. Those requesting more than $28,000 ($175,000 is the maximum) are reviewed by the Proposal Review Committee (PRC), which consists of scientific and technical staff members representing each of the Laboratory's research divisions and a member of the Office of Institutional Planning, who chairs the committee. To assist the committee, each proposal is also peer reviewed by two or three Laboratory staff members selected by the chair. Proposals requesting $28,000 or less are reviewed by the chair normally with the assistance of a technical reviewer. All Seed Money Fund proposals receiving a favorable recommendation are forwarded to the Deputy Director for Science and Technology for approval and require DOE concurrence.

In FY 2008, $4.49 million of the LDRD program was apportioned to the Seed Money Fund to support 64 projects, 41 of which were new starts (Table 2). The distribution of Seed Money Fund support by research division area is shown in Fig. 2.

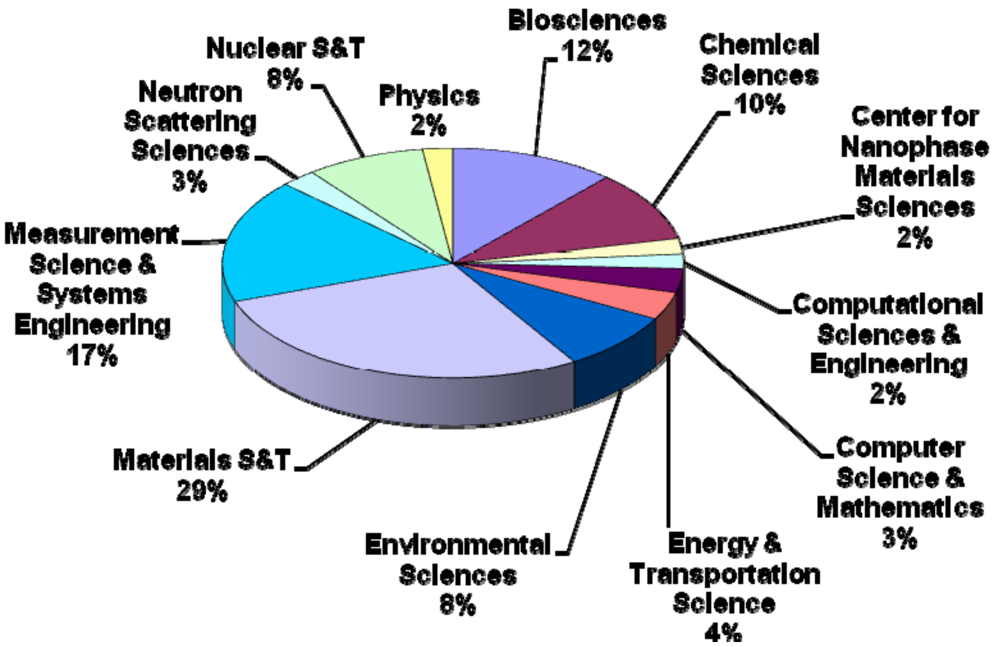

Fig. 2. Distribution of Seed Money Fund by research division for FY 2008.

Report Organization

This report, which provides a summary of all projects that were active during FY 2008, is divided into eight sections: one for each of the six Laboratory Initiatives discussed above, a General category of projects funded through the Director's R&D Fund by the Deputy Director for Science and Technology, and the Seed Money Fund. This section is further categorized by the research division of the principal investigator. The summaries are arranged by project number, and each summary contains (1) a project description, (2) a discussion of the project's relevance to the mission, and (3) results and accomplishments through the end of FY 2008. Publications resulting from the project are also listed.

Summaries of Projects Supported Through the Director's R&D Fund

ADVANCED ENERGY SYSTEMS INITIATIVE

00005

Multi-Component Fuel Spray Simulation Tools for Alternative Fuels

Joanna McFarlane, Valmor de Almeida, Johney Green, Stuart Daw, Kalyan Chakravarthy, Sam Lewis, Scott Sluder, Bill Steele, Robert Wagner, and Rolf Reitz

Project Description

A new tool set was developed for modeling combustion processes that combines knowledge of chemical physical properties, chemical kinetics, and computational fluid dynamics to simulate the performance of novel alternative fuels under realistic engine operating conditions. A database of chemical information on alternative fuels has been established from existing literature, computational analysis, and modeling. The project integrated this chemical database with various existing software components for chemical kinetics and in-cylinder combustion (CHEMKIN III, KIVA-3-ERC) to develop simulation packages of practical value for advanced engine research. A key aspect was the reduction of the chemical mechanism so that it can be incorporated into the engineering-scale simulation, and this was accomplished using a CHEMKIN-based sensitivity analysis. The new parallelized reaction-set analyses tool (XChemKin) was shown to be linearly scalable to 32 processors. The simulations were validated for advanced combustion modes by comparison with results obtained at the Fuels, Engines and Emissions Research Center (FEERC) of ORNL on biodiesel/diesel mixtures burned in Mercedes and Hatz diesel engines. Tools developed in this project, such as a multicomponent spray model, are applicable beyond biodiesel to evaluate engine performance with alternative fuel formulations such as oil sand fuels, heavy oils, and alcohol-based biofuels. Mechanisms and results from this project may also be used to benchmark Scientific Discovery through Advanced Computing (SciDAC) combustion calculations to assist in the development of supercomputing for engineering applications.

Mission Relevance

The development of non-petroleum sources of transportation fuel is an emerging national priority to reduce our dependence on foreign sources of petroleum. This project established a new research capability at ORNL of interest to two subprograms—the DOE Energy Efficiency Renewable Energy (EERE) Fuel Technology subprogram of the Office of FreedomCAR and Vehicle Technologies (OFCVT) and Fuels Combustion of the Office of Distributed Energy. The current OFCVT R&D plan specifically references the need for a predictive tool for next-generation transportation vehicles operating in advanced combustion modes on fuels derived from biomass, oil sands, or synthetic formulations. Funds from DOE EERE have been secured for continued collaboration with the University of Wisconsin beyond the scope of the project, and KIVA modeling will be supported by EERE. FEERC is also participating in an industrial consortium led by Reaction Design to model the chemical kinetics of advanced combustion.

Results and Accomplishments

This report describes the end of a 3-year project on the simulation of the combustion of biodiesel in advanced engines. Various aspects of combustion engineering were investigated, including the chemistry and physical properties of alternative fuels, computational fluid dynamics modeling of actual engines, and comparison of simulations with state-of-the-art experimental data on alternative fuels. The work was presented in four separate Society of Automotive Engineering publications in 2007 and 2008, as well as at the International Solvent Exchange Conference and the Southeastern Regional Meeting of the American Chemical Society, both in 2008. Technical gains include (1) determination of the physical properties for a variety of biodiesel components and testing of the effects of these properties on a multicomponent fuel spray model for a General Motors engine; (2) development of geometrically accurate meshes for engines and nozzles; (3) implementation of a multizone heat transfer model in a chemical kinetics framework; (4) development and scale-up of automated parallel computing software for reaction mechanism reduction and implementation with the Lawrence Livermore National Laboratory (LLNL) methyl butanoate mechanism; (5) preparation of a reduced reaction mechanism for biodiesel-diesel blends that was tested against ignition delay and NO_x emission data from a Sandia National Laboratories study; (6) chemical kinetic studies of biodiesel-diesel blends, alcohol mixtures, and surrogate n-heptane and methyl butanoate blends with comparison to FEERC and international data sets; and (7) establishment of capabilities to perform a neutron scattering study of the properties of high-pressure fuel sprays at the ORNL Spallation Neutron Source. Several graduate, undergraduate, and high school students participated in the project, demonstrating the commitment of ORNL and DOE to fostering scientific education in the United States.

Publications

Brakora, J. L., Y. Ra, R. D. Reitz, J. McFarlane, and C. S. Daw. 2008. "Development and Validation of a Reduced Reaction Mechanism for Biodiesel Fueled Engine Simulations." In *Proceedings of the Society of Automotive Engineers World Congress*, SAE 2008-01-1378.

Chakravarthy, K. 2007. "Physical Properties of Biodiesel and Implications for Use of Bio-Diesel in Diesel Engines." In *Proceedings of the Society of Automotive Engineers Fall Meeting*, SAE 2007-01-4030.

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Ra, Y., R. D. Reitz, and J. McFarlane. 2008. "Effects of Fuel Physical Properties on Diesel Engine Combustion Using Diesel and Bio-diesel Fuels." In *Proceedings of the Society of Automotive Engineers World Congress*, SAE 2008-01-1379.

Szybist, J. P., J. McFarlane, and B. G. Bunting. 2007. "Simulation of Biodiesel Blends HCCI in a Modified Hatz Diesel Engine." In *Proceedings of the Society of Automotive Engineers Fall Meeting*, SAE 2007-01-4010.

Szybist, J. P., J. McFarlane, and B. G. Bunting. 2008. "Comparison of Simulated and Experimental Combustion of Biodiesel Blends in a Single-Cylinder Diesel HCCI Engine." SAE 2007 Transactions, *Journal of Engines*. 1250–1260.

00034

Advanced Nuclear Fuel Examination and Testing

Gary L. Bell, Rick Battiste, Ralph B. Dinwiddie, and Sam Sham

Project Description

The goals of this project are to develop (1) a high-resolution, nondestructive thermography evaluation technique for imaging irradiated fuel and (2) an improved fuel cladding mechanical property testing method. The first task is to develop a high-resolution infrared (IR) surface thermal analysis system for the examination of the surface and subsurface of nuclear fuel rod cladding using active and/or passive IR thermography. This system will be installed as a diagnostic module on the new Advanced Diagnostics and Evaluation Platform in the Irradiated Fuels Examination Laboratory (IFEL) for post-irradiation examination of fuel rods; full-length light water reactor fuel rods can be examined. The second task is to develop and demonstrate full-consensus standardized mechanical testing methods for nuclear fuel cladding. This includes developing techniques to determine the elevated-temperature tensile hoop and tensile axial behavior of fuel cladding as a function of temperature and strain rate and producing an ASTM standard for the ORNL-developed expanded plug tensile hoop strength test.

Mission Relevance

The project will advance the state of the art in technologies for pre- and post-irradiation examination and testing of nuclear fuel and cladding materials. The data generated will enable nuclear fuel rods to have better fission product retention, higher plant electrical output, and improved plant reliability. This research is directly applicable to DOE's nuclear energy mission, and it directly supports the goals of the Next-Generation Nuclear Power Plant, Generation IV, and Nuclear Power 2010 programs, and the Advanced Fuel Cycle Initiative. The project will also benefit the U.S. Nuclear Regulatory Commission Loss of Coolant Accident licensing criteria program and Spent Nuclear Fuel licensing program by supporting the risk-informed, performance-based regulatory criteria obtained from a greater knowledge of the limits required to preserve fuel integrity throughout the fuel cycle. Specific examples where improved technical basis for regulation is needed are loss-of-coolant and reactivity transient accident initiators for in-core operation and improved source-term estimation for spent fuel in storage and under transportation.

Results and Accomplishments

IR Thermography. Infrared imaging of spent nuclear fuel rods was accomplished using an infrared periscope to avoid straight-line radiation exposures. This arrangement results in the IR camera being located approximately 3.5 to 5.5 m away from the fuel rod. The fuel was imaged through a 6.35 cm diam sapphire window originally installed for a gamma scanner. The combination of a small viewing area and long distance usually requires the use of an extreme IR telephoto lens, costing in excess of $50,000. This issue was overcome by the use of a $700 reflecting telescope, typically used by amateur astronomers. IR optics were not required since the telescope uses mirrors to directly image the fuel rod onto the focal plane array of the IR camera. The reflecting telescope provided a field of view of approximately 63.5 mm or about 0.18 mm per pixel. The ORNL Hot Cell Thermography System was successfully demonstrated on a North Anna irradiated fuel rod (ID No. B652A) on September 5, 2008.

Nuclear Fuel Clad Test Methods. The room-temperature expanding plug hoop tensile test method for testing irradiated fuel cladding (developed at ORNL) was extended to higher temperatures (700°C and 850°C) using a nickel plug in a stainless steel tube specimen. The load train components, plug length, specimen length, and plug geometry were investigated or optimized to reduce unwanted deformations. ORNL reports on the development/application of the expanding plug ductility test method for Zircaloy 4 fuel cladding were reviewed, and an analysis procedure was established to convert measured applied load to hoop stress in the cylindrical fuel clad specimen. It was concluded that this is a relatively simple and expedient test to evaluate the residual hoop ductility of small tubular specimens and, when applied to nuclear fuel cladding, allows a simple means to rank order the relative residual ductilities of different fuel claddings based on the measured residual hoop strains. In this regard, the test is considered to be a valuable tool for application to irradiated fuel cladding within the ASTM Standard Practice. A draft revision to the ASTM Standard E453-79 (Reapproved 2001), “Examination of Fuel Element Cladding Including the Determination of the Mechanical Properties,” was developed to incorporate the method for the “Expanding Plug Ductility Test” into the standard. A technical basis document for the Expanding Plug Ductility Test was also prepared. The draft revision of E453 and the supporting technical basis document were transmitted to S. T. Byrne, Chairman of ASTM Subcommittee E10.02 in October 2008. In addition, a proof-of-principle method for axial tensile testing of irradiated fuel cladding at elevated temperatures was developed using normal stainless steel tubing as the specimen and steel cylindrical gage blocks as plugs. Nonuniform deformation resulting from temperature variations (~25°C) in the area of interest is an issue that needs to be resolved. Due to the limited supply and cost of irradiated fuel cladding, a minimum specimen gage length study should be conducted. Also, a ceramic coating on the grip surfaces may be required to minimize damage and thus early failures of the brittle fuel cladding specimens at the ends.

00036

A Hybrid Hydrogen Storage–Generation System Based on Bi-Functional Nanostructured Photocatalysts

Panos G. Datskos, Nickolay V. Lavrik, Barton Smith, Viviane Schwartz, Costas Tsouris, and Claus Daniel

Project Description

Breakthrough technologies with application to energy systems can result from hydrogen production with photocatalytic splitting of water molecules. Our research relies on an innovative concept of a hydrogen generation system that utilizes unique properties of stressed nanostructures. The key idea of the proposed research is related to the fact that certain forms of TiO_2 are promising for photocatalytic splitting of water while others are efficient sorbers of molecular hydrogen. We focus our efforts on the recently discovered phenomenon of tailoring the energy bandgap of TiO_2 via mechanical stress. Our research encompasses several model systems that incorporate TiO_2 nanostructures with the goal of quantifying their properties relevant to hydrogen generation as a function of both externally applied mechanical stress and intrinsic strain. Evaluation of potential challenges associated with the scaling of this concept from micro- to large-scale systems will be the focus of our particular attention. The overall significance of the proposed concept lies in the possibility of creating hydrogen generation–storage hybrids capable of self-replenishing using available solar energy. Such modules are anticipated to be used in hydrogen-based transportation and other high-energy-density applications. The goal for the first 10 months of the project was to synthesize and characterize various titania phases and set up an electrochemical cell to be used in the second year for photo-electrolytic reactions.

Mission Relevance

The proposed project is relevant to the DOE Hydrogen Program and the DOE Materials Science and Technology subprogram within the DOE Office of Science. The present work will advance the science of stressed materials as catalysts and microfabrication. Several programs that are under way in the DOE Office of Science will benefit from the knowledge gained during this work.

Results and Accomplishments

During FY 2008 we made significant progress in the following four scientific and technical areas: (1) synthesis of titania phases, (2) substrate modification that promotes enhanced nanomechanical interrogation of titania phases, (3) comprehensive characterization of synthesized titania, and (4) prestressed substrate approach. Titania-based materials are known for their multifaceted functionality, excellent chemical stability, and existence of numerous nanostructured phases, including nanoparticles and nanotubes. In particular, the unique combination of physicochemical robustness and appropriate electronic structure of titania makes it promising as a material for solar energy conversion. To this point, ability to further optimize electronic properties of titania without adversely affecting its physicochemical stability is often envisioned as the most critical milestone on the way to a material capable of highly efficient solar energy conversion. We studied nanoscale mechanical and structural phenomena in order to achieve in situ reversible bandgap tuning in titania without changing its chemical composition. During this work we prepared and evaluated a series of titania thin films on nanostructured substrates with the ultimate goal of creating a system in which either tensile or compressive mechanical stress could be controllably applied to the titania phase. In addition to this ability of in situ reversible bandgap tuning, the added advantages of such as system include an increased surface area and mechanical flexibility and compatibility with many technological strategies commonly used in microfabrication.

The major thrust of our effort focused on utilization of the three distinctive technological strategies with potential to yield strained titania: (1) spontaneously formed titania nanoparticles, (2) thin film approaches, and (3) electrochemical oxidation. We have successfully implemented several technological modifications of each of these strategies and conducted further selection of most promising candidates based on our morphological, structural, and compositional analyzes of the samples obtained. Our particular goal was to identify the processes that could induce intrinsic tensile stress or facilitate application of external strain to the resulting titania phases.

Publications

Daniel, Claus, Nickolay V. Lavrik, Panos G. Datskos, Barton Smith, Vivianne Schwartz, and Costas Tsouris. In preparation. "Stress-Strain Control of Titania Thin Film on Periodically Structured Surfaces."

Daniel, Claus, Vivianne Schwartz, Nickolay V. Lavrik, Barton Smith, Costas Tsouris, and Panos G. Datskos. In preparation. "Deposition and Characterization of Photocatalytic Titania Films on Nano and Micro Structured Surfaces."

Lavrik, Nickolas V., Claus Daniel, Vivianne Schwartz, Panos G. Datskos, Barton Smith, and Costas Tsouris. In preparation. "In Situ Reversible Band-Gap Tuning with Titania Thin Films." Abstract to be submitted to the 32nd International Conference and Exhibition on Advanced Ceramics and Composites.

Lavrik, Nickolay V., Claus Daniel, Barton Smith, Vivianne Schwartz, Costas Tsouris, and Panos G. Datskos. In preparation. "Preparation of Strained Titania Films Using Pre-stressed Silicon Oxide."

00037

Modular Utility-Scale Power Converters and Controllers for the Next-Generation Grid

Leon Tolbert, Madhu Chinthavali, Burak Ozpineci, Fran Li, John Kueck, Michael Starke, Hui Zhang, and Yan Xu

Project Description

The development of a utility voltage power electronics module could be useful in a wide variety of applications, including utilizing transmission lines to their full capacity, high-voltage dc (HVDC), flexible ac transmission (FACTS), static VAR compensation, solid-state transformer, large-motor-drive applications, and aggregation of multiple distributed energy (DE) sources. The modules developed for utility applications will have high reliability owing to their durability and flexibility. Modules will have fault-current-limiting features and detection circuits such that they can limit the current through the module from external faults and can identify and isolate internal faults so that the remaining modules can continue to operate with only minimal disturbance to the utility or customer. The development of a reliable, efficient, low-cost power electronics module will be a key enabling technology for harnessing more power from distributed generation, for increasing the use of FACTS and HVDC, and for ultimately having absolute control over power flow in the grid.

Mission Relevance

The DOE Office of Electricity Delivery and Energy Reliability (OE) has interest in this research as it expands the Power Electronics and Energy Storage Program. The distributed generation (DG) program is interested in how a modular power electronic interface can aid DG sources such as solar cells or microturbines in providing additional ancillary services to the grid and making them more cost-effective. This project addresses one of the needs raised in ORNL Report ORNL/TM-2005/230, *Power Electronics for Distributed Energy Systems and Transmission and Distribution Applications: Assessing the Technical Needs for Utility Applications*, prepared in 2005 for DOE OE. Another DOE program interested in the results of this project is the Vehicle Technologies program, as this program has interest in plug-in hybrid electric vehicles and their ability to act as a distributed energy resource for the electric grid.

Results and Accomplishments

Many new-generation sources will be dc (solar panels, fuel cells) instead of ac. Interfacing these with the ac system requires a converter and incurs subsequent power electronics losses. A study was conducted comparing the dc distribution with ac distribution for ORNL's electrical system, and the advantages and disadvantages of a dc distribution system were highlighted. To safeguard power electronics used in utility applications, a fault-current-limiting and protection circuit should be provided, working independently of the gate drive circuit. A test circuit was developed consisting of an insulated gate bipolar transistor (IGBT), which is a device under test, and a switch to introduce hard switch fault (HSF) and fault under load (FUL) conditions for device testing. A special gate drive control unit was simulated to show how fault currents can be limited by controlling the gate voltage and resistance. To minimize the number of components used, the gate-under-voltage lockout feature is integrated with the gate-voltage-reduction feature. The entire operation of fault detection and current-limiting feature enabling was done within 4 μs for HSF and 2 μs for FUL conditions.

A study was conducted on the impact that silicon carbide (SiC) power electronics would have on the design of wind turbines for electricity production. The loss was reduced up to 80% when using SiC devices as compared with silicon devices. The heat sink requirements were also reduced substantially.

Further development of these devices is expected to yield efficiency and cost savings for other utility applications.

Publications

Starke, M. R., L. M. Tolbert, and B. Ozpineci. 2008. "AC vs. DC Distribution: A Loss Comparison." *IEEE PES Transmission and Distribution Conference and Exposition*, Chicago.

Xu, Y., L. M. Tolbert, J. N. Chiasson, F. Z. Peng, and J. B. Campbell. 2007. "Generalized Instantaneous Nonactive Power Theory for STATCOM." *IET Proceedings on Electric Power Applications*, 853–861.

Yu, X., M. R. Starke, L. M. Tolbert, and B. Ozpineci. 2007. "Fuel Cell Power Conditioning for Electric Power Applications: A Summary." *IET Proceedings in Electric Power Applications*, 643–656.

Zhang, H., and L. M. Tolbert. 2008. "SiC's Potential Impact on the Design of Wind Generation System." *IEEE Industrial Electronics Society Annual Conference*, Orlando, Fla.

00038

Alternative Feedstocks for the Petrochemical Industry from No-Sulfur-Added Biomass Lignins

David DePaoli, Alicia Compere, William Griffith, Chaitanya Narula, and Arpad Vass

Project Description

This project consists of initial studies for demonstrating the feasibility of using biomass lignins to extend or replace the 3.6 EJ/year of fossil resources used as feedstocks in the production of chemicals. We aim to exploit a new capability developed by ORNL for "cleaning" lignin to convert this current high-volume waste material into aromatic feedstocks for petrochemical production. We will assess the potential for conversion of biomass lignins to polyesters and other high-volume, high-valued polymers. The work includes fundamental studies of lignin properties and development of catalytic and biocatalytic processes that permit conversion of lignin into both aromatic and cyclic or aliphatic feedstocks, which are directly useful for producing a wide range of materials. Model compound systems and chemical feedstocks derived from lignin monomers will be evaluated as polymer feedstocks. Feedstock production from the lignin portion of biomass will complement the ongoing DOE initiative for cellulosic ethanol production from the non-lignin portion of biomass. The production of high-value chemicals, in addition to fuel, in a biorefinery is expected to improve the biorefinery process economics.

Mission Relevance

This project aims to develop transformational energy technology. Feedstock production from the lignin portion of biomass will complement the ongoing DOE initiative for cellulosic ethanol production from the non-lignin portion of biomass. The production of high-value chemicals, in addition to fuel, in a biorefinery is expected to improve the biorefinery process economics. DOE programs and federal agencies that will benefit from this research include the Biomass and Industrial Technologies programs of the DOE Office of Energy Efficiency and Renewable Energy; the Department of Agriculture, which is partnering with DOE on the National Biomass Initiative; and the Defense Advanced Research Projects Agency (DARPA), which currently has projects aimed at development of fuels from renewable sources.

Results and Accomplishments

This project has been successful in providing proof-of-concept data indicating that industrially viable approaches for separation of carbohydrate- and contaminant-free lignin may enable the development of routes to high-value aromatic chemical feedstocks. Excellent progress was made in experimental studies aimed at demonstrating capability to convert lignin into valuable feedstocks, including (1) demonstration of the capability for depolymerization of lignin into separable subunits by chemical processes, including catalytic and pyrolytic approaches; (2) demonstration of the capability for depolymerization and ring cleavage of lignin into a number of high-value feedstock chemicals by microbial and enzymatic conversions; and (3) initial economic analyses of lignin-to-feedstock processes.

In catalytic studies, we have clearly demonstrated that the ether linkages in lignin molecules can be cleaved under mild conditions. Our pyrolysis testing of cleaned, carbohydrate-free biomass lignin showed the feasibility of producing oxygenated phenolics analogous to those used as polyester feedstocks at relatively high yield. Several microorganisms isolated from soils were identified to have superior capabilities for lignin degradation; significantly more research will be required to determine the exact combination and concentration of microbes isolated from the consortia that will produce desired end products.

A preliminary assessment of the product mixtures generated from pyrolysis testing conducted in conjunction with industrial consultants indicates promising potential to overcome obstacles that have been identified by the DOE Biomass Program toward development of commercially viable approaches to utilization of lignin. DOE program managers have expressed interest in the results of this project, indicating potential opportunities for follow-on efforts.

Publications

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00039

Developing a Science Base for Nuclear Fuel Reprocessing Separations

Valmor de Almeida, Richard Archibald, Joseph Birdwell, Shengting Cui, David DePaoli, Robert Jubin, Bamin Khomami, Bruce Moyer, and Costas Tsouris

Project Description

This work was aimed at developing an experimentally validated computational capability for understanding the complex processes governing the performance of solvent extraction devices used for separations in nuclear fuel reprocessing. These applications pose a grand challenge due to the combination of complicating factors in a three-dimensional, turbulent, reactive, multicomponent, multiphase/interface fluid flow system. The currently limited process simulation and scale-up capabilities provide uncertainty in the ability to select and design the future separations technologies for reprocessing nuclear spent fuel in the United States. The studies undertaken in this project successfully revealed critical issues needed to be taken into account in the development of scientifically based models. These studies also initiated steps toward the development of a modern modeling approach and have positioned ORNL to address emerging opportunities in reprocessing separations.

This basic research project had three major thrusts, namely, a prototype experimental station, a continuum modeling effort, and molecular modeling and kinetics support. Excellent progress was made on corresponding activities in (1) defining, assembling, and operating a relevant prototype system for model validation and computer-aided image processing of results; (2) establishing a mathematical framework for modeling fluid flow and transport; (3) performing subscale molecular modeling and simulation.

Mission Relevance

This project is highly relevant to DOE’s Advanced Fuel Cycle Initiative and positions ORNL to play a key role in developing radiochemical separations technology required for America’s next-generation nuclear capabilities. Future radiochemical engineering science R&D activities that could use the results of this project are consistent with ORNL’s mission. These results provide ORNL with a capability to progress from basic science to engineering demonstration in this field. This work is relevant to other key national radiochemical programs, including ^{238}Pu production, and applications of National Nuclear Security Agency and Environmental Management.

Results and Accomplishments

The project gained insight into outstanding issues needed for the development of advanced modeling and simulation approaches in solvent extraction as applied to nuclear fuel reprocessing. We assembled and operated a high-speed visualization setup for analysis of microflow regimes in realistic liquid-liquid mixtures at operating conditions of centrifugal contactors. The experiments uncovered key new information on phase connectivity as a function of macroscopic parameters. We advanced the development of a systematic computer-aided image analysis code for obtaining size distribution and velocities of bubbles and drops on large data sets of noisy, low-contrast images. This information provides unique insight for the development of fluid flow models and simulation codes.

We developed an approach for structured continuum modeling able to incorporate necessary phenomena to predict realistic behavior of centrifugal contactors. The effort started here will guide the development of large-scale simulation codes for the prediction of multicomponent, multiphase field quantities representative of averages over the millimeter length scale and millisecond time scale.

In collaboration with the Department of Chemical and Biomolecular Engineering at the University of Tennessee, we explored a molecular dynamics simulation approach to obtain insight on metal ion transport at the liquid-liquid interface between the aqueous uranyl nitrate solution and the tri-butyl phosphate/dodecane solution. The simulation was the first of its kind that considered a realistic diluent (dodecane), and the largest of its kind that considered six molecular components. The experience and insight obtained from this effort will guide future developments in force field calibration, development of high-performance molecular dynamics core engines, and local experimental measurement of dynamic interfacial transport.

Publications

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00048

Theoretical and Computational Methodologies and Tools for Second-Generation Integrated Fusion Simulation

Luis Raul Sanchez

Project Description

Our project intends to lay the basis for achieving more accurate simulations of fusion experiments close to burning-plasma conditions in the near future. This predictive capability will be critical to support design decisions and to operate next-step experiments—such as the International Tokamak Experimental Reactor (ITER)—or future power-producing facilities. Due to the large disparity of relevant scales, present in the problem (over ten orders of magnitude in time scales, around six in spatial scales), direct simulation is simply impossible with present-day resources. Instead, the problem is broken down in smaller pieces that deal with reduced ranges of temporal and spatial scales that must be simulated by specialized codes. All these pieces must then be brought together, in order to perform a global simulation, in a self-consistent manner, which requires the iterative interchange of relevant information among the different codes. Many of the codes presently available to attack the partial problems are not the most appropriate to play these roles within the integrated simulation framework just described. Also, determining how information must be passed among the different codes while preserving the essential physics is still an object of active research. The current project aims at improving the present situation in both regards. First, we will attempt to lay the basis for development of a new fast magneto-hydrodynamical (MHD) equilibrium code able to tackle the complex magnetic topologies (such as magnetic islands or open field lines) relevant in these global simulations. Second, we will explore several promising methods that may act as efficient interfaces among those pieces of the problem for which they are presently unavailable. Namely, the interaction of fast scales (associated to wave-particle interactions and microturbulence) with the slower ones that determine the confinement properties of magnetic confinement devices. From these studies, fundamental insights on the dynamics of turbulence and its impact on tokamak confinement will also be gained.

Mission Relevance

DOE Office Science, Fusion Energy Sciences has recognized the need for accurate simulation capabilities with predictive power as one of its top priorities, from which major future initiatives should be expected. The development of a numerical framework as the one sketched above—in which various specific codes calculate and efficiently transfer each piece of information relevant to carry out a global simulation—is the main objective of the Fusion Simulation Project (FSP), an ambitious 15 year program being proposed for funding by DOE Office of Science. Indeed, the main goal of FSP is to "develop a fully integrated capability for predicting the performance of externally controlled fusion systems, including turbulent transport, macroscopic stability, wave-particle physics and multi-phase interfaces." The problems addressed by this project may also benefit the development of numerical tools to support the design and operation of the multinational ITER project.

Results and Accomplishments

During FY 2008 we assembled the different algorithmic pieces identified in FY 2007 and delivered a prototype of a new island MHD solver code (SIESTA). Initial exploration on its parallel capabilities and performance has been initiated, and several ways to deal with the inversion of the block-tridiagonal matrices required for the solution in a parallel environment have been investigated—mostly divide and conquer and cyclic reduction methods. We have also started testing the code beyond the simple configurations used in FY 2007. In particular, we have applied our efforts to the solution of several ITER-relevant configurations with reasonable success. Regarding the investigation on new closure methods capable of incorporating the microturbulent dynamics into MHD simulations, we have investigated how to form effective closures via fractional techniques in the case of radial transport across sheared poloidal flows using PIC gyro-kinetic codes. In particular, ion-temperature-gradient turbulence with different types of poloidal sheared flows (both self-consistently driven by turbulence via Reynolds stresses and externally driven) has been studied. The results have shown that traditional closure schemes based on reduced effective diffusivities are inadequate in this case, particularly at the short to medium timescales, and may inject the wrong type of dynamical information into the longer timescale MHD simulations. In addition, we have further developed dynamical tools based on these studies that should be usable for validation and verification (V&V) activities among codes. V&V is a DOE priority for the coming years, particularly regarding both fluid and gyro-kinetic plasma simulation in massively parallel supercomputers.

Publications

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Sanchez, R., D. E. Newman, J. N. Leboeuf, V. K. Decyk, and B. A. Carreras. 2008. "On the Nature of Transport Across Sheared Zonal Flows in Electrostatic Ion-Temperature-Driven Gyrokinetic Plasma Turbulence." *Phys. Rev. Lett.*, accepted for publication.

05011

Nanocomposites for Advanced Thermoelectrics

Brian C. Sales, David J. Singh, Hsin Wang, Jane Y. Howe, and Michael A. McGuire

Project Description

Thermoelectric devices can convert heat into useful electricity with no moving parts. Considerable progress has been made in improving the efficiency of these devices over the past 15 years. Recent improvements in thermoelectric efficiency in thin-film superlattice structures appear to be dominated by a reduction in the lattice thermal conductivity. The reduction is accomplished by the careful introduction of 0.1- to 5-nm-sized "objects" that effectively scatter acoustic phonons without significantly affecting electronic transport. This has been demonstrated convincingly in one recent thin-film superlattice study although exactly how this occurs is not understood. We propose to investigate the effects of the introduction of controlled amounts of nanoparticles into bulk samples of good thermoelectric materials. One goal is to understand how the interface scattering between nanoparticles and the surrounding crystalline solid can lower the thermal transport without significantly altering (and in some cases enhancing!) electronic transport. The effects of nanoparticle size, shape, bonding, and composition will be investigated. A second goal will be to use nanoparticles to produce a bulk thermoelectric nanocomposite that potentially can be incorporated into a usable device.

Mission Relevance

This project is relevant to DOE's energy mission. Thermoelectric materials can be used to construct all solid-state devices that directly convert heat into electricity with no moving parts. The heat can come from the sun or can be waste heat generated by a variety of sources including power plants, chemical plants, or automobiles. The basic idea is to use thermoelectric modules to convert part of the heat back into useful electricity, thereby improving overall energy efficiency. For automobiles, the net result would be to use less gasoline. The main problem with today's thermoelectric materials is poor efficiency. At the end of this project we expect to have a much better understanding of the nanoparticle-host interface and how to "tune" the properties of a nanocomposite for optimal thermoelectric performance. It is also possible that we will produce a bulk nanocomposite material that is efficient and cheap enough for some waste-heat-to-electricity applications.

Results and Accomplishments

During FY 2008, the first year of the project, we made considerable progress and were able to quickly increase the thermoelectric figure of merit (ZT) in a $Si_{0.8}Ge_{0.2}$ + clathrate phase nanocomposite by a few percent over the state-of-the-art results reported in the literature. A $Si_{0.8}Ge_{0.2}$ alloy was selected for the first nanocomposite studies because of the large amount of reliable baseline information available in the literature. To determine the correct nanocrystal size distribution, we need to know how much heat is carried by phonons with a given frequency. David Singh has started to develop the computer codes necessary to perform just such a calculation. Singh completed a calculation of the phonon density of states for a $Si_{0.8}Ge_{0.2}$ alloy. A variety of different synthesis approaches were investigated to introduce the clathrate nanocrystals (e.g., $Ba_8Al_{11}Si_{31}$) into the $Si_{0.8}Ge_{0.2}$ host phase. We found that the final densification of the material using a conventional hot-press was too slow, resulting in significant grain growth. Initial (nonoptimized) results from a more rapid densification process using a spark-plasma-sintering (SPS) system are very encouraging and have already resulted in nanocomposites with significantly higher (≈20%) values of ZT. Using theoretical input from Singh's calculations, we plan to expand the nanocomposite concept to other materials such as PbTe, where theory and recent experimental results indicate the possibility of simultaneously lowering the thermal conductivity and increasing the electronic power factor.

Publication

An, J., A. Subedi, and D. J. Singh. 2008. "Ab Initio Phonon Dispersion for PbTe." *Physical Review B*, accepted for publication.

05015

Irradiation of Advanced Light Water Reactor Fuel in the High Flux Isotope Reactor

Joel McDuffee, Jess Gehin, Randy Hobbs, Larry Ott, Lance Snead, Donald Spellman,
Dennis Heatherly, Ronald Ellis, and Kenneth Thoms

Project Description

This project will develop a new test capability at the High Flux Isotope Reactor (HFIR) that will allow testing of advanced nuclear fuels under prototypic, light water reactor (LWR) operating conditions in approximately one-half the time it takes in other research reactors. This capability will be demonstrated by irradiating test rods each containing prototypically dimensioned LWR fuel pellets in pins. We will develop the test plan and configuration for HFIR, design the test fixtures and components, complete the required calculations and safety evaluations and approvals, and fabricate the test basket and capsules. The test configuration will be used to conduct a SiC clad/uranium-fueled experiment (specimens supplied by Westinghouse and Ceramic Tubular Products [CTP]) in a HFIR Vertical Experiment Facility (VXF) position. We will irradiate the test specimens in HFIR for a period adequate to demonstrate the new HFIR capability (three cycles, ~4 GWd/MT-HM burnup) and conduct nondestructive examinations to validate the viability of the new test apparatus.

Mission Relevance

This project is focused on advanced fuel/cladding experimental capabilities in HFIR and its capability to duplicate commercial LWR operating conditions. With the resurgence of nuclear power in the world, many years of pent-up fuels testing will now have a facility at which to conduct a complete fuels experimental program, including fuel development, materials development, experiment fabrication, in-reactor testing at LWR conditions, and utilization of ORNL state-of-the-art post irradiation examination. Widespread interest in both the commercial and governmental sectors supports the development of longer-lived, robust, advanced fuel materials. Westinghouse/CTP, Knolls Atomic Power Laboratory, and the Nuclear Regulatory Commission have recently inquired about ORNL's capabilities for fuel testing and examination. The proposed project also affords ORNL the opportunity for a unique contribution to DOE's Global Nuclear Energy Partnership program.

Results and Accomplishments

Progress has essentially followed the plan developed for the LDRD project. The overall design is complete, and design drawings are being finalized. Safety calculations are ongoing but have progressed to the addressing of design-related safety issues. Most components have been ordered, and assembly will begin in the first quarter of 2009.

Each fuel pin, containing 11 fuel pellets within a SiC cladding, will be housed inside a stainless steel capsule. There will be three coolant channels in the basket, and each coolant channel will hold a stack of three capsules (upper, middle, and lower), for a total of nine capsules per HFIR experiment position.

The experimental facility will be located in the permanent beryllium reflector in one of the VXF positions. Initial irradiations will be in an outer small VXF, which allows for a step-increase in the neutron flux by migrating the capsule from an outer small VXF position to an inner small VXF. Initial calculations indicate a potential increase of 35–40% in the linear power rate with this move. A step-increase can also be imposed by replacing the shield with one of a different material or thickness. Thus, there are a number of options and methods for control of the test irradiation conditions.

Design calculations indicate that a 2.32 mm thick hafnium shield will lead to linear power generation rates in the hottest of the pins in the middle axial position that will satisfy the UO_2 safety case with a rate of 8.66 kW/ft. The depletion of the hafnium is at a rate that offsets the burnup effects of 3.8 wt % enriched UN fuel (or 4.95 wt % enriched UO_2 fuel), such that the linear heat generation rate of the fuel stays relatively constant, at least over the first few cycles. With this configuration and shield thickness, linear power ratings average 18 kW/m for the six upper and lower capsules and 26 kW/m for the three middle capsules. The linear power rate in the fuel decreases at about 1.1% per cycle. Though the hafnium is being depleted, the hafnium shield can be replaced as necessary with an even thinner shield after a selected number of HFIR fuel cycles to increase the linear power in the irradiation facility fuel pins.

There are two main design problems that are currently being addressed. First, we have found it difficult to purchase the hafnium shield. Although such shields have been fabricated and used several times in the past, hafnium supplies seem limited at this time. Second, CTP is having difficulty sealing the clad in the presence of fuel. Their initial procedure called for a slow heat-up to 400°C in an air environment. However, this process would lead to oxidation of the fuel. CTP is actively searching for an alternative method.

Publications

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Spellman, Donald, Joel McDuffee, Dennis Heatherly, Ron Ellis, Larry Ott, Randy Hobbs, Kenneth Thoms, and Doug Sparks. 2008. "Summary of March 6, 2008, ORNL Meeting on HFIR Tests for CTP/Westinghouse Advanced Fuel." Mar. 18, Oak Ridge National Laboratory.

05057

Automated Freeform Construction Technologies and Materials

François G. Pin, Randall F. Lind, Catherine H. Mattus, Dan J. Naus, Jan Kosny, Leslie R. Dole, and Robert E. Norris, Jr.

Project Description

Our objective is to investigate and develop the enabling freeform technologies for automated construction of large-scale components and structures, in particular residential and low-rise commercial buildings. The two key areas are (1) materials selection and emplacement properties and (2) the processes and devices through which these materials can be precisely deposited using automation. We will first develop the requirements relevant to the various elements of buildings (load bearing, energy efficiency, etc., for foundations, upper floors, and roof). In close coordination, we will also investigate materials that lend themselves to automated freeform construction processes as well as deposition strategies that maximize strength, geometric accuracy, and throughput. Deposition devices and processes that can efficiently support the automated layout of these materials will be developed. We will consider the paradigms of in-factory automated fabrication of building modules and on-site automated construction processes. The goals and deliverables of the project are to (1) develop, evaluate, and demonstrate a suite of materials and associated automation-suitable deposition controls that demonstrate the feasibility of the freeform automated construction concept, and (2) develop enabling science experiments and tests, including a proof-of-principle demonstration of the enabling processes at a scale relevant to building construction (e.g., 8 ft by 4 ft wall panel/module).

Mission Relevance

Automated freeform construction (AFC) has the potential to directly benefit the DOE Buildings Technology program by producing buildings with better energy efficiency, strength, environmental sustainability, material utilization, and durability while lowering waste, costs, and building time. Improved energy efficiency and reduced waste will also lower greenhouse gas emissions. The Department of Defense could benefit from the potential of AFC to produce complex, multilayer, blast resistant structures in forward areas rapidly and with limited personnel. The Federal Emergency Management Agency could benefit from the potential of AFC to produce structures rapidly for disaster relief. The Defense Advanced Research Projects Agency and the Office of Naval Research are interested in free-forming, large-scale components and molds for the casting and tooling industries. The planetary exploration programs of the National Aeronautics and Space Administration have indicated interest in in situ automated construction of extraterrestrial structures. Automated freeform systems that make use of native materials would be ideal for this application.

Results and Accomplishments

We completed a coordinated review of composite cementitious materials and related extrusion technologies, and developed target ranges of rheological, geometrical, and deposition parameters for the concept of free-form construction. Candidate component materials were acquired, and nearly a hundred mixtures were experimentally evaluated to progressively achieve fast set times, free-formability (i.e., plastic and cohesive enough for extrusion), gel time, and gel strength (to support next layer). The major result in this materials area is a basic concrete formulation that achieves both excellent extrusion and post-extrusion characteristics. An invention disclosure on this unique free-formable material formulation has being filed. We have also developed a second class of mixtures using the developed free-formable formulation and lightweight aggregates to achieve a free-formable material with higher insulating properties. To support quantitative tests of the materials, we have developed a set of basic instruments, including several penetrometers, to evaluate the gel and set strength and time histories over our time scale of interest (from seconds after mixing to a few hours). We have also developed a test stand to investigate the extrusion ability of the cementitious material mixtures as they were developed and have performed initial free-forming tests. Several nozzles and deposition heads were fabricated and tested, including some for premixed, single-strip evaluation, and others for deposition with secondary mixing of a set accelerator near the nozzle. Linear single-layer and multilayered specimens were generated and evaluated. The focus of our planned FY 2009 activities is on patterned layering and adhesion tests of multilayered specimens, evaluation of refined deposition heads for edge and end-effect control, assembly of a gantry for coordinated motion and extrusion, and three-dimensional experiments.

05075

High-Performance Proton-Conducting Fuel-Cell Electrolytes Based on Task-Specific Protic Ionic Liquids

Sheng Dai, Huimin Luo, Gary A. Baker, and Todd J. Toops

Project Description

The goal of this project is to develop alternative proton-conducting media based on task-specific ionic liquids (TSILs) possessing tunable physicochemical properties toward highly conductive and robust fuel-cell proton electrolytes. This project specifically addresses the research needs for the development of advanced hydrogen-based fuel-cell systems by employing novel protic ionic liquids (PILs). Highly conductive, PILs are proposed to replace current, conventional polymer electrolytes as advanced proton-conducting media, achieving superior and robust fuel-cell systems. The introduction of novel proton-conducting electrolytes lies at the forefront of fuel-cell technology development. This research will build upon ORNL's extensive and pioneering expertise in development of ionic liquids. This project will allow us to develop the next generation of proton-conducting media that can (1) mitigate the current problems in polymer electrolyte fuel cells (PEMFCs) associated with platinum loss induced by acid dissolution and, more importantly, (2) be interfaced with non-platinum-based electrocatalytic systems, which are incompatible to the current fuel-cell systems based on highly acidic polyelectrolytes.

Mission Relevance

To meet the specific 2010 targets of the Hydrogen, Fuel Cells & Infrastructure Technologies programs of the DOE Office of Energy Efficiency and Renewable Energy (EERE), innovative technologies are needed in development of stable and conductive electrolytes for proton conduction under non-humidified conditions. The proposed project has the potential to achieve this goal through the development of novel PILs. This approach, with its emphasis on using novel PILs and inexpensive synthesis methods to produce useful quantities of true "designer proton conductors," is a perfect candidate for new funding under the Hydrogen Initiatives recently announced by DOE EERE and the DOE Office of Science, Basic Energy Sciences. The new PILs that will be synthesized also have great potential for applications in solar cells, batteries, and supercapacitors. The proof of concept demonstrated by this LDRD project will place ORNL at the forefront of the field. This program is also expected to benefit fuel-cell and energy-storage development at the Defense Advanced Research Projects Agency, the National Nuclear Security Agency, and private industries.

Results and Accomplishments

During FY 2008, the project's first year, we made considerable progress toward a deeper understanding of two vital issues underlying the development of next-generation proton-conducting TSILs as fuel-cell electrolytes:

1. Vaporization enthalpies for two series of ionic liquids (ILs) composed of 1-*n*-alkyl-3-methylimidazolium cations, $[Im_{m1}^{+}]$ (m = 2, 3, 4, 6, 8, or 10), paired with either the bis(trifluoromethanesulfonyl)amide, $[Tf_2N^{-}]$, or the bis(perfluoroethylsulfonyl)amide anion, $[beti^{-}]$, were determined using a simple, convenient, and highly reproducible thermogravimetric approach, and from these values Hildebrand solubility parameters were estimated. Our results reveal two interesting and unanticipated outcomes: (a) methylation at the C2 position of $[Im_{m1}^{+}]$ affords a significantly higher vaporization enthalpy, and (b) in all cases, the $[beti^{-}]$ anion served to lower the enthalpy of vaporization relative to $[Tf_2N^{-}]$. The widespread availability of the apparatus required for these measurements coupled with the ease of automation suggests the broad potential of this methodology for determining this critical parameter in a multitude of ILs.

2. We introduced a completely new class of PIL based on the use of various superbase starting materials. Unlike all previously known PILs, our superbase-superacid dyads are no longer limited by proton transfer retro-reaction known to occur at temperatures as low as 100°C (or below) in conventional PIL systems. As a result, reverse proton-transfer reactions do not occur within this PIL, and vaporization losses are immeasurably low even at temperatures approaching 150°C. These features suggest outstanding potential for this new class of superbase-derived PILs in high-temperature fuel-cell applications.

Publication

Luo, H., et al. 2008. "Isothermogravimetric Determination of the Enthalpies of Vaporization of 1-Alkyl-3-methylimidazolium Ionic Liquids." *J. Phys. Chem. B* **112**, 10077–10081.

05099

Manufacturable Nanotransistors for Advanced Analog Circuits

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Project Description

For the first time since nanoscale materials took front stage on research agendas around the globe, emerging fabrication technologies may unlock the power of analog nanoelectronics by enabling true integration of novel nanodevices into functional circuits. Silicon nanowire transistors (SiNWTs) offer potentially dramatic performance improvements over CMOS (complementary metal-oxide-semiconductor) devices in terms of gain (or transconductance), power consumption, and charge sensitivity. Further, their size may allow operation in the terahertz (10^{12} Hz) frequency regime, the holy grail of high-bandwidth radio-frequency (RF) communications systems. Unlike single carbon-nanotube devices, which have shown remarkable properties but are difficult to produce consistently, our approach would extend current manufacturing methods using conventional silicon to enable high-volume, high-yield manufacturing, thus allowing widespread application and commercialization. The proposed work would go beyond the current silicon nanowire art and focus on the development of self-aligned-gate nanowire electronic structures for practical circuits, and capitalize on our strength in analog electronics. This research will produce an enabling technology for realization of a new class of high-speed, ultralow-power, highly miniaturized integrated circuits well suited for nanoscale sensing applications.

Mission Relevance

Modern CMOS integrated circuits depend on charge as the fundamental state variable where current is the motion of charge and voltage is the storage of charge. Any development that seeks to maximize the ability to sense either current or voltage in a circuit will contribute greatly to the ability to use a given device for analog processing. The proposed nanowire transistors would not just enhance the function, but their charge sensitivity would actually eliminate much circuitry presently required. For example, conventional circuits require that stages of amplification be added to handle very small signals without distortion. The next generation of nanowire devices, if properly designed, should be able to sense and process small input signals *directly* without the need for large amplification and its associated gain drift and temperature sensitivities. Two prime examples are Hall-effect sensors for automotive applications, which now need large amounts of temperature-stable gain, and direct sensing of biochemical interactions for DNA and proteomic arrays. This project applies to several DOE programs, including basic energy sciences, automotive, building sciences, and life sciences.

Results and Accomplishments

This research has enabled ORNL to fabricate its first metal-oxide-semiconductor field-effect (MOSFET) nanotransistors. During the project's first year, we focused on the design, process development, in-house fabrication, and characterization of SiNWTs that span the micrometer to the nanometer scales. A principal goal of the design is to allow eventual mass production using conventional materials. Silicon-on-insulator (SOI) wafers were chosen as the base substrates for prototype structures. Conventional optical lithography provided patterning of larger structures, such as pads and interconnect traces, while electron-beam lithography (EBL) was used to define the nanometer structures. Combining the two techniques and adding insulator, dopant, and metallization steps still require considerable process development.

We used a phased approach in the fabrication of three different generations of test structures. The first mask set focused on ohmic contact fabrication and characterization of the SOI materials. The second set of masks enabled the fabrication of N-channel micron-scale MOSFET transistors using optical lithography, which demonstrated the basic function and proved helpful in identifying problem areas and directing process refinement. The third set of masks integrated EBL and targeted a wide range of transistor sizes from 200 µm to 25 nm gate widths (200 µm, 10 µm, 5 µm, 2 µm, 1 µm, 500 nm, 200 nm, 100 nm, 50 nm, 25 nm, with a length of 1.5 µm for all devices). To date, measured characteristics of fabricated devices have shown functionality down to 200 nm widths. Additional process modifications are under way to produce working devices of less than 100 nm, with plans to reach 25 nm in FY 2009.

05115

Revolutionary Method for Increasing Efficiency of White-Light, Quantum-Dot Light-Emitting Diodes

Chad Duty, Ron Ott, Philip Boudreaux, Adrian Sabau, Gerald E. Jellison, Curt Maxey, Keith Leonard, and Biswajit Das

Project Description

The objective of the proposed research is to demonstrate a method for increasing the efficiency of white solid-state lighting (SSL). Covering a light-emitting diode (LED) with quantum dots (QDs) can produce a broad spectrum of white light. However, current techniques for applying QDs to LEDs suffer from a high density of defects and a nonuniform distribution of QDs, which respectively diminish the efficiency and quality of emitted light. ORNL has the unique capability to thermally anneal QD structures at extremely high power densities for very short durations. This process, called pulsed thermal processing (PTP), reduces the number of point defects while maintaining the size and shape of the original QD nanostructure. The proposed research uses PTP to anneal various QD systems on passive and active substrates and measure the resulting increase in photoluminescence (PL) efficiency. A multi-scale energy transport model is also being developed to understand the transport of energy within a QD structure and to take advantage of the enhanced properties of such nanostructured materials.

Mission Relevance

Light-emitting diodes are sturdy, semiconducting wafers that are vibration and shock resistant, exceptionally long lived, and an order of magnitude more efficient than incandescent lighting. Since lighting consumes about 22% of the nation's energy, DOE has established a goal of developing SSL technology by 2025 that is 50% efficient and that can accurately reproduce the solar spectrum. If this goal were attained, SSL could save the country $30 billion in annual energy costs, or the equivalent of 200 million barrels of oil. DOE recently established the Next-Generation Lighting Initiative (NGLI), representing a commitment of $350 million over the next 6 years with the goals of accelerating the development of white-light SSL and positioning the United States as a global leader in this technology. Specifically, the development of phosphors and conversion materials is considered the second highest priority (out of nine) of DOE's LED Core Technology Research Tasks.

Results and Accomplishments

During the first year of the project, the primary goal was to demonstrate that PTP could increase the PL intensity of a QD material on a passive (i.e., non-light-emitting) substrate, such as silicon or quartz. This objective was achieved by measuring an average PL increase of 17% following exposure to PTP for a given sample. In the coming year, this gain in efficiency is expected to increase dramatically as we explore additional sources of QD materials that promise lower-cost processing and higher efficiency.

Secondary goals completed during the first year were the construction of an in-process PL system and the development of an energy transport model for a QD system. When QDs are optically excited with a laser, they decay quickly and emit a photon. This required the development of a fast response PL system capable of 20 ns resolution. In addition, we designed and built a portable PL system that could be operated alongside the PTP system, giving important in-process feedback for the annealing of QD samples.

A multi-scale energy transport method was also developed for the pulsed thermal processing of QD materials. The interaction of light with a monolayer of CdSe QDs was modeled using the Schuster-Schwarzchild approximation for two-flux radiation. The primary result of the numerical simulations indicates that the PTP system is capable of heating QD samples to temperatures and time durations appropriate for thermal annealing of QDs.

Publications

Duty, C. E., et al. 2008. "Revolutionary Method for Increasing the Efficiency of White Light Quantum Dot LEDs." Presented at the International Symposium on Semiconductor Light Emitting Diodes, Apr. 27–May 2, Phoenix, Ariz.

Sabau, A. S., et al. 2008. "Numerical Simulation of Annealing of CdSe Quantum Dots for White Light LEDs." Presented at the Modeling of Multi-Scale Phenomena in Materials Processing Symposium, Oct. 5–9, Pittsburgh; to be published in the proceedings.

05179

Unmixed Combustion for High-Efficiency Energy Conversion

Josh A. Pihl, C. Stuart Daw, Veerathu K. Chakravarthy, Jim Conklin, Theodore M. Besmann, Todd J. Toops, and Ronald L. Graves

Project Description

Fossil fuel combustion accounts for more than 80% of U.S. energy consumption, and a third of that is used by the transportation sector. With conventional transportation engines able to convert less than 40% of their fuel energy to motive power, combustion engine efficiency is one of the leading barriers to reducing U.S. dependence on foreign oil and minimizing greenhouse gas production. A major source of inefficiency in current engines (20–25% of the fuel energy) is the entropy generated in unconstrained combustion. We propose to develop a novel, unmixed-combustion process that will significantly reduce entropy generation by using an oxygen storage medium (OSM) to constrain the combustion reactions in a manner mimicking the action of hemoglobin in the human body. A similar concept, referred to as chemical looping, is already being developed for stationary power generation, but it relies on continuous circulation of OSM particles. To apply this process to transportation engines, we propose to construct a combustion reactor with a fixed OSM that is cyclically exposed to alternating streams of fuel and air. We plan a combination of laboratory experiments, thermodynamic analysis, and computer modeling that will lead to a convincing prototype demonstration of the efficiency benefits of unmixed combustion. We expect this project to open a new arena of research in combustion and advanced transportation engines and to define a clear path for future research in oxygen storage materials, multi-scale simulation, and experimental engine development.

Mission Relevance

Fossil fuel combustion accounts for more than 80% of U.S. energy consumption, and a third of that is used by the transportation sector. Interestingly, very little has been done in the last 100 years to change the fundamental nature of the combustion engine itself. Car and truck engines still rely on mixing air with gaseous or liquid fuel and then reacting the fuel-air mixture inside cylinders at high temperature. The expanding combustion gases provide mechanical force to move the piston, but this work is accomplished at the expense of considerable inefficiencies. Specifically, 20–25% of the fuel energy is lost due to the entropy generated by unconstrained combustion. With the increasing concern over energy security and carbon dioxide emissions, there is a renewed focus at the DOE FreedomCAR & Vehicle Technologies program on improving fuel efficiency of combustion engines. To support this goal, we will develop a novel unmixed combustion process that will significantly reduce entropy generation by using an oxygen storage medium to constrain the combustion reactions. Preliminary calculations show that this approach could reduce by half the energy lost during unconstrained combustion.

Results and Accomplishments

A survey of the chemical looping combustion literature led to the identification of four promising OSMs, all of which have been prepared or procured. We have measured the kinetic and thermodynamic properties of three of these materials; experiments on the fourth material are under way. Equilibrium solid- and gas-phase compositions after both oxidation and reduction have been calculated for all four OSMs from thermodynamic databases. We have developed several conceptual staged combustion with oxygen transfer (SCOT) processes and analyzed their overall energy efficiency as a function of material and operating parameters, including partitioning of the reaction enthalpy between the oxidation and reduction steps, relative amounts of solid and gaseous reactants, compression ratio, air/fuel ratio, and fuel type. These analyses revealed that carefully controlling the heat transfer between the OSM solids and gas phase reactants is critical to achieving the potential efficiency benefits of the SCOT process. Strategies for optimizing the heat transfer process are under development. We have also created a conceptual design for the SCOT demonstration device, which will be built in FY 2009.

ADVANCED MATERIALS INITIATIVES

00002

Synthesis and Neutron Scattering Characterization of Ordered Self-Assembled Polymer Nanostructures and Bio-membranes

Volker S. Urban, Kunlun Hong, Phillip F. Britt, Jimmy W. Mays, and Alexander Boeker

Project Description

This project will establish new capabilities at ORNL for synthesis and neutron scattering analysis of nanostructures with controlled orientation and long-range order over macroscopic mono-domains. Block copolymer nanophases in organic solutions will be aligned in electric fields and small angle neutron scattering (SANS) will discern structural details in these field-aligned systems. The technique will also be applied to lipid bilayer membranes, which emulate the native biological environment of intact, functional membrane protein complexes. The knowledge generated in this LDRD project will advance an understanding in nanoscale science, enhance the technological capabilities at the Center for Nanophase Materials Sciences (CNMS), and highlight novel applications of neutron scattering on field-oriented systems with flagship experiments at the new ORNL SANS instruments. With alternating and crossed fields, two- and three-dimensional orientational order could be induced, enhancing the information from SANS in a similar way as single-crystal diffraction compares to powder diffraction.

Mission Relevance

This work is relevant to the Materials Science and Engineering programs within the DOE Office of Sciences Basic Energy Sciences and supports the goals of the President's American Competitiveness Initiative to develop "chemical, biological, optical, and electronic materials breakthroughs" and "overcoming technological barriers to efficient and economic use of hydrogen, nuclear, and solar energy through new basic research approaches in materials science." The project implements unique research capabilities and addresses key issues in molecular self-assembly of nanostructured and bio-inspired materials. The project will generate knowledge on molecular interactions and develop a field-alignment technology for nanophase materials with in situ structural characterization by neutron scattering. By addressing central challenges in nanomaterials and membranes, benefits will be generated in a range of highly important research programs for DOE, the Department of Defense (Defense Advanced Research Project Agency, Air Force, and Army), the National Science Foundation, and the National Institutes of Health.

Results and Accomplishments

We analyzed SANS data of deuterium-labeled, symmetric polystyrene-b-polyisoprene block copolymers that were dissolved in deuterated tetrahydrofuran and aligned in an external electric field of up to 3 kV/mm. The results are the first observations of polymer chain conformation in solvent swollen, electric-field-aligned block copolymer nanophases. We performed in situ measurements of polymer phase alignment using the in-house small angle X-ray scattering (SAXS) instrument at the ORNL Center for Structural Molecular Biology. We designed and built a new capacitor for operation in conductive (water-based) fluids. We conducted SAXS studies of protein-containing hexagonal phases prepared from Pluronic® P123 triblock copolymer (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), serving as a biological amphiphilic membrane model system. We have adapted the electric field environment to the SANS instruments at the ORNL High Flux Isotope Reactor (HFIR), and conducted successful experiments at the HFIR Bio-SANS, which explore the influence of electric fields on various self-assembled macromolecular nanostructures. We have communicated our results in several invited talks at scientific conferences and have published a paper in *Nature Materials*.

Publication

Schmidt, K., et al. 2008. "Reversible Tuning of a Block Copolymer Nanostructure via Electric Fields." *Nat. Mater.* **7,** 142–145.

00017

Nanoparticle Phase Change Materials: The Nanoscale Science Basis for Gigajoule Energy Storage

Miroslaw S. Gruszkiewicz, Ariel A. Chialvo, David R. Cole, and Michael J. Simonson

Project Description

The goal of this project is to advance fundamental understanding of solid-solid transitions and interactions at the solid-fluid interface in concentrated nanoparticle dispersions as the foundation for novel, high-temperature thermal energy storage. Inorganic phase-change materials (PCMs), stabilized by optimized carrier solutions that remain liquid at high temperature, can provide the unique properties promising a dramatic increase in solar energy efficiency. Indirect experimental evidence exists for phase stability reversals driven by large differences in surface energies between nanophase polymorphs. Several questions need to be answered before the optimal combination of nanosolid and liquid can be found with tunable thermal properties. Important problems include transition kinetics and reversibility over multiple cycles, stability of the nanophase in the liquid matrix, determination of the mechanism of solid-solid transformations in nanoparticles at various temperatures, and the atomic-scale source of high heat effects. The principal focus is to (1) experimentally demonstrate the principle of using high-energy inorganic solid-solid transitions in stable nanoparticles for energy storage and (2) investigate the key phenomenon of nanosolute solvation by the method of constraint molecular dynamics (MD). Success of this project will contribute to the advancement of nanoscience and enable more efficient utilization of solar thermal energy by providing a breakthrough pathway for thermal energy transfer and storage.

Mission Relevance

The "Basic Research for Solar Energy Utilization" program of the DOE Office of Science, Basic Energy Sciences is most likely to benefit from this project. Other target programs include Materials under Extreme Environments and Advanced Nuclear Energy Systems, with subtopics related to the role of surface energy and chemistry at interfaces in confined systems. Both thermal storage and efficient characterization of nanomaterials are currently of interest to the DOE Office of Energy Efficiency and Renewable Energy. The DOE Office of Electricity Delivery and Energy Reliability initiatives (Distributed Energy program, Thermally Activated Technologies, and Recycling Thermal Energy for Combined Heat and Power Systems) could also benefit. Operation of fuel cells is part of the mission of the Department of Defense (DOD). The goal of the DOD distributed energy program is to advance technologies using thermal energy storage to improve overall energy efficiency and reduce pollution. The outcome of this project may also be of interest to National Aeronautics and Space Administration, where it could lead to development of a simpler solution than currently used molten-salt-based energy conversion systems.

Results and Accomplishments

We developed an automated high-temperature, high-precision scanning calorimeter as a new ORNL experimental capacity for rapid detection of phase transitions in nanomaterials. The instrument was tested using prototype nanoparticle samples of TiO_2 (anatase and rutile) and ZrO (monoclinic and tetragonal), 5 to 50 nm. Sample characterization and synthesis of uniform 5 nm ZrO_2 nanoparticles were carried out at ORNL Center for Nanophase Materials Sciences. The points of zero charge were measured to assess the size stabilities as a function of pH. Suspension viscosity varied with pH, but 20% to 46% solid loadings were practical. A unique transitiometer was used for simultaneous calorimetric and volumetric scanning to 400°C. An exothermic phase transition accompanied by an isochoric pressure effect was found at 237°C. Several scans to 300°C were made using our own twin-cell heat-flux calorimeter with new pressure cells. Suspension of 10 nm anatase showed a large, reproducible, endothermic effect when cooling below 270°C. The proof-of-principle results indicate that higher temperature closed cells will be needed to eliminate end effects and reduce the noise originating from convection. For interpretation of experiments, molecular dynamics simulations based on the "blue-moon" ensemble were used to determine the potential of mean force between pairs of nanoparticles surrounded by an aqueous electrolyte solution. Our findings provide the stepping stone for development of crucial coarse-graining inter-nanoparticle potentials based on molecular-based hydration-force profiles to overcome the high CPU requirements of the explicit-water simulations, while capturing the contributions from surface charge and the local aqueous environment.

00018

Apertureless Near-Field Desorption/Ionization Mass Spectrometry for Nanoscale Chemical Imaging at Atmospheric Pressure

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Project Description

Prerequisite to creating and using nanomaterials to control molecular processes is the capability for nanoscale chemical imaging. Although scanning probe microscopy techniques enable the framework of matter to be ascertained at the atomic scale, the associated images inherently provide no information about chemical composition and molecular structure. More recently, near-field scanning optical microscopy has been combined with fluorescence, Raman, and infrared systems to produce spectroscopic information at unprecedented spatial resolution (~100 nm). In the techniques, a laser-illuminated metal probe acts as an optical antenna to produce enhancement of radiation intensity in a localized region at the apex and comparable in diameter to the tip (as small as 20 nm). Although mass spectrometry (MS) has been enormously successful for chemical analysis and molecular structural characterization, its viability for high-resolution chemical imaging has been hampered by the limited applicability and spatial resolution of available sampling/ionization techniques. However, the optical near fields responsible for high-resolution optical spectroscopy also can produce nanoscale surface effects. Thus, the tip can presumably function as a near-field, desorption/ionization source for MS chemical imaging at unprecedented nanometer-scale spatial resolution. Therefore, this effort seeks to demonstrate near-field desorption/ionization MS under atmospheric pressure conditions and to apply the process to nanoscale chemical imaging.

Mission Relevance

Revolutionary technologies are needed to address this country's continually increasing energy demand. One promising area for development is the creation of nanoscale materials to control molecular processes in areas such as fuel cells, catalysis, and photovoltaic cells. However, the full promise of nanoscience will not be realized without the capability for investigation of chemical processes occurring on individual nanoparticles or at isolated active sites. The understanding garnered from such studies will guide researchers in the DOE Office of Science in tailoring and optimizing nanosystems for control of reaction paths and kinetics. Direct MS imaging with subcellular spatial resolution would likely be of interest to the National Institutes of Health for investigation of the molecular and biochemical nature of soft matter, such as plant and biological tissue. In addition, the potential analytical capabilities of near-field desorption/ionization MS might be valuable to the Defense Advanced Research Projects Agency in regard to classified measurement problems requiring the capability for nanoscale chemical imaging.

Results and Accomplishments

The instrumentation previously developed for demonstration of proof of principle for tip-enhanced, near-field ablation was upgraded to enable surface regions up to 100 μm × 100 μm to be imaged using the process. A Veeco MultiMode atomic force microscope (AFM) head combined with an nPoint closed-loop sample stage comprised the new tip/sample mechanical subsystem. The setup enabled nanometer-scale *x,y* sample movement with little drift and hysteresis, thereby allowing for reproducible positioning. The tip-surface laser interaction region was coupled to a Thermo Electron LCQ ion trap MS via a ~15 cm stainless steel capillary to enable direct sampling and analysis of desorbed material. AFM control and data acquisition were performed using a Nanonis controller and software; its programming interface was employed to create custom LabVIEW codes that allowed for array-based sampling protocols using tip-enhanced, laser ablation.

For a model surface, Sharpie® Red marker (known to contain Rhodamine B dye) was swiped onto glass cover slips and vacuum dried, creating a dye layer tens of nanometers thick with 25–100 μm^2 regions of relative smoothness (±0.5 nm). For reproducibility assessment of near-field ablation, the above apparatus was used to create an array of 225 craters (~100 nm diam × 5 nm deep) in the surface, each resulting from a single ~15 nJ pulse of 532 nm laser radiation. Standard AFM imaging of the sample surface revealed a variation of ~50% in crater depth. Preliminary mass spectra of the ablated material showed an ion signal at a mass/charge value corresponding to that of the protonated Rhodamine B molecule.

Publication

Goeringer, D. E., et al. 2008. "Toward Nanoscale Chemical Imaging: Investigation of Tip-Enhanced, Near-Field Optical Methods for Desorption/Ionization Mass Spectrometry at Atmospheric Pressure." *Proceedings of the 56th ASMS Conference,* June 1–5, Denver.

00027

Fundamental Mechanisms of Self-Assembly of Ordered Nanostructures in Heterogeneous Ceramic Materials

G. Malcolm Stocks, Amit Goyal, Jianxin Zhong, and Yanfei Gao

Project Description

Successful fabrication of ordered arrays of nanostructures of one multicomponent ceramic material embedded in another multicomponent ceramic matrix provides enormous application opportunities in high-temperature superconductors, multiferroics, and many other materials systems with high potential for technological applications. Motivated from the recent demonstration of nanoscale self-assembly of $BaZrO_3$ nanodots in a $YBa_2Cu_3O_{7-\delta}$ superconducting ceramic thin film using pulsed laser deposition, this project examines the simultaneous phase separation and strain ordering (SPSO) of embedded nanostructures in heterogeneous ceramic materials, via synergistic efforts in fundamental theoretical formulations, simulations, and experiments. The project scope includes the development of a continuum-based, nonequilibrium thermodynamics model as well as atomistic models to study the growth kinetics, complemented by experimental fabrication and validation of novel self-assembled nanostructures. The outcome of this research provides guidance in the development of material selection and controllable nanostructural evolution for fabrication of novel materials.

Mission Relevance

This project is directly relevant to DOE Office of Science, Basic Energy Sciences programs in high-temperature superconductivity, advanced nanostructured materials, computational science, and material theory. At ORNL this work is particularly relevant to stated goals of the Center for Nanophase Materials Sciences and the Leadership Computing Facility. For nonsuperconductivity applications, we can directly extend our work to incorporation of oxide nanodots/nanorods within a ceramic matrix for energy applications such as energy-efficient solid-state lighting (SSL) and photovoltaic cells, which are of great interest to the DOE Offices of Science and Energy Efficiency Renewable Energy, as well as the Department of Defense, National Science Foundation, and many high-technology companies.

Results and Accomplishments

In this project, the key accomplishments to date are (1) the mechanism of SPSO resulting in self-assembly of $BaZrO_3$ (BZO) nanodots within $YBa_2Cu_3O_{7-\delta}$ (YBCO) was understood and theoretically modeled; (2) via control of strain, it was shown experimentally that the self-assembly could be altered or modified to result in alignment of nanodots in different directions; and (3) using this theoretical understanding and via the experimental control of strain, optimal arrangements of insulating nanodots within the YBCO matrix were demonstrated to result in very high performance superconducting films, with excellent flux-pinning in high, applied magnetic fields. Synergistic experimental and theoretical efforts established that the nanoscale BZO patterns form to minimize the combined free energy of mixing, phase boundary, and elastic interaction, which originates from the lattice mismatch. A phase-field model was developed to study the kinetics of this ordering process. While the vertical ordering is governed by the strain-mediated surface nucleation mechanism, the long-range lateral ordering is primarily determined by lattice symmetry and elastic anisotropy. A kinetic mechanism map has been constructed that illustrates the competition between deposition rate and surface diffusion on the SPSO process. Ordered nanocomposites of $BaTiO_3$-$CoFe_2O_4$ mixtures were also fabricated using pulsed laser ablation. Composites of 4 vol %–35 vol % $CoFe_2O_4$ in $BaTiO_3$ were fabricated. Domain switching mechanisms have also been studied in line with the recent experimental work on the composite film of $BaTiO_3$-$CoFe_2O_4$ as part of this project.

Publication

Gao, Y. F., J. Y. Meng, A. Goyal, and G. M. Stocks. 2008. "Spatial Ordering and Anisotropy in Surface Stress Domains and Nanostructural Evolution." Invited paper to JOM **60**, 54–58.

00029

Imaging Energy Materials In Operandi with Atomic Resolution Scanning–Transmission Electron Microscopy

Albina Y. Borisevich, Niels De Jonge, Andrew Lupini, Stephen J. Pennycook, and Gabriel M. Veith

Project Description

In this project, we are aiming to provide an atomic-level characterization of dynamic structure evolution and electron transfer processes in materials that are central to the energy mission of DOE. This goal will be achieved by conducting atomic-resolution scanning-transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) within local environmental and/or electrical cells. Composition and pressure of reactive gases, temperature, and bias will be varied across the sample to induce controllable changes in chemical composition and oxidation states. With these techniques, we will study charge collection in solar cells via electron-beam-induced current, to observe interface evolution under bias, and to study heterogeneous catalysis in action. This project will provide crucial information about processes in advanced catalysts, solar cells, and fuel cells, at present invisible to atomic-scale study. We will observe structural changes and electron transfer processes in materials as they happen, in their native environment. Mechanisms and limitations of energy conversion processes in catalysts, solar cells, and fuel cells will be revealed.

Mission Relevance

This project will provide crucial information about processes in advanced catalysts, solar cells, and fuel cells, which are critical to the energy mission of DOE but at present invisible to atomic-scale study. Mechanisms and limitations of crucial energy conversion processes will be revealed, enabling more efficient processes and materials to be developed for the benefit of DOE and the nation. This program will extend ORNL's leadership in aberration-corrected STEM into the field of in situ imaging. The subject matter has direct relevance to many energy materials systems of importance to the DOE Office of Science, Basic Energy Sciences. Depending on the progress in specific directions, the developed techniques of real device characterization will allow us access to the more applied branches of DOE and external funding from the Office of Naval Research, the Army Research Office, and other sources. The fundamental scientific advances will also be useful to all federal agencies undertaking basic scientific research in materials, including the National Science Foundation, the National Aeronautics and Space Administration, and the Department of Defense.

Results and Accomplishments

This project has allowed us to develop the instrumental and methodological infrastructure for probing dynamic processes in energy materials. This development effort was focused on three primary directions: (1) in situ transport imaging using electron-beam-induced current (EBIC) mode, (2) in situ mapping of bias-induced changes using NanoFactory STEM-STM, and (3) detection of bias-induced changes in material structures and phase transformations. Complementary to this is the development of methods for three-dimensional focal series reconstructions necessary for analysis of morphologies of reaction products. As the result, we have (1) developed and successfully tested an EBIC-enabled sample holder for the VG601 and (2) acquired, installed, and collected preliminary transport data on ZnO nanowires using STEM-STM. The applicability of this technology to in situ transport probing in TiO_2/CdSe photovoltaic structures was explored, and associated limitations were elucidated. We have also demonstrated a potential to map the ferroelectric polarization (displacement) field using Z-contrast STEM. Ferroelectrics are an important model system for electrochemical processes and ferroelastic materials used in energy storage. Previously, only bright field TEM mapping was reported. The principal investigator and co-principal investigator gave multiple invited talks at conferences and were also invited to give a seminar on mathematical methods in microscopy.

Publications

Borisevich, A. Y., A. R. Lupini, A. F. Koschan, M. Mercimek, M. A. Abidi, and S. J. Pennycook. 2008. "3D Scanning Transmission Electron Microscopy for Catalysts: Imaging and Data Analysis." *Microsopy and Microanalysis 2008,* Aug. 4–7, Albuquerque, N.M.

Pennycook, S. J., M. Varela, M. F. Chisholm, A. Y. Borisevich, A. R. Lupini, K. van Benthem, M. P. Oxley, W. Luo, S-H. Oh, D. Kumar, D. L. Sales, S. I. Molina, A. G. Marinopoulos, and S. T. Pantelides. 2007. "Functionality of Nanostructures Through Aberration-Corrected Microscopy and First-Principles Theory." *International Conference on Advanced Materials 2007,* Oct. 8–12, Bangalore, India.

Pennycook, S. J., M. Varela, M. F. Chisholm, A. Y. Borisevich, A. R. Lupini, K. van Benthem, M. P. Oxley, W. Luo, Z. Sefrioui, J. Santamaria, D. L. Sales, S. I. Molina, A. G. Marinopoulos, and S. T. Pantelides. 2008. "Interfaces Under the Microscope—New Insights into Device Physics." *2008 International Workshop on Nanomaterials, Devices and Physical Properties, Part 2,* July 5, Kunming, China.

00030

Antiferroelectric Thin-Film Capacitors for Ultrafast High-Power Energy Storage

Ho Nyung Lee, Matthew F. Chisholm, and David J. Singh

Project Description

Complex oxide antiferroelectrics (AFEs), such as (doped-)$PbZrO_3$, offer the potential for high energy storage densities due to the characteristic increase of dielectric constant and electric polarization with applied field—opposite to the behavior seen in relaxor ferroelectric (FE) capacitors. Due to ultrafast response, they have great promise for potential application in microelectronic devices. The delicate interplay between long-range electrostatic forces and local electric/elastic configurations plays a critical role, with a real possibility to artificially generate the AFE phase from otherwise FE material. In this project, therefore, we search for novel properties and unobserved behaviors of complex oxide perovskite thin films and heterostructures that have an AFE-to-FE transition under the applied electric field. Piezoelectric strain induced in epitaxial FEs and functionally cross-coupled nanoscale heterostructures are also being investigated under extreme conditions, such as at high electric fields and with nanoscale capacitors, in order to explore unprecedented behaviors and/or properties. State-of-the-art capabilities for thin-film growth by pulsed laser deposition and an "all-electron, general potential linearized augmented planewave method" for first-principles theory as well as Z-contrast scanning transmission electron microscopy for imaging and chemical analyses are employed. With these tools, this project will contribute to discovering novel materials and functionalities that provide revolutionary advances in high-power-density storage.

Mission Relevance

The work proposed here is an ORNL opportunity for world leadership in understanding materials for high energy and power-density storage. Because the quest for new energy storage materials is central to a broad range of research programs, the prototype epitaxial ferroelectrics developed in this project undoubtedly will also open doors to follow-on funding in both directly (i.e., current and future calls from the DOE Office of Science, Basic Energy Sciences, as well as interest by the DOE Office of Energy Efficiency and Renewable Energy in vehicular energy storage) and indirectly related areas (i.e., electronic materials, sensors, and resistive switching/data storage) that currently are supported by several sponsors.

Results and Accomplishments

The primary focus during FY 2008 was on exploring the materials nanoscale functionality under extreme conditions. First, the ultrahigh piezoelectric strain has been determined from $Pb(Zr,Ti)O_3$ (PZT) ultrathin thin films by time-resolved hard X-ray microdiffraction. We found that an extremely large piezoelectric strain can be induced in PZT epitaxial films by applying very high electric fields up to 8 MV/cm, well above the dielectric breakdown field. The use of very short pulses (a few nanoseconds) made it possible to apply such a high electric field that was turned off before the thermal breakdown. The film used for this experiment was only 35 nm thick. It was also found that the PZT film responds piezoelectrically (up to ~3% strain) within a few nanoseconds. This provides important evidence that a ferroelectric capacitor with such a fast response time can charge and discharge at a similar timescale. Therefore, this implies that when PZT epitaxial films are used in capacitors, not only a high-power energy density but also a strong piezoelectric response useful for many applications such as medical imaging can be readily achieved. Moreover, by first-principles super-cell calculations used to investigate the lattice distortions in $BaZrO_3$ heavily codoped with potassium and lanthanum, we found that nonferroelectric $BaZrO_3$ can be made ferroelectric in this way. The ferroelectricity was the result of lanthanum off-centerings and can be understood using ionic size considerations. In particular, we found that the size disorder on the perovskite *A* site suppresses the tendency toward octahedral tilts with substitution of the small lanthanum ion. This results in *A*-site driven ferroelectricity.

Publications

Grigoriev, A., R. Sichel, H. N. Lee, E. C. Landahl, B. Adams, E. M. Dufresne, and P. G. Evans. 2008. "Non-linear Piezoelectricity in Epitaxial Ferroelectrics at High Electric Fields." *Physical Review Letters* **100**, 027604.

Kagimura, R. and D. J. Singh. 2008. "*Ab initio* Study of Pb Antisite Defects in $PbZrO_3$ and $Pb(Zr,Ti)O_3$." *Physical Review B* **78**, 174105.

Kagimura, R. and D. J. Singh. 2008. "First Principles Investigations of Elastic Properties and Energetics of Antiferroelectric and Ferroelectric Phases of $PbZrO_3$." *Physical Review B* **78**, 104113.

Kagimura, R., M. Suewattana, and D. J. Singh. 2008. "$(Ba,K,La)ZrO_3$ as a Possible Lead Free Ferroelectric: Density Functional Calculations." *Physical Review B* **78**, 012103.

Yang, S. M., J. Y. Jo, D. J. Kim, H. Sung, T. W. Noh, H. N. Lee, J. G. Yoon, and T. K. Song. 2008. "Domain Wall Motion in Epitaxial $Pb(Zr,Ti)O_3$ Capacitors Investigated by Modified Piezoresponse Force Microscopy." *Applied Physics Letters* **92**, 252901.

00031

Energy Flow and Conversion on the Molecular Level: A View at Molecular Photoelectromechanical Machines

Sergei V. Kalinin, Gilbert M. Brown, Ilia N. Ivanov, and Stephen Jesse

Project Description

The convolution of societal, economic, and political factors in the last several years has propelled global warming to the forefront of public awareness, stimulating the search for renewable green energy sources and efficient energy utilization. Organic molecular systems suggest a possible solution, instigating a massive effort to develop novel materials and device structures for organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs). Very often, these systems demonstrate extremely high (50–90%) quantum yields in molecular form, which drops to 1–5% in device structures.

The crucial task in maximizing the efficiency of molecular systems is developing the capability to measure, on the nanometer and ultimately molecular levels, the individual processes involved in energy conversion, including (1) photon absorption and exciton formation, (2) exciton diffusion and separation, and (3) charge transport and effects of molecular organization surrounding medium and substrate on these processes. This project has the objective of separating these systems into individual functional components assembled in two-dimensional molecular layers that are amenable to scanning probe imaging and spectroscopic measurements. In this way the individual processes involved in solar energy conversion can be addressed separately. Observing and understanding these steps will allow materials with increased efficiencies and extended lifetimes to be designed for OPV and OLED systems. This project will establish the foundation for the new area of molecular electromechanical machines (i.e., a means for actuation and manipulation on the molecular level).

Mission Relevance

Understanding fundamental mechanisms of energy conversion between light, electrical, and chemical in organic and bio-inspired systems is one of the highest priorities for the DOE Office of Science, Basic Energy Sciences (BES). Optimization of energy efficiency in OPV and OLED devices is a priority for the DOE Office of Energy Efficiency and Renewable Energy (EERE). This project directly addresses these missions by (1) creating the model systems that allow nanometer- and molecular-scale studies of energy conversion phenomena in molecular systems and assemblies, (2) studying their self-assembly as a route for self-repairing devices, and (3) studying electroluminescent and photovoltaic phenomena on the nanoscale in both molecular systems (BES) and realistic multicomponent devices (EERE). Beyond DOE, this project is directly relevant to the mission of the Defense Advanced Research Projects Agency (i.e., artificial vision, molecular optoelectronics, molecular electromechanical machines) and optical data storage. The electrical SPM in liquid environment and shielded probes developed here are an enabling component for probing cellular and biomolecular systems, relevant to the National Institutes of Health.

Results and Accomplishments

The primary effort during FY 2008 focused on the design and synthesis of molecular platforms to carry OPV and OLED functionality, and development of experimental methods for macroscopic and nanoscale probing of photovoltaic and electroluminescent phenomena. We designed the tripod-based molecular structures for self-assembly and synthesized the prototype compound. Dr. M. Nikiforov, who has prior experience in molecular-resolution imaging of porphyrins, joined the group in May 2008 and is now primarily supported by this project. We are building the deposition system for molecules in ultrahigh voltage (UHV), complementing the standard liquid-phase self-assembled monolayers formation. We extended the previously developed band excitation method for imaging in fluids (Asylum MFP-3D system) and UHV (Omicron VT-SPM system equipped with Nanonis controller, installed in June 2008). The methods were verified using a model ferroelectric system, and their sensitivity and resolution limits were established. In parallel, we developed a data analysis method based on principal component analysis that allows rigorous deconvolution of the data. This direction led us to a set of impressive results, including (1) direct mapping of thermodynamics of bias-induced phase transitions, (2) robust dissipation imaging in liquids and vacuum, (3) probing voltage-dependent contact mechanics in UHV, and (4) preliminary results on dissipation in molecular unfolding. The project has resulted in (fully or partially) five publications, including one in *Nature Materials* and one in *Physical Review Letters*, and three invited talks at international conferences. Brian Rodriguez, a postdoctoral fellow supported by this project, was awarded a Humboldt fellowship at MPI Halle, and Sergei Kalinin received the AVS Peter Mark award for young scientists.

Publications

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00032

Nanostructured Thermoelectrics for Power Generation: Smaller Is Cooler

Rongying Jin, Ho Nyung Lee, Sheng Dai, Gyula Eres, and Brian C. Sales

Project Description

This project focuses on synthesizing novel thermoelectric materials (co-based layered oxides) with one-dimensional (1-D) and two-dimensional (2-D) nanostructures and developing state-of-the-art techniques to measure their thermopower and thermal and electrical conductivities so that the efficiency of these nanostructured materials can be determined accurately. The results include (1) detailed studies of thermoelectric, structural, and magnetic properties of bulk Na_xCoO_2 and $Ca_3Co_4O_9$, which serve as reference and foundation for comparison with their counter nanoforms; (2) systematic investigations of thermoelectric properties of $Bi_2Sr_2Co_2O_9$ epitaxial thin films that show the power factor can be enhanced more than double of that obtained from bulk single crystals; (3) development of measurement capabilities, allowing us to measure three thermoelectric quantities of individual nanorods Bi_2S_3.

Mission Relevance

The proposed capability for thermoelectric property measurements on 1-D and 2-D nanomaterials will serve basic research needs for nanoscience and nanotechnology development, particularly for power generation. This research will benefit the Solar Energy Utilization and Energy Efficiency program of the DOE Office of Science, Basic Energy Sciences and the FreedomCAR and Vehicle Technologies Program of the DOE Office of Energy Efficiency and Renewable Energy. This project will also benefit programs of other federal agencies, such as the Direct Thermal to Electric Conversion Program of the Defense Advsnced Research Projects Agency and Power and Propulsion programs of the National Aeronautics and Space Administration.

Results and Accomplishments

We made significant progress in five aspects.

1. Thermoelectric, structural, and magnetic properties of single crystalline Na_xCoO_2 and $Ca_3Co_4O_9$ were studied, aimed at understanding the mechanism for having high thermopower with low thermal conductivity and electrical resistivity.
2. Using pulsed laser deposition, high-quality $Bi_2Sr_2Co_2O_9$ epitaxial thin films were successfully grown under various growth conditions by tuning either growth temperature or O_2 atmosphere. Our measurements reveal that both electrical conductivity and thermopower vary nonmonotonically with the growth temperature. What is surprising is that samples with the best electrical conductivity also exhibit the highest thermopower, in contrast to that in the bulk counterpart. As a result, the power factor obtained from our films is more than double that of the single crystal form.
3. Several nanothermoelectric materials with 1-D character were grown, including $LiCoO_2$ nanowires with diameters in the range 7 to ~9 nm, and $Ca_3Co_4O_9$ nanotubes with diameters smaller than 500 nm.
4. The effect of zero-dimensional nanostructures (Ag nanoparticles with diameters <10 nm) on the thermoelectric properties of $Ca_3Co_4O_9$ powders was explored.
5. Nanodevices for measuring three thermoelectric quantities of an individual Bi_2S_3 nanorod were fabricated and tested.

00041

Smart Materials Toward a New Paradigm of Super-Efficient Separations Using Only Energy Input: Conformational Switching Based on Magnetic Nanoparticles

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Project Description

This work will introduce a revolutionary new class of molecular switches based on the hypothesis of magnetically induced conformational change. This concept will be exploited to bring about a dramatic increase in the efficiency of separations, a critical energy technology area. If extractants could be switched "on and off" using only energy input, vs. chemically based cycling, binding-release cycles would be so efficient that huge concentration factors would be achievable in small equipment with no secondary waste. That is just what is needed for transforming chemical separations in the nuclear fuel cycle and in many other applications. Specifically, we aim to tether a selective metal ion receptor between an anchor substrate and a magnetic nanoparticle (NP) such that the stretching effect caused by the force acting upon the NP in a magnetic field leads to an unfavorable conformational change in the receptor, resulting in the release of its bound metal ion. The prototype switchable system will employ $CoFe_2O_4$ NPs tethered to selected extractive agents such as polyethylene glycols (PEGs), crown ethers, or calixarenes, which are additionally anchored to a solid surface such as quartz or silicon. The synthesized materials are being characterized by scanning electron microscopy, transmission electron microscopy, X-ray and neutron scattering and reflectometry, FTIR reflectance-absorption spectrometry, ellipsometry, and tracer distribution measurements.

Mission Relevance

This work will benefit the DOE Office of Science, Basic Energy Sciences (BES); however, spin-offs can be expected in separations, decontamination, environmental cleanup, and detection, benefiting programs in the DOE Office of Nuclear Energy, DOE Office of Environmental Management, and National Nuclear Security Administration. Other likely beneficiaries of this technology are the Defense Advanced Research Projects Agency and the Strategic Environmental Research and Development program (both of the Department of Defense) and theDepartment of Homeland Security, particularly in developing technologies for radionuclide decontamination or detection. A follow-on proposal has been submitted to the BES Advanced Nuclear Energy Systems program.

Results and Accomplishments

We have successfully(1) prepared cobalt ferrite nanoparticles up to 15 nm and coated them with a reactive layer of isocyanate-terminated propylsilane groups; (2) coated silicon wafers with amine-terminated PEG molecules; and (3) demonstrated the attachment of the NPs to the PEG-coated silicon wafers. Batches of 3–5 nm cobalt ferrite NPs were prepared; these were covalently coated with reactive isocyanate groups for further derivatization. Larger 15 nm NPs were prepared by successive growth layers upon the unfunctionalized 3–5 nm seeds. Transmission electron microscopy with elemental analysis showed well-dispersed NPs with clear indication of silicon on the surface. Silicon wafers with a SiO_2 polished coating on one side were employed as substrates for surface modification, resulting in attachment of the NPs to surface-bound PEG. Wafers were first functionalized with Si-$(CH_2)_n$-NCO ($n = 3$ or 10) moieties through Si-O-Si linkages. X-ray reflectometry detected the organic silane monolayer. Attachment of PEG was achieved by soaking the coated wafers in a solution containing mono-protected diamino PEG under dry conditions. Ellipsometry (VASE) indicated PEG layers of 1.5–2.3 nm thickness. The reactive NPs described above were tethered to the amine-terminated PEG layer on the wafers by soaking the wafers in a dilute dispersion of the NPs in chloroform, either with or without the presence of a magnetic field. VASE indicated the presence of the NPs on the surface of the wafer to give a NP layer of thickness 14 nm; a void volume of 79% was consistent with the electron microscopy, showing separated rafts of closely packed NPs.

00042

Design of Point-Defect Trapping Centers in Nanostructured Nickel for Advanced Nuclear Applications

David T. Hoelzer, James Bentley, Chong Long Fu, Michael K. Miller, Xingqiu Chen, and Xun-Li Wang

Project Description

The purpose of this project is to achieve scientific knowledge for designing a high number density of nanoscale clusters, or nanoclusters, in a prototype face-centered cubic (fcc) metal based on nickel that will provide significant strengthening at high temperatures and will also greatly improve the tolerance to neutron irradiation damage in advanced nuclear reactors. This project focuses on nickel since nickel-based superalloys have immense strategic importance in high-temperature, nonnuclear applications and corrosive environments but do not perform well in neutron-irradiation environments. The nanoclusters will have a unique defective structure based on atomic bonding with vacancies that will act as potent trapping centers for neutron-irradiation-induced point defects and helium generated traps in some reactor concepts. These trapping centers will mitigate the harmful effects of neutron-irradiation damage in nickel by catalyzing the recombination of point defects and preventing the formation of helium bubbles on grain boundaries.

Mission Relevance

This project is relevant to the DOE Office of Science, Basic Energy Sciences initiative on Advanced Nuclear Energy Systems (ANES). Advanced nuclear reactors (ANRs) are one of the few energy sources that can meet the steadily increasing global demand in new electric generation capacity while simultaneously reducing harmful emissions of greenhouse gases and the dependence of the U.S. economy on foreign oil. However, the ANRs being considered by the Generation IV (GEN-IV) and Global Nuclear Energy Partnership (GNEP) programs will require significant advancements in the performance of existing structural materials. These programs have interest in nickel-based superalloys, but their poor behavior to neutron irradiation damage limits their consideration for use. This project focuses on the science of nanoclusters for improving the high-temperature strength and tolerance to neutron irradiation damage of structural materials in ANES. The scientific understanding achieved for stable nanoclusters in body-centered cubic (bcc) iron alloys will guide the design of similar nanoclusters in fcc nickel. The successful completion of this project may lead to a more radiation tolerant nickel-based alloy, which could have a significant impact on future decisions by the GEN-IV and GNEP programs.

Results and Accomplishments

Although the first year results of this project showed that it may be possible to form oxygen-rich nanoclusters in fcc nickel, the theoretical and experimental results obtained in the second year suggest that this goal may be difficult to achieve. The theoretical modeling first showed that titanium was more effective than zirconium in stabilizing O-vacancy clusters in nickel, but that the titanium oxide (TiO_2) was still more stable than all possible Ti-O-vacancy configurations. Recently, the theoretical modeling showed that while the addition of yttrium makes the Ti-O-vacancy cluster more stable, it is still not as stable as TiO_2. The same conclusion was obtained with the addition of lanthanum to Zr-O-vacancy clusters. Thus, the theoretical modeling indicates that stable O-rich nanoclusters may be difficult to form in fcc nickel. The experimental study, including advanced microstructural characterization of ball-milled and heat-treated powders, showed initially that it was possible to form a high number density of Ti-, Y-, and O-rich or Zr-, La-, and O-rich particles in nickel after 1 h at 800ºC and 750ºC. However, recent results show that these nanoscale particles increased noticeably in size after exposure for 1 and 10 h at 1000ºC to 1200ºC. Thus, the experimental results are consistent with the conclusions obtained by theoretical modeling. However, the agreement between the theoretical and experimental studies is a significant achievement since it further substantiates the new theory showing the important role of vacancies in stabilizing nanoscale clusters of atoms, or nanoclusters, in metallic matrices.

00045

Molecular Fragment Databases for De Novo Structure-Based Design

Benjamin P. Hay

Project Description

The objective of this project is to create a series of novel molecular-fragment libraries for use in computer-aided molecular design (CAMD) applications. These libraries, which will contain atomic coordinates and structural descriptors for tens of thousands of unique organic scaffolds, provide building blocks for constructing molecules on the computer using de novo structure-based design techniques. The process of generating the molecular-fragment libraries will be automated through the development of library-building software. This tool will operate by functionalizing an existing hydrocarbon library with synthetically attractive terminal groups such as ethers, amines, and amides. The utility of each new library will be verified through trial runs with the in-house CAMD tool *HostDesigner*. Methodology resulting from this study has a broad potential application. CAMD provides a rational approach to identify molecular architectures for radionuclide receptors used in nuclear separations (advanced nuclear energy systems), highly specific receptors for detection and analysis of chemical and biological agents (national security, medicine), model systems to study enzyme function (catalysis), and molecular components that self-assemble to form functional materials (solid state lighting, solar energy, nanoscale materials).

Mission Relevance

The deliberate design of molecules and materials with desired physical and chemical properties is a current challenge that cuts across scientific disciplines. This project develops new CAMD capabilities to address this challenge. DOE Office of Science Basic Research Needs workshop reports, generated in support of recent initiatives, document pervasive opportunities for CAMD application. Examples include the design of actinide sequestering agents (Advanced Nuclear Energy Systems); molecular configurations for electric field enhancement (Solid-State Lighting); light absorbers, photovoltaics, and photoelectrodes (Solar Energy); and components for self-assembled nanostructured materials (Nanoscience Research). Results from this project have potential application in any research program that entails design of organic compounds and materials. Given that such activities occur in many research programs, there is broad potential for benefit to other federal agencies. Examples would be the design of molecular-scale machines (National Science Foundation), magnetic resonance imaging agents (National Institutes of Health), and components for nanoscale computer processors (Defense Advanced Research Projects Agency).

Results and Accomplishments

A set of library-building codes, *makelinks* consisting of 15,327 lines of Fortran, has been extensively tested, and production versions have been completed. Performance has been validated by comparing the output for specific test hydrocarbons against data generated systematically by hand and against output from conformational searches performed with commercial modeling software, PCModel. Starting from the original HostDesigner hydrocarbon library, containing 8,265 fragments, *makelinks* has been used to create seven large libraries containing hydrocarbon fragments terminated with one or two functional groups. The fragment libraries that have been completed and tested to ensure that they are compatible with the HostDesigner code include (first functional group, second functional group, number of new fragments): (1) ether oxygen, none, 30,335; (2) ether oxygen, ether oxygen, 31,557; (3) secondary amine nitrogen, none, 56,791; (4) secondary amine nitrogen, secondary amine nitrogen, 96,565; (5) secondary amine nitrogen, tertiary amine nitrogen, 183,333; (6) tertiary amine nitrogen, none, 55,763; and (7) tertiary amine nitrogen, tertiary amine nitrogen, 111,661.

An additional utility code, *splice*, has been created to combine these large libraries. This code was used to unite the initial hydrocarbon library with the seven new ones, yielding a master library containing a total of 574,270 fragments. Tests have confirmed that this master library functions correctly with HostDesigner.

Scientific and technical significance of this work has not substantially changed since the project was approved. As planned, remaining effort will focus on completing the library development by creating fragment libraries based on the amide functional group and combining them with those already developed.

00049

Transfer of Vertically Integrated Carbon Nanotube Arrays for Sensors and Thermal Management

Jeremy J. Jackson and David B. Geohegan

Project Description

Vertically aligned carbon nanotube arrays (VANTAs) are self-supporting, nanotube carpets which grow in high densities by chemical vapor deposition (CVD) at high temperatures on substrates that are prepatterned with metal catalyst films or nanoparticles. While research worldwide (and in our group at ORNL) concentrates on the basic science of their growth and characterization of their outstanding thermal, optical, mechanical, and electrical properties, their high-temperature synthesis conditions prohibit their use in many application areas such as electronic wafers, sensor components, optical elements, or biological probes. Methods of transferring, patterning, and bonding VANTAs to supports are desperately needed to enable new explorations of their functionality and new applications of carbon nanotubes in these areas. In this research project, we will develop experimental techniques for the transfer and bonding of VANTAs to enable the exploration of several application areas involving sensors, optical coatings, and thermal management.

Mission Relevance

The outstanding thermal, electrical, mechanical, and sensory properties of VANTAs have a wide variety of applications of interest to DOE. These materials have been specifically identified as a highly promising solution to provide thermal management for both large-scale composite materials, such as hydrogen storage tanks, and in specific locations onboard microelectronic chips or light-emitting diodes. Similarly, these materials are of interest to DOE and the Department of Homeland Security as a means of incorporating vertical thermal and electrical characteristics to polymer films for everything from aerospace composites to functional skins for next-generation prosthetics.

Results and Accomplishments

Growth techniques of VANTAs were modified to permit simpler delamination and transfer of the aligned arrays to secondary substrates. Aluminum oxide buffer layers were found to nearly self-release the VANTAs after chemical vapor deposition, permitting the use of a mild acid solution or evaporated gold overlayers to remove the intact VANTAs. After removal of the aluminum oxide buffer layer, the VANTAs with gold electrodes attached to their tops were flipped over and used to explore a variety of applications, including acting as substrates to attempt electropolymerization of polymers in solution to form infiltrated, aligned nanotube-conjugated polymer composites. Scanning electron microscopy verified excellent encapsulation of the nanotubes within the array using this procedure, thereby enabling methods for preservation of aligned nanotubes for bulk heterojunction formation. Modifications of the procedures were developed for large-diameter single-wall VANTAs.

00050

Structure of Fluids Confined in Nanoporous Materials Using Neutron Scattering

Gernot Rother and Ariel Chialvo

Project Description

Confinement of fluids in porous materials plays an important role in many natural and technical systems, for instance carbon sequestration in rock formations, component separation, and hydrogen storage for fuel cells. The properties of fluids confined in spaces of nanoscopic size often deviate significantly from bulk, which is due to sorption and finite size effects. Neutron scattering techniques are perfectly suited for the study of sorption effects, which allow for the first time the measurement of the mean density and volume fraction of the sorption phase. We study the properties of the sorption phase of pure fluids systematically for different fluid-matrix combinations and different conditions of pressure and temperature. For confined fluids, small angle neutron scattering (SANS) is used, which allows us to measure structural properties of pore fluids exhibited in the nanometer range. To separate confinement effects from interface effects, we also study fluid-solid interactions at flat interfaces using neutron reflectivity. Experimental work is complemented by classical molecular modeling to give detailed insight into the origins of the complex sorption patterns found in many systems with emphasis on high-density depletion effects.

Mission Relevance

Research on fluid-solid interactions under controlled conditions of pressure and temperature is central to a number of important nanoscience challenges receiving funding consideration from the DOE Office of Science, Basic Energy Sciences, including those identified in the "Workshop Report: Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems." Fundamental understanding of the structure and dynamics of fluids in confinement is currently lacking; therefore, successful completion of this project will promote future opportunities for follow-on funding in neutron-based nanoscience. The study of fluid-solid interactions using neutron scattering techniques has recently been proposed by our group in two Energy Frontier Research Center proposals.

Results and Accomplishments

During FY 2008 progress was made in the following areas. The automated gas dosage system for neutron experiments in the pressure range 0–1200 psi is now fully operational. We started to build a high-pressure SANS cell with extended Q-range capabilities. Two neutron reflectometry experiments studying the sorption of SF_6 to Si covered with a thin layer of native SiO_2 and thermally grown thick layers of amorphous SiO_2 have been performed at HMI Berlin. One SANS experiment to study confined fluids in porous silica has been performed. The data from these experiments are currently being analyzed. We find interfacial fluid depletion at high fluid densities at both free interfaces and under confinement. Our experimental results were qualitatively interpreted by Brovchenko and Oleinikova, who suggest that high-density depletion may be a general phenomenon for systems with weakly attractive fluid-solid interaction potential. Modeling work using classical molecular dynamics simulation techniques is under way for CO_2 in mesoporous silica to verify and rationalize experimental findings.

Publications

Cole, D. R., E. Mamontov, and G. Rother. 2008. “Structure and Dynamics of Fluids in Micro-porous and Mesoporous Earth and Engineered Materials.” In *Neutron Applications in Earth, Energy and Environmental Sciences, Series: Neutron Scattering Applications and Techniques,* L. Liang, R. Rinaldi, and H. Schober (eds.), Springer.

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Rother, G., et al. 2008. “Microstructural Characterization of Fluids in Pores: A Combined Study Using Neutron Scattering and Molecular Dynamics Simulation.” *American Conference on Neutron Scattering,* May 11–15, Santa Fe, N.M.

05034

Single Molecular Imaging and Spectroscopy of Adsorbed Molecules

Minghu Pan, Stephen Jesse, Petro Maksymovych, Vincent Meunier, and J. F. Wendelken

Project Description

We are implementing a new, ORNL-designed, scanning tunneling microscope (STM) based on the designs of our collaborators but with significant improvements in both the hardware and software. A key aspect of this project is the intimate and demonstrated coupling between experiment and theory. Our theoretical effort will allow us not only to use the STM images to determine bonding site and configuration but also will guide the interpretation of inelastic signal strengths as a function of bonding configuration and tip position over the molecule. We will use this new capability to explore the dependence of vibrational modes, strength, energy, and lifetime (energy transfer) of adsorbed molecules bound to different substrates. In addition, the instrument will be utilized to examine with atomic resolution the vibrational (or bosonic) coupling in high-temperature superconductors.

Mission Relevance

The project is relevant to DOE Office of Science, Basic Energy Sciences program. The promise of nanotechnology will be realized only through continued advancement and utilization of techniques capable of imaging materials properties on the nanoscale. Our goal in this project is to push the theme of imaging functionality at the nanoscale to the limit of single-atom or molecular imaging and spectroscopy. What we can see, we can then control, and engineer the chemistry, energy flow, light absorption, mechanical response, electronic states, spin, and transport. This new instrument coupled closely with theory and modeling can be a kingpin for bringing the ORNL Center for Nanophase Materials Sciences (CNMS) into the forefront of imaging functionality and lead to the expansion of the CNMS by creating the Center for Imaging Functionality at the Nanoscale.

Results and Accomplishments

We have designed, constructed, and tested a new variable-temperature STM. This STM has the capability not only to image with atomic resolution but also to simultaneously record the electronic and vibrational spectra at temperatures ranging from 8 K to room temperature with highly stable temperature control. We demonstrated our variable-temperature STM by studying the spatial and temperature dependence seen in the newly discovered iron-based, high-technicium superconductors, using samples grown at ORNL. We are the first to report high-energy resolution STM and spectroscopy (STS) measurements on $Nd(O_{0.86}F_{0.14})FeAs$. We found that the tunneling spectrum at 15 K shows a suppression of spectral intensity indicative of the opening of a superconducting gap. A slightly different shape and size of the gap for different locations may be an intrinsic phenomenon or the result of sample inhomogeneities. Also observed is a pseudogap at a temperature above T_c. On the theory-simulation side, we have performed a complete analysis of the treatment of many-body effects governing the physical phenomena occurring in a low-temperature STM experiment where inelastic effects are present and have a significant signature on the spectroscopy. Working in parallel with the above experimental and theoretical work, progress has been made in developing novel SPM-based measurement techniques compatible with ultrahigh voltage environments. The additional challenges posed by interfacing high-frequency probe and measurement signals through the vacuum chamber walls and to the SPM tip have been met through a careful balance between sufficient cable shielding and mechanical isolation of the tip.

Publications

Jayasekera, T. 2008. "Effect of Phase Breaking Events on Electron Transport in Mesoscopic and Nano Devices." *International Journal of Quantum Chemistry* **108**, 2896.

Jesse, S. 2008. "Rapid Multidimensional Data Acquisition in Scanning Probe Microscopy Applied to Local Polarization Dynamics and Voltage Dependent Contact Mechanics." *Applied Physics Letters*, accepted for publication.

05054

Bandgap Narrowing of Oxide Semiconductors Using Noncompensated n-p Codoping for Enhanced Solar Energy Utilization

Zhenyu Zhang, Gyula Eres, M. Parans Paranthaman, Baohua Gu, and Wenguang Zhu

Project Description

Bandgap narrowing of oxide semiconductors has been recognized as the main avenue for enhancing their performance in photoelectrochemical solar energy conversion. This project is centered on a conceptual breakthrough, termed noncompensated n-p codoping, for controlled reduction of the bandgap of TiO_2 and ZnO for a wide variety of catalytic and optical applications. Rather than doping an element individually by trial-and-error, this novel concept embodies two essential ingredients: an n-p pair is kinetically and energetically easier to be doped into the host, and the noncompensated nature of the dopant pair creates an extra band in the gap region, effectively narrowing the bandgap. The validity of the concept is supported by preliminary first-principles calculations. Systematic modeling will be carried out to determine the optimal synthesis conditions for efficient codoping, to establish the quantitative dependence of the bandgap narrowing on the codopant concentration, and to investigate the catalytic properties of the new class of materials. Critical materials synthesis using two distinctly different methods with unique advantages will be performed to firmly establish the principle of noncompensated n-p codoping in host materials. Complementary characterization techniques will be used to systematically study the correlations between the chemical composition and optical and photochemical properties, as well as the energy conversion efficiency and chemical stability of the new materials. This project represents an important step toward developing a strong ORNL program for solar energy conversion based on integrating advanced materials synthesis capabilities and fundamental understanding of materials properties for high-efficiency solar energy utilization, guided by predictive theoretical modeling and simulations.

Mission Relevance

This work is directly relevant to DOE's research portfolio in basic science. It is particularly relevant to DOE initiatives in materials science and fundamental research for alternative sustainable energy.

Results and Accomplishments

The results can be summarized as follows. On the theory side, we used different schemes of first-principles density functional theory (local density approximation plus onsite Coulomb repulsion, and hybrid approaches) to establish the dependence of the bandgap narrowing of TiO_2 on the different combinations of the n-p codopants. We predicted that the codoping of Cr and N will have substantially enhanced thermodynamic and kinetic soluability to be substitutionally doped in TiO_2. We found that TiO_2 codoped with Cr-N pairs exhibits a novel "half semiconducting" feature, potentially offering new research opportunities for developing new materials for spintronics. We extended the noncompensated n-p codoping concept to other systems, including diluted magnetic semiconductors. On the experimental side, we used wet chemistry synthesis approaches to fabricate a variety of TiO_2 nanoparticles, all in anatase phase, but either pure, or doped with Cr or N, or codoped with Cr-N pairs. We characterised the nanoparticles using a line of spectroscopic and structural techniques, including optical absorption, Raman scattering, X-ray photoelectron spectroscopy, scanning tunning spectroscopy, and electron paramagnetic resonance, and confirmed many of the salient features predicted in the theory part. We used a complementary growth technique of pulsed laser deposition to fabricate anatase-phase thin films with different dopant combinations and densities, and confirmed many of the structural and spectroscopic properties as observed from the wet-chemistry samples. We obtained preliminary results indicating substantially enhanced efficiencies for water splitting on the surfaces of the Cr-N codoped TiO_2 nanoparticles under light irradiation in the visible region.

05061

Nanostructured Mesoporous Photocatalysts for CO_2 Reduction

A. C. Buchanan III, Michelle Kidder, Gilbert Brown, Reza Dabestani, and Edward Hagaman

Project Description

Photoreduction of CO_2 by visible light is one the most challenging processes in solar energy-to-fuel conversion. The goal of this project is to design and construct organized assemblies of metal reaction centers in mesoporous silica scaffolds that will serve as efficient photocatalysts for CO_2 reduction employing visible light. Two distinct oxo-bridged metal reaction centers will be covalently grafted to the pore surface of an SBA-15 mesoporous silica. The two metal centers will be designed such that, upon irradiation with visible light, a metal-to-metal charge transfer (MMCT) band can be excited, resulting in electron transfer and generation of a metal center in an oxidation state capable of CO_2 reduction. The flexibility in selection of metals and oxidation states, diverse synthetic strategies for tethering metal centers to the surface, control over metal ratios and grafting densities, and the ability to tune interfacial properties such as polarity through further chemical modification provides great opportunity for the design of efficient new photocatalysts for CO_2 reduction. These materials will be characterized by an array of techniques including X-ray diffraction, BET analysis, NMR and FTIR spectroscopies, and ICP elemental analysis. The photochemical properties of these materials and the details of the MMCT step will be examined by steady-state and time-resolved optical spectroscopic techniques. Finally, we will examine the photocatalytic reduction of CO_2 with these designed catalysts to determine conversion efficiencies and product selectivities.

Mission Relevance

Carbon dioxide utilization for the production of (1) fuels such as methane and methanol, (2) fuel and chemical feedstock precursors such as CO, and (3) other value-added chemicals remains a major scientific challenge and opportunity. DOE has major programs focusing on carbon dioxide capture, storage, and conversion (Fossil Energy), as well as the use of solar energy for production of electricity (Basic Energy Sciences, Energy Efficiency and Renewable Energy) and fuels (Basic Energy Sciences). Hence, this project, which aims to design and produce new nanostructured photocatalysts for the conversion of carbon dioxide into fuels using visible light, has direct relevance to these DOE program goals. In addition, the DOE Basic Energy Sciences program has a significant programmatic mission for fundamental research resulting in the design of novel catalysts for energy applications, and this project is directly relevant to that mission.

Results and Accomplishments

Studies in FY 2008 focused on a detailed examination of the synthesis and characterization of Ti(IV)-O-Sn(II) hetero-bimetallic catalysts tethered to the pore surface of SBA-15 mesoporous silica. Several methodologies for introducing the titanium and tin sites were successfully evaluated for the ability to control site densities, Ti:Sn ratios, and dispersion on the SBA-15. We have also examined the use of a Ti-O-Ti dimer organometallic precursor to prepare Ti(IV)-O-Sn(II) grafted catalysts and probe the significance of titanium site isolation on MMCT formation and catalytic activity. Solid state ^{119}Sn NMR is being employed to provide insights into the tin bonding environment on the surface, and it is showing promise for providing novel structural insights. The materials have also been characterized by elemental analysis, FTIR, and nitrogen physisorption measurements. We found that the photocatalysts maintain their mesoscopic order with high surface areas and large pore diameters. The materials were also examined by diffuse reflectance ultraviolet-visible spectroscopy. The SBA-15 attached Ti-O-Sn catalysts show extended optical absorption to about 450 nm in the visible region. This is characteristic of the desired MMCT process {Ti(IV)-O-Sn(II) → Ti(III)-O-Sn(III)}, and the MMCT band intensity is dependent on the Ti:Sn ratio. The Ti(III) site produced by the MMCT process is in a tetrahedral environment on the silica, and it is known to be able to reduce CO_2. We are continuing to explore the most favorable titanium grafting densities, Ti:Sn ratios, and the influence of titanium dimer structures for optimization of the MMCT band for this photocatalyst. Designing new solar photocatalysts based on oxo-bridged heterobimetallic chromophores (M-O-M') is drawing increasing attention (e.g., for water oxidation) because of the versatility in their design. We have now expanded our investigations to explore additional M-O-M' clusters grafted to SBA-15 to design improved photocatalysts for CO_2 reduction.

05079

Supra-macromolecular Assembly of Artificial Photoconversion Units

Hugh O'Neill, Kunlun Hong, William Heller, and Bernard Kippelen

Project Description

The goal of this project is to gain a molecular level understanding of the design principles that support and promote the assembly of an artificial photosynthetic unit for the conversion of light into electric or chemical energy. A synthetic system is sought that is capable of self-assembly into a biomimetic membrane structure and is able to incorporate functional catalytic units within a supra-macromolecular structure. Synthetic electroactive block copolymers can provide a biomimetic environment and self-assemble into nanostructures with tunable phase morphology. Their functionality can be widely varied through choice of monomers and polymerization reactions (e.g., incorporation of binding sites for chromophores and catalysts). We propose to use photosynthetic proteins to understand the fundamental principles of synthetic architectures suitable for solar energy applications. This will lead to an in-depth understanding of the weak intermolecular forces that govern supramolecular assembly and result in a block copolymer system that can perform in a manner analogous to the natural photosynthetic membrane. This project brings together ORNL's recognized expertise in photosynthesis, polymer synthesis, and neutron science. In addition, our collaboration with the Georgia Tech team (part of the AtlantICC Alliance; http://www.atlanticcalliance.org/index.html), who have expertise in organic photovoltaics, will further strengthen our ability in this area.

Mission Relevance

This project primarily deals with the control of molecular processes at interfaces. It is focused on bioinspired molecular assemblies, novel nanoscale and self-assembled materials, self-repairing conversion materials, and solar fuel concepts. At the end of this work, we will have an in-depth understanding of the design principles required for the development of a membrane system for artificial photoconversion applications. As this project primarily deals with the control of molecular processes at interfaces, it addresses the solar energy research component of ORNL's Advanced Materials Initiative. This work is also relevant to the Solar Energy Initiative and the Division of Materials Sciences and Engineering, both of the DOE Office of Science, Basic Energy Sciences.

Results and Accomplishments

Light harvesting complex II was isolated using two different procedures. The first step in both procedures was solubilization of thylakoid membranes with Triton X 100. In the first procedure the LHC II complexes were separated from other components by appression of the LHC II followed by centrifugation. In the second procedure, which resulted in a purer preparation of the protein, the solubilized thylakoid membranes were subjected to density gradient centrifugation. To study the interaction of block copolymers with LHC II, experiments were carried out using Pluronic block copolymers. The interaction of LHC II with Pluronic L62 at low polymer to protein ratio (10:1) resulted in a change in the shape of the CD spectrum. Other studies have reported that such changes indicate that the LHC II complexes form lamellar sheets in solution.

This result provides insight into the features that will be important for the design of electroactive block copolymer systems. We also studied the synthetic analogues of LHCII. The genes that encode all three LHC II polypeptides have been cloned. In addition, a truncated gene that consists of helix 1 of LHCII has been cloned, and cloning of the variant encoding helices 1 and 2 is under way. This approach will allow us to investigate if individual LHCII subunits and their truncated derivatives have the ability to alter the phase behavior of membrane-forming lipids and also determine the minimum polypeptide sequence capable of binding chlorophyll.

The solution structure of LHCII in detergent solution was investigated using small angle neutron scattering. Contrast matching in 15% D_2O was used to eliminate the scattering signal from the detergent. The data is consistent with an LHC-II trimer extracted from the published crystal structure. The radius of gyration of the trimer is 27.9Å. This study will form the basis for understanding how LHC II complexes can be incorporated into artificial membranes formed by block copolymers.

05090

Synthesis, Assembly, and Nanoscale Characterization of Confined, Conjugated, and Charged Polymers for Advanced Energy Systems

Jimmy W. Mays, John F. Ankner, Philip F. Britt, Mark Dadmun, Kunlun Hong, and S. Michael Kilbey II

Project Description

Conjugated polymers hold the key to future fundamental advances in science and technology. A major barrier that hinders the application of conjugated polymers for energy conversions has been a lack of understanding how conjugation affects structure and properties, which springs directly from a lack of well-defined materials. The objectives of this project are to develop the chemistry necessary for creating tethered, interfacial layers of poly(para-phenylene) (PPP) and their derivatives on solid substrates and to study how the self-organization, confinement of these polymers impact their nanoscale structure and properties. The surface-tethered layers will be created by functionalized polycyclohexadiene (PCHD) chains with complementary functionality on the substrate. Then they will be converted to PPP brushes by aromatization. Doping of PPP brushes will yield highly ordered arrays of conducting polymer chains. These materials will be the first well-defined conjugated polymer brushes, and the study of their structure and properties will provide unique insight into the impact of nanoscale confinement on their properties. The proposed work will focus mainly on synthesis of these novel materials, structural characterization via neutron reflectometry/scanning probe microscopy, and conductance measurements. Efforts to study the electrochemical behavior of the systems will also be advanced.

Mission Relevance

This project is relevant to programs at DOE, the Department of Defense (DOD), and the Department of Homeland Security (DHS). We are creating novel polymer brushes derived from poly(cyclohexadiene), including poly(cyclohexadiene sulfonate), poly(phenylene), and poly(phenylene sulfonate), where we will have control over the polymer molecular weight, microstructure, grafting density, and substrate, and will develop fundamental understanding of the correlation between the structure of the polymer chains and the structure and properties of the polymer brushes. This foundation will then be utilized to develop future research projects focused on charged or conducting polymer brushes with specific properties (e.g., photovoltaic, proton conducting) of interest to DOE, DOD, and DHS. The Army Research Office Broad Agency Announcements indicate that conjugated polymers are of interest to several programs. One is Dr. Michael Gerhold's program on optoelectronics, where novel optoelectronic materials are sought. The other is the Polymer Chemistry program of Dr. Douglas Kiserow, which describes an interest in such materials for a range of applications.

Results and Accomplishments

Two trichlorosilane end-capped poly(cyclohexadienes) with high 1,4-microstructure, one perdeuterated and the other protonated, were synthesized by anionic polymerization. The nondeuterated sample was reacted with a silicon oxide substrate to create PCHD brushes. The brushes were aromatized and sulfonated. All materials were characterized by a combination of ellipsometry, atomic force microscopy (AFM), contact angle measurements, and neutron reflectivity. A very dense, but not homogeneously uniform, monolayer of grafted PCHD has been formed from the grafting of trichlorosilane end-capped PCHD polymers to a silicon oxide surface. With a PCHD chain of 11,000 daltons, a layer that is approximately 6 nm thick is attained. Neutron reflectivity shows that this layer has a roughness that is greater than the thickness, indicating that a monolayer has not been attained. Additionally, the results indicate that aromatization to PPP does not change the gross characteristics (thickness, density, roughness) of the grafted polymer layer. Ellipsometry, AFM, and reflectivity indicate that the sulfonation reaction alters the thickness of the layer, extending it away from the surface. This makes sense, as the incorporation of charges along the chain should stretch the chain. Unfortunately, it appears that the sulfonation reaction utilized also removed a significant portion of the grafted chains. Further work will concentrate on developing a sulfonation procedure that incorporates charges onto the chain while minimizing chain scission. Analysis of the electrical properties of the isolated sulfonated poly(p-phenylene) domains could provide an intriguing method to monitor the effect of confinement on the properties of these unique systems.

05372

Drawn Field Emitters, Vertically Aligned Carbon Nanotubes, and Related Nanostructures

John Thomas Simpson and Ilia N. Ivanov

Project Description

This research project proposed to combine and extend two existing ORNL technologies: fabrication of high-quality carbon nanotubes and drawing nanostructured materials. By combining these two technologies in a synergetic way, we were able to demonstrate new forms of composite materials and structures that are capable of exhibiting new capabilities in a variety of areas including high-current, low-turn-on field emission and display devices. This project explored field emission fabrication and characterization of drawn wire, and carbon nanotube (CNT) arrays based on unique fabrication techniques developed at ORNL. Our existing drawn wire array fabrication techniques were used and expanded to include tip sharpening and backplane activation. Furthermore, we explored the use of conductive carbon nanotubes as electrical elements in vertically aligned, individually addressable, field emitter arrays. We demonstrated new ways to simultaneously disperse and align CNTs using glass fiber drawing. Since CNTs burn up in air at glass drawing temperatures, we first sealed to CNTs using "liquid glass" and used a resultant dry glass/CNT powder to fill a capillary tube. The tube was then drawn, cut into segments, bundled, and cut into wafers. The wafers contained aligned and mechanically dispersed conductive CNTs.

Mission Relevance

The potential new devices stemming from this research will have a variety of scientific and commercial applications. The ones most aligned with DOE missions involve new high-efficiency photovoltaic devices and low powder display systems. The Defense Advanced Research Projects Agency will very likely be interested in this new technology and the associated devices due to reduced energy footprint and/or their higher energy density. Our demonstration of this fabrication process opens up a whole new set of opportunities to produce electronic devices based on field emission array technology and high-efficiency light-emitting diode lighting systems. For example, high-definition, low-voltage activated display technology will be one of many new applications of this new field emission array technology.

Results and Accomplishments

Wire Drawing. We demonstrated field emission of sharpened tungsten wire arrays which can be used as field emission cathodes. To create these arrays we used a modified fiber drawing process. Micron-sized tungsten wire was coated with glass and then cut into segments. The segments were bundled and fused together to make a single piece of glass with uniformly distributed parallel tungsten wires. Wafers were then cut perpendicular to the wire axis. In a three-step process, the glass was removed at one end, the exposed tungsten wire tips were sharpened, and the pointed tips were further exposed by removing more glass. These wire tips have a radius of curvature smaller than 200 nm. Finally, the samples were placed under vacuum and connected to a voltage source. The lowest amount of applied potential (i.e., voltage) to detect electron flow for the individual tungsten wires was measured. Results showed that reasonable potentials need to produce emission and that this process can be used to create tungsten field emission cathode arrays using an easily scalable process.

Drawing Glass Containing Carbon Nanotubes. We explored new ways to simultaneously disperse and align CNTs using a glass fiber drawing without burning up the CNTs. Once drawn, fiber segments were then bundled together and placed inside a glass tube and drawn a second time and third time. Scanning electron microscope (SEM) images verify that the CNT did not burn up in the drawing process. Additionally, SEM images of the second and third draws show that the CNTs are becoming more dispersed and starting to align in the axial direction of the fiber. Measurements of the axial conductivity showed that the drawing process increased the conductivity from a single draw to a double draw. This is due to the drawing process dispersing and aligning the CNTs along the fiber axis.

05373

Investigating the Role of Physical Interactions and Block Sequence Tailoring on Macromolecular Self-Assembly Through Micellar Systems

S. Michael Kilbey II

Project Description

In this project the role of sequence tailoring and reversible physical interactions on the self-assembly of polymer micelles in aqueous solutions is being studied. A new modular approach for creating centro-symmetric three-armed stars will be developed and used to create star-like polymers that change their configuration in response to external stimuli. The flexibility enabled through the modular approach is key, allowing diverse sets of materials to be easily created from a library of constituents. By controlling the composition and sequence of the constituents, the structure, dynamics, and response of the star copolymers can be tailored. In addition to complete and rigorous characterization of the novel materials synthesized, the structure and dynamics of the self-assembled micelles will be examined using dynamic and static light scattering. This project is transformative in that by tailoring sequence and composition, we are able to isolate the role of molecular-level design on self-assembly, nanoscale structure, and dynamics, paving the way for designed materials for a variety of applications.

Mission Relevance

A grand challenge in materials science and chemistry is to understand how the chemical information and interactions encoded into materials through synthesis drives their assembly, nanoscale structure, and function. The knowledge gained from this fundamental research program will significantly contribute to our understanding of soft matter (polymers), providing crucial information into how to design novel materials with specific properties and structure, ultimately enabling breakthroughs in next-generation materials and devices, including materials for solar energy conversion, fuel cells, and battery technologies. This work is also enabling for processing via self-assembly, which capitalizes on free energy gradients and weak interactions. As a result, this research aligns with programs of the DOE Office of Science, Basic Energy Sciences, particularly in materials and chemical sciences, and it may, by paving the way for understanding structure-function relationships in bio-inspired systems, benefit agencies having missions in national security and defense (e.g., Defense Advanced Research Projects Agency, Defense Threat Reduction Agency).

Results and Accomplishments

Efforts since the inception of the project in July have focused on (1) synthesis of constituent "arms" of the stars and their characterization and (2) preparation of the central linking core necessary for realizing the novel three-arm star-block copolymers. Three different types of end functionalized polymers to be used as building blocks for the stars have been made and characterized. The central linking core (based on trimelletic anhydride chloride) was successfully modified to accept linking of the first arm in the multistep approach. Furthermore and key to the project, a first attempt to demonstrate the linking approach (arm to central core) using these materials was successful. This augurs well for continued advances using responsive polymeric materials that interact via hydrogen bonding and electrostatic interactions and the modular approach that is central to the novelty of the synthetic route. From findings to date, it appears that this novel synthetic approach for making complex copolymers will enhance ORNL capabilities for creating tailored polymeric materials. Specific to the project, once a base set of those responsive polymers are synthesized and the three-arm star polymers constructed, efforts to characterize thermodynamic behavior of these star-block copolymers when manipulated by triggering phase transitions of the constituent materials will begin. These studies will engender insight into how chemical information and interactions integrated into the molecular assembly affects nanoscale structure and dynamics.

05374

Materials Behavior Underlying the Electrochemical Performance of Advanced Batteries

Sheng Dai, Nancy Dudney, Karren More, Ed Hagaman, Bob Shaw, De-en Jiang, Andrew Payzant, Claus Daniel, and Edgar Lara-Curzio

Project Description

This work undertakes two research thrusts aimed at developing underlying knowledge of basic materials behavior that governs lithium battery electrochemical performance and lifetime. Specific objectives include (1) dynamic characterization of the initial development of the solid-electrolyte interphase (SEI) in terms of morphology and molecular composition at a heretofore unattained level of resolution, thus demonstrating the ability to fundamentally relate these characteristics to energetics and kinetic factors; and (2) development of an understanding of the evolution of stress states and mechanical behavior of electrodes and the SEI in order to directly connect structure and materials processing routes to the factors that make major contributions to a lithium battery's durability (lifetime) and safety. To accomplish these goals, it will be necessary to (1) tailor advanced, in situ characterization tools for effective use with battery material systems that utilize ORNL's capabilities in electron microscopy, molecular spectroscopies (e.g., nuclear magnetic resonance, electron spin resonance, vibrational spectroscopies), X-ray diffraction, and mechanical behavior; (2) establish the necessary suite of instruments to conduct standard electrochemical characterization of battery cells (or half cells) in order to relate in situ microscopy, molecular spectroscopies, X-ray, and mechanical observations and measurements to macroscopic current-voltage performance; and (3) develop processing routes to synthesize model systems that facilitate analysis of the results in terms of thermodynamic, kinetic, and stress factors.

Mission Relevance

It is readily apparent that efficient, affordable electrical energy storage is the key to meeting the challenges of future energy security and climate change in the transportation and stationary and portable power generation sectors (http://www.sc.doe.gov/ bes/reports/files/EES_rpt.pdf). It is also clear that, particularly for transportation, an enormous improvement in battery performance is needed to displace fossil-based fuels for everyday needs. The technical challenges to reach the necessary level of ultimate performance of electrical energy storage devices (batteries and supercapacitors) are daunting; none are more so than the need for materials (both electrodes and electrolytes) that exhibit long-term stability at high rates of charge transfer under both oxidizing and reducing conditions. The needed advances will require basic and applied research in materials science and electrochemistry as well as extended materials and systems development and testing. In this project ORNL will undertake initial steps to grow a robust program of research devoted to materials for future electrical energy storage devices by focusing on a few key processes that underlie the electrochemical performance of advanced lithium batteries.

Results and Accomplishments

The key objective of this project is to establish the key infrastructure for ORNL to conduct research in electrical energy storage. However, because this project was started very late in the year, we have no results or accomplishments as yet. The funds awarded for FY 2008 were used to procure materials and equipment for research to be conducted during FY 2009–2010.

05375

Attoliter Droplets on Demand in Nanochannels: New Opportunities for Investigating Chemical Reactivity and Catalysis in Nanoscale Reactors

Charles Patrick Collier, Seung-Yong Jung, and Scott Retterer

Project Description

We propose a new method for producing submicron, *attoliter-scale* (10^{-17} L) aqueous droplets on demand at the intersection of nanochannels. At the intersection of two apposed aqueous channels with an immiscible oil channel, two submicron, oil-dispersed aqueous droplets containing different reactants can be forced to collide with each other and fuse, completely mixing their interior contents by diffusion in less than a millisecond. This can be used to produce monodisperse reaction vessels two orders of magnitude or smaller in volume than in current state-of-the-art microfluidic devices, while satisfying the constraints of perfect sealing and passivation against nonspecific adsorption of large macromolecules like proteins at the droplet periphery. The resulting surface-to-volume (S/V) ratios of droplets at this scale will be in excess of 10^6, which may open up new areas of research across several fronts, in particular the study of catalysis and reaction dynamics of transient chemical and biochemical intermediates in confined environments. As a proof-of-principle demonstration of the method, we will measure single-enzyme kinetics in the nanoreactors with a well-defined time zero for initiating the reaction, and with sub-millisecond temporal resolution.

Mission Relevance

The ability to probe reaction dynamics of highly reactive, transient chemical, biochemical, and electrochemical species in confined environments with unprecedented temporal resolution will provide important new capabilities vital to next-generation DOE missions. Results from this work will add to our fundamental understanding of catalysis, chemical synthesis, and energy in nanoscale confined systems, and thus may be directly applicable to targeted DOE initiatives such as advanced materials, advanced energy systems, and systems biology. In addition, practical technological advances, such as in sensors and detection technology, resulting from this research may be exploited for cross-cutting programs such as national security.

Results and Accomplishments

Three approaches are being pursued in the Nanofabrication Research Laboratory to create sealed nanochannels on fused quartz or silicon substrates. Each approach offers its own unique set of advantages and disadvantages; the activity performed for FY 2008 has been directed toward finding the best balance of performance metrics at this early stage of development, for optimal integration of nanochannels in the completed device. The three approaches explored are (1) reactive ion etching (RIE) of nanotrenches directly *into* quartz substrates, followed by capping of the trenches with thin silicon oxide or nitride films grown via plasma-enhanced chemical vapor deposition (PECVD); (2) wet etching of sacrificial amorphous silicon wires, encased in PECVD-grown oxide or nitride tubes, to form hollow nanochannels *on top of* quartz substrates; and (3) dry etching with RIE of nanotrenches into silicon substrates, followed by sealing of the trenches with PECVD-grown oxide or nitride films. Option 3 is almost identical to option 1, except that silicon is used as the substrate instead of quartz.

The use of transparent quartz substrates would be ideal for optical access to the nanochannels; however, growth of “RIE grass,” which are high aspect ratio, needle-like features in the trench that form during etch due to micro-masking of the substrate by transient fluorocarbon polymer species, limits the ability to form clean, well-defined nanochannels in quartz (option 1). RIE etching of silicon substrates (option 3) is much easier and more established than etching in quartz for this reason. Highly anisotropic nanochannels, centimeters long and with widths from 200 to 1000 nm, have been formed from trenches etched into silicon in this manner, and sealed with PECVD oxide. However, the silicon substrate is not transparent to uv-visible light, which will preclude the ability to use inverted optical microscope objectives without additional fabrication steps, such as back-etching of silicon. Option 2 may be a good compromise between the other two approaches. It keeps the transparent quartz substrate without the associated problems inherent with RIE etching of quartz. In addition, the fabrication should be somewhat less complex than option 3.

NATIONAL SECURITY SCIENCE AND TECHNOLOGY INITIATIVE

00024

NanoePower—Nanocatalytic Direct-Fuel Thermoelectric Generator

Zhiyu Hu

Project Description

The goal of this project is to develop a solid-state power generation system based on microelectromechanical systems (MEMS) that is fully automatic and fueled directly and has a high specific power and a long operational life. In addition, the system will be mechanically simple; man-portable; and able to power electronic devices such as computers, sensors, and communication gear using methanol, ethanol, or hydrogen. NanoePower is a new class of solid-state power generation that operates at ambient temperature and pressure in which the fuel's chemical energy spontaneously releases to thermal energy at predefined localized nanocatalytic heating zones without conventional ignition or high temperature gas-phase burning/combustions while the entire system maintains ambient bulk temperature. NanoePower is a fully scalable distributed power system that could have specific power and energy 10–100 times better than existing batteries. The first goal of this project is to fabricate a postage stamp–size DC power generator with output power of 1–10 W and an operational life of 1000 hours.

Mission Relevance

NanoePower uses innovative approaches in nanoscale energy conversion and transport to address urgent needs for reliable portable power systems. Using environmentally friendly, high-energy-density fuels such as methanol, ethanol, or hydrogen, NanoePower could potentially replace low-energy-density chemical batteries, which have many adverse environmental effects. This project is well-fitted with DOE missions in improving environmental quality, utilizing alternative energy/bioenergy, and achieving excellence in science. As a high-specific-power and high-energy-density portable power system, NanoePower will also benefit federal agencies, such as the Department of Defense, that are interested in reliable, portable power.

Results and Accomplishments

In FY 2008 we successfully demonstrated the concept of direct energy conversion using nanacatalytic room-temperature combustion. Using the latest nano/microfabrication technology, we have designed and fabricated the second-generation NanoePower test chip, which greatly improved the power generation efficiency and stability. Our laboratory prototype is able to continually produce steady electrical power from methanol vapor directly at room temperature over several days. Technological breakthroughs were achieved in the following areas: (1) high-performance nanostructured thermoelectric nanofilms, (2) innovative nano-heating-zone MEMS solid-state nanostructures, and (3) immobilized nanocatalytic heterostructures. A multi-target physical vapor deposition (PVD) method was employed to build high-performance thermoelectric nanofilms. Metals and semiconductors were used to nanocomposite p-type and n-type thermoelectric nanofilm structures (<1000 nm). Our second-generation MEMS platform employed an innovative first-surface nano-heating-zone structure that is able to achieve remarkable thermal gradient up to 30,000 K/mm near room temperature. Two types of test chips were fabricated. One is designed for the nanostructure and material property measurement. Another chip contains 400 NanoePower element units in a one-inch-square die. We also investigated several methods of coating and localizing a nanocatalytic layer onto our test chip. Two methods were developed for patterning catalytic nanoparticles on various substrates: direct dispersion of prefabricated nanoparticles and on-site synthesis via a chemical reaction. In our experiment, autoignition of nanocatalytic reaction was achieved in a methanol vapor/air mixture under ambient conditions and produced stable electrical power output for days. Since some nanocatalytic particles synthesized more than 3 years ago are still very active, the NanoePower system would have an operational life of at least a few thousand hours under a continuous fuel and air supply with a power density up to 1 kw/kg.

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00028

A Novel Process of Thick Nanocomposite Surfaces for Defense Applications

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Project Description

Wear and friction are critical issues for many defense applications. The purpose of this work is to develop a novel surface engineering technique to form a highly wear-resistant nanocomposite surface for lightweight alloys, such as those of aluminum and titanium. Friction stir processing (FSP) is used to stir and mix ceramic nanoscale particles into a metallic surface to form a nanocomposite layer to improve the surface hardness, strength, and wear resistance without sacrificing the bulk ductility and conductivity. Unlike most other surface engineering techniques, FSP can form very thick layers, up to millimeters in thickness, and avoid delamination because of the inherent material continuity. This project is focused on developing the surface nanocomposite process and understanding the inherent mechanisms by taking advantage of the state-of-the-art characterization capabilities at ORNL. This surface engineering technique has great potential for many military applications to provide energy savings through friction and weight reductions and safer, longer lasting, and more reliable service as a result of the harder, stronger, and more wear-resistant surfaces.

Mission Relevance

Friction and wear are estimated to cost 6% of the U.S. gross national product, or around $700 billion annually. The terms wear and friction appeared 25 and 19 times, respectively, in the 2005 Military Critical Technologies List of the Department of Defense. This proposed nanocomposite surface engineering technique is expected to save energy through friction and weight reductions and to provide safer, longer lasting, and more reliable service as a result of the harder, stronger, and more wear-resistant surfaces. The successful development of this technique will have great potential in aviation, ship machinery, and ground transportation applications. Particularly, this surface engineering process has great potential for many military applications that require hard, strong, or wear-resistant surfaces, such as submarine mast fairing guiderails and MCM ship main propulsion shafts (Naval Sea Systems Command), carrier landing cable-guiding sheaves (Naval Air Systems Command), and lightweight armor (Defense Advanced Research Projects Agency).

Results and Accomplishments

A novel surface engineering process based on FSP has been developed successfully to improve surface hardness and wear resistance without sacrificing bulk ductility and conductivity. Nanoscale ceramic (Al_2O_3 and SiC) particles have been stirred and mixed into aluminum surfaces to form nanocomposite layers of up to several millimeters thick. The concentration of the hard phase was in the range of 5–25 vol %. Major challenges that were encountered and overcome in the process development include the low densities of nanopowders, powder placement, and the excessive wear of FSP tools. For pure aluminum, the nanocomposite layer significantly increased the hardness (by 3×) and yield strength (by 10×), and reduced the friction coefficient (by 55%) and wear rate (by 100×) when rubbing against a bearing steel. For Al 6061-T6511 alloy, the nanocomposite layer improved the wear resistance by more than one order of magnitude. A post-FSP heat treatment (T6) provided an additional 50% enhancement of the wear performance of the nanocomposite surface. Transmission electron microscopy revealed much higher matrix dislocation densities in the nanocomposite zone compared to the nonprocessed aluminum alloy; this is believed to be largely responsible for such significant property improvements. Neutron diffraction measurements conducted at the High Flux Isotope Reactor suggested mild tensile residual stress in the aluminum matrix, which was mainly induced by thermal expansion mismatch between aluminum and alumina.

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00035

Cognitive Radio for Transformational Logistics

Mark A. Buckner, Michael R. Moore, Michael J. Vann, Nageswara S. Rao, Lawrence P. MacIntryre, Miljko Bobrek, Benjamin E. Huey, and Donald P. Bouldin

Project Description

Our national transportation infrastructure, composed of complex, interdependent components, presents a particular challenge to national security because it is both a critical asset and a key vulnerability. To address this vulnerability, we propose cutting-edge information and communication technologies based on a synergy of novel algorithms and electronic circuits employed in cognitive radios (CRs). A CR can learn and dynamically adapt its communication parameters based on interaction with its environment through active negotiation with other spectrum users and/or passive sensing of the environment. Though not a requirement, most CRs are software based and implemented on software-defined radio platforms. For transportation security applications, CR technologies can provide the capabilities required of fourth-generation logistics tracking by adapting to nonexistent or rapidly changing infrastructures. Such systems will make use of a variety of standards-based radio frequency identification and communications waveforms, global positioning system and other sensors, and computational intelligence to dynamically alter its waveform and routing schemes to facilitate connectivity over a variety of disparate communication links, including cell phones, satellite communications, and radio links. This capability will enable total in-transit visibility, automated generation of manifest (e-manifests), mission-based logistics responses, and automated repair scheduling.

Mission Relevance

This project is relevant to a variety of DOE national security missions, including monitoring of special nuclear materials and critical infrastructure. Technology developed under this project will provide military convoys with automated sensor and communication connectivity both among the trucks and back to oversight locations (e.g., command posts.) It will provide in-transit visibility for logistics support missions. Domestically (e.g., Department of Homeland Security/disaster response), it will provide similar visibility and connectivity for convoys and teams responding to large disasters in which the existing communication infrastructure has been destroyed and which may require, chemical, biological, radiological/nuclear, and explosive sensing. We anticipate the results of this project will also benefit DOE's Spectrum Management program, NA-42, and several other federal agencies including CIA, DIA, FBI, NSA, DOD, DEA, ATF, DHS, DNDO, and NIJ, each with a variety of tagging, tracking, and locating needs. Finally, the scientific/technical mission relevance involves the leap ahead in the amount of signal processing (communication at multiple layers plus sensor fusion) that can be achieved on small, portable platforms.

Results and Accomplishments

Significant progress was made in waveform implementation, mobile ad hoc routing, and cognition and parameter optimization.

Waveforms. Four waveforms are now fully demonstrable on our software defined radio (SDR) platform: (1) Iridium paging, (2) Savi active Radio Frequency ID (aRFID), (3) Wherenet aRFID, and (4) an ORNL custom waveform (DSSS-based). The status of other key waveforms is as follows: (1) Iridium Short-Burst Data (SBD), 95% complete; (2) Zigbee, 25% complete; and (3) 802.11b, 25% complete. The first three waveforms have been demonstrated on integrated hardware.

Mobile Ad Hoc Routing. Various existing ad hoc routing algorithms, including the Optimized Link State Routing (OLSR) protocol, the Ad hoc On-Demand Distance Vector (AODV) routing protocol, and MITRE’s MobileMesh protocol, were briefly evaluated for use in this project. Source code for each of these algorithms was available, but it was written in C++, or specifically for Linux, and would have required substantial effort to port to code to run on the Xilinx FPGA embedded processor. In addition, OLSR and AODV are complex and have large memory requirements, making them ill-suited for our prototyping platform.

A careful evaluation of the present requirements revealed a very simple protocol could be devised which would be better suited for this application, requiring less time to implement and fewer system resources to operate than OLSR and AODV. The purpose of the CR tag-to-tag network is quite simple. It exists to provide dynamic routing of information from/to CR and non-CR nodes (aRFID tags, sensors, etc.) to CR nodes that are currently providing “gateway” services to remote locations/collection points via Iridium. Ultimately, the routing protocol will be incorporated as a CR service that dynamically learns and adapts to optimize local connectivity, gateway services for in-transit visibility, and power leveling among the nodes in the local mesh network.

A new routing protocol was developed to satisfy these simple connectivity requirements. The protocol, which was implemented in C, has the following properties: (1) nodes periodically broadcast a “Hello” message so that all nodes can keep track of their adjacencies; (2) nodes periodically broadcast their routing tables so that they can maintain a list of their available full-duplex communication paths; (3) nodes may request a path to the nearest available CR node providing active gateway services; (4) nodes may request a path to any node in the network; (5) nodes only maintain route tables for adjacent nodes, satellite transceivers, and nodes for which they have recently relayed messages; (6) nodes can request sensor readings or confirmations from adjacent nodes and perform information fusion to validate sensor readings; and (7) nodes can spontaneously report sensor values to remote collection points based on schedule reporting intervals or triggered-threshold events. The protocol was designed to be scalable and easily extended to provide additional features such as encryption, power conservation, and message precedence.

Cognition and Parameter Optimization Algorithm. An effort conducted in that the first year of the project resulted in some modeling and prototyping efforts of relevant circuits needed to support parameter optimization algorithms. The follow-on effort in the second year involved two items: (1) successful demonstration of the ability to use the CR program’s digital design process/tool-flow from Xilinx FPGA implementation for rapid prototyping to an Application Specific Integrated Circuit in the TSMC (Taiwan Semiconductor Manufacturing Company) 180-nm process when very low power or large volume production is needed and (2) bio-inspired signal processing and cognition/learning program. The bio-inspired signal processing and cognition effort included leading a nationwide team in development and submitting of a proposal to the Defense Advanced Research Projects Agency (DARPA). Although the proposal was not selected, this effort is being leveraged for potential follow-on opportunities with DARPA, the National Science Foundation, and the Office of Naval Research.

Publications

Buckner, M. A., et al. 2008. “From Requirements Capture to Silicon: A Model-Driven Systems Engineering Approach to Rapid Design, Prototyping and Development in the Oak Ridge National Laboratory’s Cognitive Radio Program.” *Proceedings of the SDR ‘08 Technical Conference*, Nov. 27–30, Washington, D.C.

Moore, Michael, and Dan Archer. 2008. “Mobile Urban Radiological Survey System (Real-Time Pedestrian Mapping for Search-ORNL).” Report delivered to DOE/NN-42 in September.

00046

Combustion of Nanostructured Metal Fuels: Towards Designing Optimized Combustion Chambers

M. P. Paranthaman, A. L. Qualls, B. G. Sumpter, and S. D. Labinov

Project Description

This project will (1) create a new metal fuel for anaerobic combustion that could be used in unmanned, high-altitude air vehicles and possibly hypersonic engines and (2) conduct initial combustion proofing. A Department of Defense (DOD) aluminum combustor design is projected to have an in-vehicle energy density near 1200 W·h/L. In contrast, a boron-fueled sterling- or turbine-powered design can produce an energy density of greater than 2500 W·h/L because boron is more energetic and can be burned in a low-pressure power plant of lesser weight. The aluminum combustor uses 800°F steam in heavy, thick-walled pressure vessels, carries an oxidizer separately, and is projected to require a vehicle of 38 in. in diameter—much larger than most deployment platforms can handle. The more powerful but lighter boron plant will enable the use of smaller vehicles without sacrificing tactical capability and endurance, enable wider deployment options, and potentially be safer than aluminum-powered alternatives. Our scientific approach is based on previous ORNL work on the combustion of engineered clusters of metallic nanoparticles. Initial results have shown complete and rapid solid phase oxidation at temperatures of 1000–1400 K without chamber-fouling condensation or sintering—critical for multiuse, high-endurance engines.

Mission Relevance

DOE's overarching mission is to advance the national, economic, and energy security of the United States and minimize dependence on imported oil, which requires alternative energy sources and carriers. This project opens the possibility of an energy carrier and heat engines more powerful than both gasoline and internal combustion, and independent of the carbon cycle. While the project focuses on high-performance military applications of interest to DOD and the National Aeronautics and Space Administration, the follow-on implications for civil applications are enormous. While military designs may not be recyclable, civil ones could be done easily. Just as electricity moves energy from generation to point of use, nanostructured metal fuels can carry energy from centralized reduction facilities (using nuclear, coal, solar, geothermic, or water energy) to locations that need the transportation and portable power. As an alternative to fossil fuels, metal fuels would be safer, potentially easier to store and transport, have much greater power density, not pollute the environment during combustion, and be less costly to produce from metal ores than gasoline is from crude oil. This project addresses unfilled technology requirements for propulsion engines that have more power and energy density than those currently available so as to enable development of specific classes of unmanned vehicles. In particular, anaerobic engines could be developed that could be used in situations where either the induction of air or the exhaust of hot gas is foreclosed by either mission requirements or the operating environment.

Results and Accomplishments

During FY 2008 we made progress in identifying an alternate fuel based on porous silicon that may be significantly better than the ones we studied in FY 2006–07. The self-ignition temperature of these porous nanostructured silicon particles was experimentally determined to be around 500 K. Porous nanostructured silicon potentially could be used as an anaerobic fuel instead of the metallic iron, aluminum, and/or boron nanofuels. The enthalpy of silicon oxidation reaction is 14 kJ/g, which is comparable to the aluminum oxidation of 16 kJ/g or carbon oxidation to carbon dioxide of 9 kJ/g. Silicon is 200 times more abundant than carbon, 6 times more than iron, and 3 times more than aluminum. A working metal fuel combustor was also fabricated and successfully tested with aluminum/air and boron/air aerosols mixed with hydrocarbon fuel. Experimental results compared favorably with the mathematical model of a 1000-W metal fuel combustion chamber.

05068

Novel Alternative Signatures for Radiation Detection

John S. Neal, Lynn A. Boatner, and Slobodan Rajic

Project Description

This project directly addresses the need for providing alternative signatures for the detection of nuclear materials via new and innovative radiation detection concepts and by harnessing expertise within ORNL in the areas of glass science, fiber optics, and radiation detection materials and systems. Our work investigates the effects of gamma rays and neutrons on fiber-optic transmission with the goal of optimizing the sensitivity and specificity of the glass systems to both ionizing radiation and the displacive effects produced by neutrons. In our work, we propose to (1) maximize the sensitivity and specificity of optical fibers to varying forms of radiation (including neutrons), (2) develop a new deployable method for detecting individual ionizing radiation events (real-time neutron detection) in optical fibers, and (3) develop a fieldable method for physically and precisely locating radiation sources by measuring the localized response of optical fibers to radiation using the established technique of optical time-domain reflectometry (OTDR). This new technology will provide alternative signatures for the presence of nuclear materials and can be used in either a real-time or dosimetric mode. The successful completion of this work will provide a new and novel technology with the potential for overcoming the current constraints of an inability to readily distinguish radiation types and to physically locate the position of radiation sources—plus it will offer size, weight, cost, and power consumption advantages.

Mission Relevance

The nuclear detection community has an increasing need to identify alternative signatures for the presence of nuclear materials and the application of these alternative signatures to advanced radiation sensors and systems. This project directly addresses the need for providing alternative signatures via new and innovative radiation detection concepts and by harnessing expertise within ORNL in the areas of glass science, fiber optics, and radiation detection materials and systems. Our work will benefit (1) the DOE/NNSA Office of Nonproliferation Research and Development (NA-22), which conducts applied research and development, testing, and evaluation to produce technologies that lead to prototype demonstrations and resultant detection systems, thereby strengthening the U.S. response to current and projected threats to national security worldwide posed by the proliferation of weapons of mass destruction and the diversion of special nuclear material; and (2) the Domestic Nuclear Detection Office, which develops, acquires, and supports the deployment of new systems to detect and report attempts to import or transport a nuclear device or fissile or radiological material intended for illicit uses.

Results and Accomplishments

Multiple glass systems have been synthesized and fabricated as both fibers and billets (small cylinders). Some of the glass systems have shown sensitivity to neutrons or gamma rays. Of particular note, we have prepared and fabricated an optical fiber system that contains depleted uranium (DU). A miniature drawing tower and furnace have been installed for the fabrication of DU-containing fibers and billets. All required safety documentation and permissions have been obtained, and we expect to begin the fabrication of fiber-drawing DU-containing pre-forms in early 2009.

We have used ^{60}Co gamma rays, ^{252}Cf fission spectrum neutrons, and Am-Li thermal neutrons for irradiating optical fiber and bulk test glass samples. For subtle effects, including gamma-induced chromatic effects in fibers, we have access to a highly modified spectrophotometer that is fiber coupled and has a very sensitive photomultiplier tube that spans a wavelength range from 400 nm to almost 1000 nm. This instrument has provided detailed absorption and scattering information before and after irradiation exposure. We are also using a commercial spectrophotometer to measure optical absorption spectra before and after irradiation of glass billets doped with a variety of impurities for the purpose of increasing the sensitivity of the glass to radiation-induced effects. We have built and tested an instrument to be used in situ during irradiation. To determine if there is an effect in the optical fiber under irradiation, we have developed a special test station that compares a reference fiber to a segment of optical fiber under test (irradiation). To meet our goals to use OTDR methods for the detection of both gamma rays and neutrons, we have acquired an industry standard OTDR in the form of a Tektronix TFP2A Fibermaster.

05142

Enabling Ubiquitous Information Flows: Real-Time Data-Streams Instantiation and Agent-Based Forward-Analysis

Mallikarjun Shankar, Yu Jiao, Ryan Kerekes, Rick Lusk, Thomas Potok, Timothy Rhyne, and Vladimir Protopopescu

Project Description

We address two interdependent grand challenges in enabling access to real-time information or processed data when such information is dynamic (i.e., streaming and real-time), distributed, and voluminous. These grand challenges have come into sharp focus with the current price points of computing and communications allowing ubiquitous sensing, because the best distributed computing technologies have not kept apace with the volumes and dynamics of data. We pose and address the wide-area dynamic-data instantiation challenge: Given a search query specification (i.e., an event or data of interest) and a set of data descriptors, how does a system automatically instantiate a real-time data overlay network to collect, organize, semantically tag, and retrieve the data? We then address the question of how a distributed processing capability based on an agent paradigm evaluates or "forward analyzes" instantiated streaming data flows in a heterogeneous, distributed, low-bandwidth environment to support the created real-time overlays.

Mission Relevance

There is a growing need for national real-time dynamic data linkage: local, state, and federal information sharing and dissemination. For the Departments of Energy, Homeland Security, and Defense, decision makers (e.g., in emergency response or the military theater) and analysts must review vast amounts of information. Data flowing from different sources at high rates can and does easily overwhelm human analysts in the military or in national security organizations. When the amount of data gets large or the network bandwidth is limited (e.g., in wireless settings), the traditional approaches of crawl-index-search breaks down. In addition, the typical approach of pulling data from a central repository creates a single point of failure and generates unnecessary transmission of data through the network. Also, network traffic to a centralized data repository can be used by an enemy to predict future action. Our effort develops solutions that strategically anticipate the data ingest and analysis challenges facing the above agencies.

Results and Accomplishments

We have formalized and accomplished specific goals in our proposed plan by the creation of a design architecture supported by a preliminary implementation of the infrastructure. As the first step to formalization, we have developed a set of scenarios (or use cases) that make the requirements and problem statement concrete and specific. The scenario for the military creates a stream of SALT—size, activity, location, time—reports arriving according to chosen distributions, event types (e.g., fire, improvised explosive devices, locations [latitude, longitude, altitude], and time). The scenario for homeland security applications involves a distributed network of cameras which allow a user to task and process data streams of images in an efficient manner. The tasking step here is a search for a particular image. In both cases, the forward and distributed processing of the data enables the vision of a ubiquitous information processing infrastructure.

Our completed preliminary implementations are in two categories: an application realization and, one of the first of its kind, a true distributed mobile agent framework. The application allows images to be processed and dispatched to a mobile device test platform (cell phone and palm-top devices). The new Java-based mobile agent framework, called Knowledge Acquisition Ubiquitous Agent Infrastructure (KAUI), runs on both standard J2SE Java Virtual Machine (JVM) and a mobile JVM for Windows Mobile called CrE-ME. Response times (time between initiating the search and having received all the search data) ranged from 6 to16 s for our sample queries, where the deployment time of the infrastructure only took 4 s of the total search time. Distributed solutions outperform the centralized solution in terms of speed for each query, and the speed of the distributed search depends on the amount of query-relevant data in the system (which traverses the primary bottleneck—the wireless network capacity).

Publications

Chen, Ming, Xiaorui Wang, Raghul Gunasekaran, Hairong Qi, and Mallikarjun Shankar. 2008. "Control-Based Real-Time Metadata Matching for Information Dissemination." *IEEE Real-Time Computing Systems and Applications,* Aug. 25–27.

Kerekes, Ryan, and Yu (Cathy) Jiao. 2008. "Image Analysis on the PlayStation 3: A System-Level Performance Study." *2008 IEEE International Conference on Image Processing.*

Kerekes, Ryan, Yu (Cathy) Jiao, Mallikarjun Shankar, Thomas Potok, and Rick Lusk. 2008. "Agent-Based Forward Analysis." *IEEE/SIMA at MILCOM,* Nov. 16–20.

NEUTRON SCIENCES INITIATIVE

00001

Infrastructure Development for Neutron Scattering for Biomembranes and Biomimetic Membranes

William T. Heller, Yiming Mo, Dean A. A. Myles, Greg S. Smith, and John F. Ankner

Project Description

Biological membranes and biomimetic systems are topologically complex and incredibly dynamic systems where function is largely effected through complex interactions between components of the system, such as lipids and proteins in biological membranes. The study of biological membranes and biomimetic systems is important to a variety of scientific disciplines, and it is an area of key strategic interest to the DOE and National Institutes of Health (NIH). ORNL currently lacks the infrastructure to effectively support this science at its two neutron sources. We propose to develop the preparative capabilities, sample environments, analytic and modeling tools, and the core expertise required to support a strategic program of biomembrane, membrane protein, and biomimetic membrane research at ORNL and to facilitate user community science at the Spallation Neutron Source and the High Flux Isotope Reactor. Specifically, we will establish facilities and expertise for the expression and purification of membrane proteins and sample preparation for neutron reflectometry experiments. Additionally, sample environments for the neutron reflectometers will be developed that are optimized for investigations of the structure and function of biological membranes and biomimetic systems. Data analysis and modeling tools needed to interpret the data collected from these complex systems will be identified. We will demonstrate these capabilities by studying the association of specific lipids with the membrane-integral protein porin. Establishing this platform and capability at ORNL will leave us optimally positioned to contribute to the programmatic goals of DOE and NIH in this exciting field of science.

Mission Relevance

The project addresses mission goals of the Genomics: Genomes to Life program, funded by the DOE Office of Science, Biological and Environmental Research, by developing the sample preparation and neutron scattering infrastructure needed to develop a molecular-level understanding of biomembranes, a critical and complex system possessed by every living cell, and biomimetic systems having technological applications. The work is also relevant to the missions of NIH. The NIH's Structural Biology Roadmap resulted in the programs Membrane Protein Production and Structure Determination (RM-04-026) and Centers for Innovation in Membrane Protein Production (RFA-RM-04-009). The NIH program call (PA-06-119) for studies of the structural biology of membrane proteins is a continuation of a long-running program announcement serving several institutes of NIH. By providing the infrastructure that researchers need, we will make it possible to use neutron scattering as another structural characterization tool for studying these challenging systems.

Results and Accomplishments

The project completed in March 2008, with the final six months of funding allowing Yiming Mo, the postdoctoral research associate on the project, to complete his efforts and participate in the development of a manuscript. Reduction of small angle neutron scattering (SANS) data collected at HFIR in September 2007 was completed. The experiment probed detergent-associated states of two membrane proteins, the porin OmpF and bacteriorhodopsin. While one of the samples was not well-behaved, the bacteriorhodopsin data was excellent. SANS was used to study lipid mixtures at a series of temperatures and concentrations, building on the reflectometry studies performed earlier in the project to better understand the nature of the unexpected phase-separation phenomenon observed. The results suggest that the effect seen is also concentration dependent, with the neutron reflectometry studies (where the phase separation was observed) utilizing a much higher lipid-to-water ratio than the SANS studies. Additional research would be required to complete the effort. Strategies continue to be pursued for building a clear proposal, but a stronger scientific case with clear ties to an NIH priority will need to be found that builds on the biophysical studies performed so far.

Publication

Mo, Y., B.-K. Lee, J. F. Ankner, J. M. Becker, and W. T. Heller. 2008. "Detergent-Associated Solution Conformations of Helical and Beta-Barrel Membrane Proteins." *J. Phys. Chem. B.* **112,** 13349–13354.

00013

High-Temperature High-Pressure Studies of Dynamics of Fluids in Nanopores Using the Spallation Neutron Source Backscattering Spectrometer

Eugene Mamontov, David R. Cole, Peter T. Cummings, Kenneth W. Herwig, and Louis J. Santodonato

Project Description

The purpose of this project is to determine the key features of dynamics of water and aqueous solutions confined within nanoporous materials under extreme temperature-pressure conditions encountered outside the explored regions of the phase diagram. We will achieve this goal by designing unique sample environment equipment and utilizing the best-in-class neutron spectrometer—the BASIS at the Spallation Neutron Source (SNS)—with unprecedented capabilities. We will perform scattering experiments and computer simulations to quantitatively assess molecular properties of confined fluids. Successful development of this project will demonstrate the capabilities of the first operational SNS neutron spectrometer to a broad group of prospective instrument users and showcase the capabilities of the SNS to conduct research at the forefront of chemical physics, physical chemistry, and materials science.

Mission Relevance

This project is directly relevant to the energy resources DOE mission. The need for characterization of potential hydrogen-storage materials, including nanoporous oxides at extreme conditions, was described in the document derived from the workshop on Basic Research Needs for the Hydrogen Economy sponsored by the DOE Office of Science, Basic Energy Sciences (BES). A preliminary draft agenda for the next BES-sponsored workshop on Basic Research Needs for Advanced Nuclear Energy Systems indicates that investigations of materials and chemical systems under extreme conditions are two of the six thematic science areas to be addressed. In addition, users of the SNS will be utilizing the capabilities developed in the course of the project. Thus, their research activities supported by the federal agencies other than DOE (e.g., National Science Foundation) will benefit from this project.

Results and Accomplishments

During FY 2008, the project's second and final year, we accomplished the following.

1. We summarized and published results of our quasielastic neutron scattering (QENS) experiments on water and aqueous solutions in silica pores at the backscattering spectrometer (HFBS) at the Center for Neutron Research at the National Institute of Standards and Technology (NIST) (see the publication below).
2. We completed molecular dynamics simulations of water and aqueous solutions in silica pores at various temperatures (to be published).
3. We performed QENS experiments on water and aqueous solutions in silica pores at the SNS BASIS and compared the data to those obtained at the NIST HFBS (to be published).
4. We built and tested a dedicated furnace to be used in conjunction with the high-pressure cell.
5. Perhaps most important, we built several high-pressure cells suitable for high-temperature experiments. Some of these cells are made of sapphire, as was planned before. However, some other cells are made of TZM (titanium-zirconium-molybdenum) alloy, which promises excellent performance (QENS measurements at 1.5 kbar at 500°C should be feasible). The cells are currently evaluated and will be tested shortly.

To summarize, in the course of this project we have accumulated substantial knowledge of the behavior of aqueous solutions in confinement, while the newly built high-temperature, high-pressure cells uniquely position us to make further advances into the previously unexplored regions of phase diagrams of various fluids.

Publication

Mamontov, E., D. R. Cole, S. Dai, M. D. Pawel, C. D. Liang, T. Jenkins, G. Gasparovic, and E. Kintzel. 2008. "Dynamics of Water in LiCl and $CaCl_2$ Aqueous Solutions Confined in Silica Matrices: A Backscattering Neutron Spectroscopy Study." *Chemical Physics* **352**, 117.

00015

A Robust Polymer Scaffold System for Bio-inspired Membranes

J. F. Ankner, J. W. Mays, J. M. Messman, D.A.A. Myles, S. M. Kilbey II, and B. S. Lokitz

Project Description

The objective of this project is to develop expertise in the preparation and investigation (using neutron scattering) of soft material scaffolds that can be used to create bio-inspired membranes. Interfaces play a key role in biological processes, and many biological molecules function at interfaces and in confined environments. Therefore, developing robust platforms that can be used to examine structure-property-function relationships of biomolecules attached to and penetrating into interfaces is crucial to ORNL taking a leadership role in bridging biology and biological processes to the development of next-generation materials and devices.

Mission Relevance

The expertise we are developing in creating synthetic bio-inspired membranes made from novel polymers and our leadership in using neutron reflectometry to investigate structure property-function relationships of these bio-inspired films will create a foundation from which future research projects focused on more complex scaffolds with novel or multiple biological functions can be proposed. This capability will benefit the DOE Office of Science, Basic Energy Sciences program, and other federal agencies such as the Department of Defense and the National Institutes of Health.

Results and Accomplishments

During FY 2008, the project's second year, optimization of polymer synthesis, deposition, and surface functionalization and characterization has been achieved. This was accomplished by utilizing the controlled free radical polymerization technique known as reversible addition-fragmentation chain transfer (RAFT) and through polymer chain end attachment in a "grafting to" approach. Specific accomplishments include:

1. We have attached polymers of 2-vinyl-4,4-dimethylazlactone (VDMA) to silicon substrates via a novel, "universal" approach using "click" chemistry: the PVDMA chains have an azide end group because they are synthesized using an azide-functional chain transfer agent (CTA). This azide functionalized PVDMA is reacted with an alkyne group deposited on the silicon substrates. In the presence of a catalytic amount of copper, a triazole is formed, thereby covalently anchoring the PVDMA chains to the surface. This approach provides control of both molecular weight (through the RAFT polymerization) and tethering density (by manipulating the areal density of alkyne on the surface or the reaction time).
2. We have successfully functionalized surface-bound PVDMA brushes (e.g., *N*-*N* bis(carboxy methyl)-lysine-hydrate) and are currently preparing to perform model protein binding studies. The modified surfaces have been characterized utilizing ellipsometry, GeATR-FTIR spectroscopy, and atomic force microscopy.
3. In addition, several of the modified surfaces have been characterized on the Spallation Neutron Source Liquids Reflectometer in both solid and liquid cells in order to observe in situ structural changes induced at the polymer/solution interface. Currently, we have measured the alkyne base layer on the silicon substrate, PVDMA brushes, hydrolyzed PVDMA brushes, and *N*-*N* bis(carboxy methyl)-lysine-hydrate functionalized PVDMA brushes in air and various deuterated solvents.

Publication

Messman, J. M., A. Banaszek, J. Barringer, J. W. Mays, S. M. Kilbey II. 2007. "Synthesis, Assembly, and Bio-functionalization of Stimuli-Responsive Polymer Brushes." *Proceedings of the 34th Annual International Waterborne, High-Solids and Powder Coatings Symposium* **2007**, 77–88.

00019

Probing Molecular Interaction Between Microbial-Cell Protein and Mineral Surfaces with Neutrons

Liyuan Liang, Baohua Gu, John Ankner, Dean Myles, Wei Wang, and Alex Johs

Project Description

The purpose of the project is to investigate interactions between microbial-cell proteins and mineral surfaces, which are critical to understanding the electron transfer mechanisms and microbial ecosystem reactions/responses in subsurface environments. We hypothesize that direct contact between microbial-cell proteins and minerals is necessary for electron transfer along a respiratory chain to mineral iron. We use neutron reflectometry (NR) in combination with aqueous chemical and surface analytical techniques to study the effects of surface charge, chemical affinity, and specific hydrophobic/hydrophilic interactions on binding between mineral functional groups and cell proteins when embedded in membrane lipids. Iron oxide nanoparticle films and cytochrome proteins derived from the outer walls of microbial cells (e.g., sulfate- or iron-reducing bacteria) are used as a model for the study.

Mission Relevance

This project is relevant to both Genomics: GTL and the Environmental Remediation Sciences Program (ERSP) of DOE. Contributions to understanding the process of electron transfer and mineral respiration are related directly to the Genomics: GTL program. Microbial and mineral interaction has profound implication to bioremediation and is therefore relevant to ERSP. Recent data in the literature suggests that outer membrane cytochromes may also be involved in the reduction of Hg(II) species by dissimilatory metal-reducing bacteria. Thus this work is particularly relevant to the Science Focus Area on Hg(II) transformations in environments sponsored by the DOE Office of Science, Biological and Environmental Research. This project also should be beneficial to National Science Foundation programs on Cellular Systems and the Interagency Opportunities in Multi-Scale Modeling in Biomedical, Biological, and Behavioral Systems, and to National Institutes of Health programs on Research on Microbial Biofilms and Quantitative Approaches to the Analysis of Complex Biological Systems.

Results and Accomplishments

The second year effort focused on (1) optimizing procedures to fabricate uniform iron oxide thin films on silicon substraces; (2) preparing biomimetic phospholipid membrane bilayer films on solid supports and iron oxide thin films; (3) isolating, purifying, and characterizing outer membrane cytochrome proteins from pure cultures of metal-reducing bacteria; and (4) creating suitable interfacial and computational models for interpreting neutron reflectivity (NR) data in future experiments. We accomplished all these tasks. The uniform deposition of thin films on a large-area (>20 cm^2) substrate is required for structural investigations by NR. First, we developed a novel method to fabricate a hematite (α-Fe_2O_3) nanoparticle layer(s) on a solid substrate by the Langmuir-Blodgett (LB) technique. Second, within the framework of a user program of the Environmental Molecular Sciences Laboratory, we obtained uniform hematite thin films on solid supports by pulsed laser deposition. The structure and morphology of the thin films were characterized using scanning electron microscopy, X-ray diffraction, atomic force microscopy, and Raman spectroscopy. A manuscript (in press) reports new procedures developed in our laboratory and characterization results of iron oxide nanoparticle thin films. Conditions for a homogenous and reproducible deposition of phopholipid bilayers on hydrophilic silicon or iron oxide–coated silicon wafers using the LB technique were established. In addition to LB deposition we develped a method to deposit phospholipds on solid substrates in aqueous solutions. The outer membrane cytochrome OmcA from *Shewanella oneidensis* MR-1 has been isolated and purified. Detailed characterization for OmcA is being performed to obtain a high-resolution crystal structure. The expertise obtained so far will contribute to the construction and optimization of more complex systems, where information on spatial arrangement and of biomolecules near the mineral interface can be obtained. A book chapter is in press (Springer) for publication.

Publications

Johs, A., L. Liang, B. Gu, J. Ankner, and W. Wang. 2008. "Application of Neutron Reflectrometry for Studies of Biomolecular Structures and Functions at Interfaces." Chapter 16 in *Neutron Application in Earth, Energy, and Environmental Sciences,* Liang, Rinaldi, and Schober (eds.), Springer (in press).

Wang, W., L. Liang, A. Johs, J. Ankner, and B. Gu. 2007. "Controlled Synthesis, Manipulation of Surface Hydrophobicity, and Self-Assembly of Hematite Nanocrystals." *Geochim. Cosmochim. Acta* **72**(12): A1001.

Wang, W., L. Liang, A. Johs, and G. Bu. 2008. "Thin Films of Uniform Hematite Nanoparticles: Control of Surface Hydrophobicity and Self-Assembly." *J. Mater. Chem.* (in press).

00022

High-Throughput Neutron Crystallography for Macromolecular Structure, Function, and Design

Dean Myles, Hugh O'Neill, and Edward Snell

Project Description

This project addresses the last remaining challenge and bottleneck in neutron protein crystallography—the rational growth of single crystals of soluble and membrane-bound proteins that are suitable for neutron analysis. Traditional screening methods are inefficient, slow, and labor intensive, with often lag times of 2–4 years before successful structure determination. We are radically transforming this process by harnessing the high-throughput, robotic protein crystallization screening techniques that have transformed crystal growth in the structural genomics world. The effects of varying multiple parameters can be screened and evaluated rapidly, systematically, and with dozens of proteins assayed against thousands of variables at the same time. Success in developing this rational approach will deliver huge reward, making the unique capabilities of the Macromolecular Neutron Diffractometer (MaNDi) at the Spallation Neutron Source (SNS) accessible and available to thousands of structural molecular biologists.

Mission Relevance

This project will support and develop new strategic capabilities in neutron protein crystallography at ORNL that will allow us to target cellular, signaling, and membrane-bound proteins and enzymes of interest in medical, pharmaceutical, industrial, biodefense, and bioenergy research. Success in developing this rational approach will deliver huge reward, making the unique capabilities of the MaNDi and TOPAZ diffractometers at SNS accessible and available to thousands of structural molecular biologists. The ability to target and analyze these proteins and enzymes will be of broad and specific interest to many individual researchers working in other government, industrial or academic laboratories on projects for the National Science Foundation and the National Institutes of Health, and for the development of bio-inspired materials and systems for the solar, hydrogen, bioenergy, and nuclear programs at DOE.

Results and Accomplishments

We developed this work in two phases: the first, to develop protocols, and the second, to apply them to proteins of biological interest. In FY 2008 we completed, and are currently analyzing, the results of ~108,000 individual crystallization screening experiments. Discernable patterns and shifts in protein solubility are emerging in comparative phase diagram analyses of H_20 versus D_2O crystallization conditions and of H-protein vs D-protein solubility. With the data accumulated thus far, these patterns appear predictable for inorganic salt and precipitant combinations, but behaviour and shifts in the popular polyethylene glycols crystallization systems are proving to be more complex. A manuscript describing these analyses is in preparation. The protocols and crystallization rules learned in the second phase of the project were used through FY 2008 to guide the application and development to targets of high value and interest to ORNL researchers. Five projects are developed to the point of neutron analysis. Conditions have been optimized for predictable growth of large neutron size crystals of several proteins, and neutron data either have been collected or planned. Novel crystallization conditions have been established for five other second phase proteins of specific programmatic interest to research programs at ORNL and to our collaborators at partner institutes.

00023

Magnetic Structure Under Simultaneous Ultrahigh Pressure and High-Temperature Conditions: 200 kbar and 1500 K

Chris A. Tulk, Antonio Moreira Dos Santos, Jamie Molaison, Bryan Chakoumakos, Juske Horita, and Dave Cole

Project Description

This project is aimed at expanding the range of phase space that could be investigated with neutron diffraction by using the high-pressure diffractometer (SNAP) at the Spallation Neutron Source (SNS) and developing heating capabilities that enable simultaneous generation of high temperature and high pressure. This would require designing a system that is compatible with SNAP, procuring it, and assembling the components for testing. The high-pressure, high-temperature system has been finished, constructed, and tested to temperatures approaching 1000 K. Several samples have been run at the High-Flux Isotope Reactor (HFIR) over the past year to study the onset of a pressure-induced ferromagnetic phase of CoO. This work is complemented by high-energy X-ray scattering studies and maximum entropy analysis, where we were able to show the tetragonal lattice distortion and the transfer of electronic charge into the *ab*-plane. Additional experiments were performed by the postdoctoral fellow working on this project on semiconductor clathrate crystals at high pressure. These samples were observed to undergo a series of transformations as the pressure is increased to above 22 GPa, and analysis of these structures are under way. In addition, we have identified benefits of cooling the Paris-Edinburgh cell and have designed, constructed, and tested a cryogenic cooling system for the Paris-Edinburgh cell. Furthermore, six presentations of this work have been given at international conferences, and five manuscripts are being prepared.

Mission Relevance

This project explores the behavior of magnetic materials at high pressures by neutron diffraction, so it naturally falls under one of the major research areas of ORNL, namely neutron science. This also fits into the broader DOE mission to operate world class neutron scattering facilities in this country and into the Materials Science and Technology program of the DOE Office of Science, Basic Energy Sciences. This project has its focus on providing a fundamental understanding of the magnetic properties of materials under extreme conditions, and we fully expect these results to be relevant to understanding complex magnetic interaction in applied systems. More specifically, the high-pressure sample environments developed for this project provide unprecedented pressure ranges for doing neutron diffraction in the United States. Not only does this project provide the basis for postdoctoral research, but it also will provide tools that will benefit the SNS and HFIR user facilities.

Results and Accomplishments

High-Pressure Magnetic Systems Scientific Overview. During the past year work has continued well with activities on a number of fronts. We have continued to investigate the magnetic properties of cobalt oxide with increasing pressure. Cobalt monoxide orders antiferromagnetically at 290 K with a tetragonal distortion. More interesting, the magnetic spin is not oriented along the tetragonal unique axis but at an angle of about 27° (and at 8° from the (111) plane) corresponding approximately to the [113] direction. This exceptional occurrence is likely due to a competition of effects between the Jahn-Teller distortions of the high spin d^7 ion with the spin orbit coupling resulting from its unquenched angular momentum. While some explanations were suggested for such a unique feature, such as multiple k-vector (later disproved), asymmetric cation-cation superexchange, and noncollinear alignment of the spin and orbital angular momentum, experimental evidence for the cause is still lacking.

Experiments conducted as part of this project have included the study of the onset of magnetization as both temperature and pressure are increased, thus mapping the Neal transition, as well as extensive and complementary high-energy X-ray scattering studies and Maximum Entropy Methods (MEM) analysis, which have illustrated the pressure-induced tetrahedral lattice distortion. These results were obtained from four experiments on the wide-angle neutron diffractometer at HFIR, and two experiments on the H-E beamline at sector 1 at the Advanced Photon Source at Argonne National Laboratory, as well as a trip to a laboratory at the National Research Council of Canada to learn the MEM data analysis techniques. This work is now being prepared for publication.

Semiconductor Clathrate Materials, the $Ba_8Ga_{16}Ge_{30}$, and the $Sr_8Ga_{16}Ge_{30}$ Systems. Semiconductor clathrate systems are structurally analogous to the water hydrate systems and form a possible thermoelectric compound. These semiconductor clathrates are compounds consisting of an open framework lattice of mainly Si, Ge, and Ga, containing a second large cation (alkali or alkali-earth) trapped in its cages. The vibrational freedom that the guest atoms experience allows such materials to behave like "phonon glasses" and usually show promising thermoelectric properties. In this work, in situ high-pressure powder diffraction was performed in two Ge clathrates: $AE_8Ga_{16}Ge_{30}$, where AE = Sr, Ba. The pressure was applied to the samples by means of a diamond anvil cell (DAC) up to 25 GPa, and powder diffraction data was collected in a high-energy (100 keV) synchrotron beam line, allowing a data collection over a wide q range [0.2 $Å^{-1}$–50 $Å^{-1}$]. Both structures were analyzed as a function of pressure, particularly with respect to the influence of the charge transfer of the guest atoms to the host lattice during compression and phase transformation.

Two papers detailing these data are being prepared—one on the high-pressure isostructural and bonding transformations in the crystalline forms and the other on the structure of the high-pressure structural forms. Further experiments are planned to be conducted on SNAP this fall/winter.

Publications

Brandao, Cu P., J. Rocha, M. S. Reis, A. M. dos Santos, and R. Jin. 2008. "Magnetic Properties of $KNaMSi_4O_{10}$ Compounds M = Mn; Fe. *Journal of Solid State Chemistry* **182,** 253–258.

Souza, A. M., D. O. Soares-Pinto, R. S. Sarthour, I. S. Oliveira, M. S. Reis, P. Brandao, and A. M. dos Santos. 2009. "Entanglement and Bell's Inequality Violation Above Room Temperature in Metal Carboxylates." *Phys. Rev. B,* accepted for publication.

00025

A Helicon Ion Source for the Spallation Neutron Source Upgrade

Robert F. Welton, F. Wallace Baity, and Richard H. Goulding

Project Description

The overall scientific capability of the Spallation Neutron Source (SNS) can be greatly enhanced by increasing neutron production. One approach to increasing neutron production is making available proton beams of greater intensity and reliability than can be achieved now using conventional ion sources. The goal of this project is to develop a new type of H^- ion source using a helicon-generated plasma closely coupled to the state-of-the-art SNS H^- ion source. The helicon hydrogen plasma generator, recently developed by the ORNL Fusion Energy Division (FED), has the capability to produce plasmas ~10× more dense than today's H^- sources using about one-tenth the radio frequency (rf) power. If successful, this project will provide a prototype ion source for SNS operations as well as future upgrade projects and advance the state of the art for positive and negative ion sources. The approach would be applicable to other accelerators and may also allow the high-power rf plasma generators now being developed for use in the neutral beam injectors of the International Thermonuclear Experimental Reactor (ITER) to be replaced with higher-reliability helicon generators.

Mission Relevance

The development of reliable neutron production is critical to the success of the SNS and future power upgrade projects. Consequently, this project, if successful, will greatly benefit the DOE Office of Science. In addition, the development of a high-brightness, multipurpose plasma ion source capable of achieving significantly higher beam currents, duty factor, and lifetime than currently available will benefit many areas of science and technology, including (1) future high-power accelerator facilities, (2) industrial applications such as ion implanters and neutron sources, and (3) H^- ion sources for high-energy neutral beam injectors for fusion devices such as ITER.

Results and Accomplishments

In FY 2007 we achieved plasma densities $>10^{13}$ e/cm^3 inside the ion source: ~10× greater than values typically measured in conventional rf-driven H^- sources using much less rf power (<10 kW) and much less gas consumption (<5 sccm), meeting all our goals. In FY 2008 two changes were made and approved by the LDRD review committee at the midpoint review: First, due to unanticipated heavy use of the test stand at SNS, it was necessary to perform all beam extraction measurements at the FED facility. This required that a completely new H^- extraction module be designed and constructed. Second, due to the cost and schedule impact of this requirement, it was necessary to drop the task to design a prototype helicon source for actual use on SNS. Detailed plasma density measurements of the source region, including the cesium collar, were performed and the original source design improved by adding a permanent magnet to improve plasma mapping to the collar. In FY 2008 the extraction module was employed for the first beam extraction measurements from the helicon-driven H^- source. Without cesium, the maximum H^- beam current measured to date was 12 mA, with 9 kW of rf input power at 13.56 MHz using ~3 sccm of gas flow. We anticipate higher beam currents once cesiated tests are performed, which are currently being undertaken using follow-on funding.

Publications

Goulding, R. H., R. F. Welton, F. W. Baity, and D. O. Sparks. 2007. "A Helicon Ion Source for the SNS." *Proceedings of the Topical Conference on Radio Frequency Power in Plasmas,* Clearwater, Fla.

Welton, R. F., M. P. Stockli, S. N. Murray, Jr., J. Carr, Jr., and J. R. Carmichael. 2006. "A Proposed Helicon Driver for the SNS Ion Source." *Proceedings of the International Linear Accelerator Conference*, Knoxville, Tenn., p. 367.

Welton, R. F., M. P. Stockli, S. N. Murray, D. Crisp, J. Carmichael, R. H. Goulding, B. Han, O. Tarvainen, T. Pennisi, and M. Santana. 2008. "H^- Source Developments at the SNS." *Rev. of Sci. Instruments* **79** (2008), 02C721-1.

Welton, R. F., M. P. Stockli, S. N. Murray, D. Crisp, J. Carmichael, R. H. Goulding, B. Han, O. Tarvainen, T. Pennisi, and M. Santana. 2008. "Next Generation Ion Sources for the SNS." *Proceedings of the 1st Conference on Negative Ion Beams and Sources*, Aix-en-Provence, France.

05004

Neutron Scattering Study of Magnetic and Spin Dynamic Behavior in Amine-Stabilized Transition Metal and Transition Metal Oxide Nanoparticles

Andrew Christianson, Sheila Baker, William Heller, Mark Lumsden, Stephen Nagler, Brian C. Sales, and Thomas Schulthess

Project Description

We propose to study amine-stabilized transition metal-based nanoparticles for novel, size-dependent magnetic effects and spin dynamics. Metallic nanoparticles are active fields of research in the basic and applied sciences. These materials are being intensively studied for a wide variety of applications, including catalysis and advanced functional materials. The physical constraints resulting from the size of such systems have produced new behaviors, some of which have the potential to be of industrial interest. Recent advances in synthesis now produce highly uniform and stable nanoparticles enabling studies that aim to observe and explain novel phenomena of interest to a variety of disciplines and technologies. ORNL is well positioned to take a leadership role in the study of nanoscale magnetism due to the combination of world class materials synthesis and neutron scattering instrumentation.

Mission Relevance

The proposed research will provide key additional knowledge of the physical behavior of magnetic nanoparticles and as such has direct relevance to the mission of the Division of Materials Sciences and Engineering in the DOE Office of Science, Basic Energy Sciences.

Results and Accomplishments

We have successfully synthesized MnO magnetic nanoparticles with both hydrogenated and deuterated capping ligands using the following strategy. A capping ligand was prepared by neutralizing a fatty acid (stearic or myristic acid) with tetramethylammonium hydroxide in methanol. To this solution, manganese chloride was added, forming a manganese fatty acid precipitate. The precipitate was washed thoroughly with methanol and dried under vacuum. The manganese fatty acid was then mixed with an additional activating/directing agent in 1-octadecene solvent and heated to 305°C for 2–4 hours. The resulting MnO nanoparticles were precipitated using acetone. After centrifugation and removal of the supernatant liquid, the particles were redispersed in toluene and precipitated again with acetone or methanol. This procedure was repeated no less than three times to obtain uncontaminated MnO nanoparticles. An analysis using transmission electron microscopy measurements indicated no statistical difference between nanoparticles capped with either hydrogenated or deuterated ligands. Initial X-ray diffraction and small-angle neutron scattering measurements have been completed, and analyses are under way.

05028

Rotating Solid Target Design Development for the Spallation Neutron Source

Thomas J. McManamy, Roy K. Crawford, Phillip D. Ferguson, James Janney, and Mark J. Rennich

Project Description

A rotating solid target could provide a simple, robust, highly flexible, and long lifetime alternative for the second Spallation Neutron Source (SNS) target station that is insensitive to the selection of long pulse (~1 ms) or short pulse (~1 µs) operation. Even slow rotation (a few hertz) would greatly reduce the average power density and radiation damage. As a result, the cooling requirements are relaxed and target lifetimes are greatly increased (years) with increased neutron production due to the use of tungsten with a small coolant fraction. Efficient coupling to the moderators can be achieved using smaller beam spot sizes. The issues are principally developing the mechanical design including target seals, cooling, handling methods for the target, moderators and reflectors, and optimizing the source geometry to fit the desired suite of neutron instruments. This effort includes the following tasks: (1) neutronic and mechanical evaluation and optimization of major design options, including wing or slab moderator neutronic performance, horizontal or vertical axis mechanical evaluation for a range of disk radii from 0.25 to 1 m, and radiation damage and heat loads estimates as a function of disk radius; (2) design optimization for a selected axis and moderator configuration, including target and moderator mechanical layout and neutronic performance optimization, target structural and thermo-hydraulic preliminary design, and concept development for remote handling; (3) concept development for target bearing and sealing methods; and (4) mockup of design solutions for key technical problems.

Mission Relevance

This project will benefit the DOE Office of Science, Basic Energy Sciences program, which is interested in building a second target station at SNS. There is a risk that cavitation damage with a target like the presently used mercury target may restrict the allowable beam power for reasonable target lifetimes at the second target station without development of a gas mitigation scheme. Having in hand a design solution for the target may help expedite approval of the second target station. In addition to potential simplicity of design, long lifetimes, and higher reliability, the solid rotating target may also offer significant advantages in improved neutronic performance. Without conceptual design, it is unlikely that the rotating target concept would be considered mature enough to support such a major funding decision.

Results and Accomplishments

A solid rotating target design for 3 MW at 20 Hz with a realistic mechanical design has been shown to have approximately 7% better neutronic performance than a mercury target and a life of approximately 6 years for a 10 dpa window limit compared to less than 1 year for a mercury target. Some details of our design and calculated performance are as follows:

1. A 3 MW tantalum-clad tungsten target design concept rotating at 30 rpm was developed with a midplane cooling arrangement that gives peak temperatures of only about 150°C and relatively low target material stresses (~100 MPa).
2. A peak decay heat of approximately 35 kW was calculated for 3 MW operation.

3. A target diameter of 1.2 m was chosen to allow this 35 kW of decay heat to be removed by radiation and gas conduction to the reflector assemblies (with no primary cooling or secondary cooling) while maintaining peak temperature below the threshold for the tungsten, steam reaction (800°C).
4. A design layout was developed for the motor, seals, and bearings; the layout locates them on a vertical shaft about 3.5 m above the target where "hands-on" maintenance will be possible with the beam off.
5. An overall target station layout and remote handling configurations for the target and moderators were developed to allow the target to be replaced as part of a large vertical plug and the moderators to be maintained independently with horizontal plugs since they are expected to have a shorter lifetime than the target.

DOE Critical Decision 1 planning for the second SNS target station has incorporated conceptual design development and safety studies for a rotating target, leading to a decision between mercury and a rotating target after the first year. Another potential application should be the European Spallation Source, planned for long pulse operation at 5 MW, which should be possible with minor extensions of the present design concept.

Publication

McManamy, T. J., M. J. Rennich, J. Janney, and P. Ferguson. 2008. "3 MW Solid Rotating Target Design." *Proceedings of the 9th International Workshop on Spallation Materials Technology.*

05029

Pushing the Limits: High Impact Neutron Protein Crystallography

Leighton Coates

Project Description

Our objective is to enable neutron analysis on the structure and function of two novel proteins at atomic levels of detail, each of which will push neutron protein crystallography into new areas. Neutron protein crystallography produced several high impact scientific publications in the 1990s, exciting the biological community about the possibilities of using neutron science. Although there has been a steady trickle of neutron structures since the advent of neutron crystallography, the number of proteins studied by neutron diffraction remains low. The development and publication of high impact projects utilizing neutron protein crystallography to address new sorts of biological questions will be a key asset to stimulate and build the biological user community for the single crystal diffactometers that will operate at the Spallation Neutron Source and the High-Flux Isotope Reactor. The study of complex proteins using neutron science offers novel applications for neutron protein crystallography, which can provide answers to key biological questions that cannot be answered even with near atomic resolution X-ray structures.

Mission Relevance

At the time of writing, only nine unique proteins, whose atomic coordinates are deposited in the protein data bank, have been studied to high resolution using neutron diffraction. These proteins share a number of similarities; they are all stable proteins that diffract X-rays to well beyond atomic resolution (1.2 Å) and have been studied for many years. Many of the nine proteins studied are available for purchase from all major suppliers of biochemical reagents. Studies on these types of proteins, while providing interesting science, will never yield the high impact results or publications necessary to stimulate wider interest in neutron protein crystallography and recent developments in it. The chances of obtaining peer-reviewed funding to work on proteins of this type are minimal at best. Most peer-reviewed research in the structural biology area is conducted on proteins overexpressed within a host system. Understanding membrane protein structure and function remains an outstanding grand challenge in biology, and its strategic and fundamental importance in human health, medicine, agriculture, and bioenergy cannot be overstated.

Results and Accomplishments

The main target protein has now been successfully subcloned into a PET based expression vector, and protein has been overexpressed and purified to greater than 95% purity These crystals have been checked at the Advanced Proton Source at Argonne National Laboratory, and they diffract X-rays to 1.5Å. A full data set was collected, and crystallographic refinement confirms that this is indeed the protein of interest. These data have been used to refine a model that will be used as a starting point for joint neutron X-ray refinement. Further crystal growth optimization has been performed to generate the much larger crystal volumes required for neutron studies.

The initial protein crystals obtained have been significantly enlarged using macro-seeding techniques. The largest crystals produced so far have come from the second generation of macro seeding and are much larger in volume than the original crystals. We intend to attempt to collect data as soon as TOPAZ is available. The initial results have helped generate a funding proposal to the National Science Foundation (NSF). The proposal has been set up in collaboration with the University of Alabama at Huntsville, enabling NSF-funded postdoctoral fellows to be based at ORNL if successful.

05045

Neutron Structural Virology

Flora Meilleur, William Heller, and Dean Myles

Project Description

Arthropod borne viruses (Arboviruses) are major sources of human disease. Their natural vector is blood-sucking insects, and they cause some of the most devastating infectious diseases known to human and veterinary medicine, including yellow fever, dengue fever, and West Nile fever. Collectively, arboviruses are second only to malaria as a threat to global health. Arboviruses share certain properties of structure and function, suggesting that information gained about any one of these viral agents may be applicable to other members of this virus family that includes human and animal pathogens. Sindbis virus is prototypic. Its structure comprises two nested icosahedral shells that sandwich a lipid membrane bi-layer and protect a single-stranded RNA core. Cellular interaction and infection involves dramatic structural reorganization of the virus. Our objective is to model and understand the structural changes that are associated with virus assembly, attachment, and infection at cell membranes using neutron solution scattering and reflectometry. A detailed understanding of the mechanism by that these structurally unique groups of infectious agents gain entry to cells is essential for the successful pursuit of pharmaceutical development of antiviral compounds that block the infection process to treat and prevent infection by the members of this viral family.

Mission Relvance

Arboviruses are major sources of human disease. Collectively, arboviruses are second only to malaria as a threat to global health. Worldwide, approximately 2.5 billion people are at risk of contracting this disease annually. Despite the enormous economic and medical impact of these agents, very few effective vaccines exist for their control. Therefore, this work will be of strong interest to the biomedical community, showcase the capabilities of the Spallation Neutron Source and the High-Flux Isotope Reactor, and generate interest in neutron techniques among biomedical researchers in a manner that will drive cross-cutting science and expand the user community of these facilities, thus benefitting programs of the DOE Office of Science, Basic Energy Sciences. This work will also benefit agencies that are concerned with human health and veterinary medicine, such as the Department of Agriculture and the National Institutes of Health.

Results and Accomplishments

During the first year of the project, we focused on small angle neutron scattering (SANS) with contrast variation to sequentially track, characterize, and model structural conformation and rearrangement undergone by the inner protein capsid, the outer protein shell, the lipid bilayer, and the RNA core, respectively. Sindbis was produced in large amount from tissue-cultured mammalian cells and mosquito cells. The virus was purified by density gradient centrifugation in 100% hydrogenated buffer and 100% deuterated buffer to prepare a series of eight contrasts. We performed SANS neutron experiments on free-virus particle solution on the BIO-SANS instrument at HFIR. Analysis of the virus samples after completion of the experiment revealed that there was no loss of infectivity during the course of the measurements. We also determined that there was no loss of protein through interactions with the cuvettes. This is critical and illustrates the unique potential of neutron scattering techniques to study large and complex infectious and/or functional entities. The high-quality data collected were reduced, and interpretation and modeling are in progress. In parallel, we produced milligram amounts of the virus envelop glycoprotein E1 hydrophobic fragment involved in cells attachment. Characterization of the oligomerisation state of E1 under different environments is in progress using circular dichroism and small angle X-ray scattering. This study, combined with analysis of E1 insertion in model lipid bilayers, will provide new information on the role of E1 in the infection mechanism of Sindbis virus.

05088

Inelastic Neutron Scattering from Magnetic Heterostructures

Randy Fishman, Lee Robertson, Mark Lumsden, and Jian Shen

Project Description

Inelastic neutron scattering is the world's most powerful tool to study the magnetic dynamics of solids. But only with the recent development of improved neutron optics and more powerful neutron sources such as the Spallation Neutron Source (SNS) has it become feasible to study the magnetic dynamics at interfaces and in confined geometries. We propose to develop the technique of inelastic neutron scattering from magnetic heterostructures consisting of alternating magnetic and nonmagnetic layers. To demonstrate the feasibility of this technique, we will study Dy/Y and Ho/Y multilayers, which were chosen for the close lattice matches and the large dysprosium and holmium moments. Molecular-beam epitaxy will be used to fabricate heterostructures by repeating bilayers with roughly 45 Å of dysprosium or holmium and 30 Å of yttrium. Magnetic characterization will be performed using the magnetism reflectometer at SNS, and inelastic measurements will be performed at the High-Flux Isotope Reactor (HFIR). Simultaneously, we will develop the theory of inelastic neutron scattering from magnetic heterostructures by using a coupled Green's function technique.

Mission Relevance

The development of an inelastic neutron-scattering technique for the study of magnetic heterostructures will have wide-ranging implications for a variety of materials of technological and scientific interest. This new technique will enhance the potential applications of SNS and HFIR, both of which are central to the DOE mission.

Results and Accomplishments

The synthesis efforts of Jian Shen and his group have suffered several setbacks due to poor control of the substrate quality. Cosequently, our inelastic neutron-scattering measurements of Dy/Y multilayers have been delayed. We are currently trying to procure a Dy/Y sample from external sources.

In our modeling efforts, we have developed a general Green's function technique to evaluate the spin-wave frequencies and intensities of an arbitrary noncollinear magnet. As a test case, we studied the frustrated antiferromagnet $CuFeO_2$, which exhibits two collinear magnetic phases: a ↑↑↓↓ phase below 7 T and a ↑↑↑↓↓ phase between 13.5 and 20 T. The aluminum-doped material $CuFe_{1-x}Al_xO_2$ ($x > 0.016$) exhibits a noncollinear magnetic ground state, which we are examining with numerical techniques. One way to determine the nature of the noncollinear phase is to examine the nature of the spin-wave instabilities of the collinear ↑↑↓↓ phase. We also have applied this Green's function technique to a simple model noncollinear antiferromagnet, called the generalized Villain model.

Those two sets of calculations set the stage for applying this coupled Green's function technique to inelastic scattering from magnetic heterostructures. We have recently started to study the relaxed helix that appears in the dysprosium spacers of Dy/Y multilayers.

Publication

Fishman, R. S., F. Ye, J. A. Fernandez-Baca, J. T. Haraldsen, and T. Kimura. 2008. "The Importance of Stacking to the Collinear Magnetic Phases of the Frustrated Antiferromagnet $CuFeO_2$." *Physical Review B: Rapid Communications* **78**, 140407.

05125

An Experimental, Theoretical, and Molecular Modeling Approach to Characterize the Structure and Dynamics of Charged PAMAM Dendrimers in Solution

Wei-Ren Chen, Gregory S. Smith, Kenneth W. Herwig, Kunlun Hong, William A. Goddard, Yi Liu, Yun Liu, and Lionel Porcar

Project Description

Poly(amidoamine) dendrimers (PAMAM) with ethylenediamine (EDA) cores and amino groups are synthetic, nanoscale macromolecules with promising potential for use in biomedical applications. While a number of studies have focused on the structure of dendrimers in solution, several questions pertaining to aqueous PAMAM solutions remain unanswered. A combined experimental, theoretical, and molecular modeling study is conducted to understand how charge and counterion condensation affect the single-molecule structure, the interaction potential between PAMAM dendrimers, and relevant dynamic processes. The dynamic behavior of interest includes backfolding and confined water migration relevant at the single molecule level as well as the self-diffusion of dendrimers in concentrated solutions where inter-dendrimer interactions play a dominant role. Specially tailored dendrimers with molecular architectures selectively highlighted by hydrogen isotopic labeling will be synthesized and utilized for small-angle neutron scattering (SANS), neutron spin echo (NSE), and neutron backscattering spectroscopy measurements. A theoretical description of the effective interaction will be used to model the neutron scattering results. Significantly, we will carry out multiscale simulations of a dendrimer in solution to elucidate structural and dynamical details not accessible experimentally. This work will reveal fundamental scientific behavior critical for assessing the therapeutic potential of dendrimers.

Mission Relevance

The focus of this project is placed on understanding the rich phase behaviors of PAMAM dendrimers, a novel macromolecule possessing both polymeric and colloidal structural natures, via a synergetic approach combining neutron scattering, molecular dynamics (MD) simulations, and material synthesis. The overarching goal of our work is consistent with the mission of the DOE Office of Science, Basic Energy Sciences, which fosters and supports discovery, dissemination, and integration of results in the natural sciences and engineering, via the utility of world-class scientific user facilities.

Results and Accomplishments

In our experimental study, a SANS technique is used to explore the various structural aspects of the PAMAM dendrimer solutions at their charged states. We developed a mean-field model for the SANS coherent scattering cross section $I(Q)$. Based on the results of our data analysis, we first found that the inter-dendrimer interaction is greatly influenced by their polymer-colloid structural duality. Second, an unexpected generational dependence of the counterion association is revealed, which is attributed to the backfolding of the dendrimer molecule. A SANS-contrast variation method was employed to quantitatively evaluate the volume of the intramolecular cavity of the PAMAM dendrimer in terms of the associated water molecules number. Last, we found that, upon increasing the dendrimer concentration in aqueous solutions, the molecular size, parameterized by radius of gyration R_G, is found to remain invariant, an observation manifesting its colloidal structural nature. The experimental focus of the second year will be placed on understand the effect of the functionlization of the PAMAM molecular architecture to its structural and dynamical properties.

A new force field for the charged PAMAM dendrimer, in which all the constituent atoms of dendrimer, water, and counterions are incorporated explicitly, was developed during the first year of this project. In comparison to the SANS experimental results, the new MD simulation algorithm is found to describe the structural properties in a more realistic manner. At present, new computational works are being carried out to understand the peculiar dynamical features observed by the NSE and backscattering experimental works.

Publications

Chen, W.-R., et al. 2007. "Small Angle Neutron Scattering Studies of the Counterion Effects on the Molecular Conformation and Structure of Charged G4 PAMAM Dendrimers in Aqueous Solutions." *Macromolecules* **40**, 5887.

Chen, W.-R., et al. 2009. "Effect of Counterion on the Structural Properties of Charged PAMAM Dendrimer Aqueous Solutions Revealed by Small Angle Neutron Scattering." *Macromolecular Symposia*, accepted for publication.

Li, T., et al. 2008. "Assess the Intra-molecular Cavity in PAMAM Dendrimers by Small Angle Neutron Scattering." *Macromolecules* **41**, 8916.

Liu, Y., et al. 2009. "Conformational Invariance of PAMAM Dendrimer Revealed by Atomic Simulations." *Journal of the American Chemical Society*, accepted for publication.

Porcar, L., et al. 2008. "Structural Investigation of PAMAM Dendrimers in Aqueous Solutions Using Small Angle Neutron Scattering: Effect of Generation." *Journal of Physical Chemistry B*. **112**, 14772.

05140

Mapping the Protein Structure-Function-Dynamics Landscape

Pratul K. Agarwal

Project Description

This project will dramatically impact and extend the use of neutron scattering techniques in the structure-function-dynamics analysis of biological materials by developing experimental, analytical, and computational techniques that exploit residue-specific H/D-labeling techniques to systematically target, highlight, and distinguish the dynamics of individual H-labeled residues in otherwise functional deuterated protein systems. We will develop and apply these capabilities in model systems and demonstrate their combination and use in neutron spectroscopy, neutron crystallography, and molecular dynamics (MD) simulation. As a test system, we will use a small 53-residue protein rubredoxin from *Pyrococcus furiosus* (RdPf), the most thermostable protein characterized to date. Specifically, we will (1) develop protocols for expression and production of site-specific H/D-labeled RdPf, (2) explore the residue-specific temperature dependence of protein dynamics using neutron spectroscopy, (3) determine neutron crystallographic structures at identical temperatures to locate and model H-labeled residues, and (4) analyze this information with respect to high-performance MD simulations. Once developed, we will apply these techniques to analyze the specific structure-function-dynamics of the medically important enzyme, DHFR, which is a major target for drug design.

Mission Relevance

This project will dramatically impact and extend the use of neutron scattering techniques in the structure-function-dynamics analysis of biological materials by developing experimental, analytical, and computational techniques that exploit residue-specific H/D-labeling techniques to systematically target, highlight, and distinguish the dynamics of individual H-labeled residues in otherwise functional deuterated protein systems. This effort will deliver new scientific capabilities and results of particular interest to National Institutes of Health, National Science Foundation, and DOE programs in biomedicine, bioengineering, and biotechnology, specifically for biomedical, pharmaceutical, and bio-inspired design, and will greatly extend the capabilities of the Spallation Neutron Source and the High-Flux Isotope Reactor and the user base in the biosciences.

Results and Accomplishments

This ongoing project is investigating the interconnection between protein structure, dynamics, and function using a multidisciplinary approach. As proposed, we have used RdPf as a test system for the first phase. We have expressed, purified, and crystallized (1) hydrogenated RdPF, (2) deuterated D-RdPf, and (3) specifically CH_3-labeled deuterated Hmethyl-D-RdPf. We have collected neutron data to 1.65 Å from large crystals of both D-RdPf and Hmethyl-D-RdPf. Neutron data were collected at room temperature. Preliminary analysis confirms that the methyl-specific labeling protocol has been successful. In order to perform joint X-ray/neutron refinement of the structures, room temperature X-ray crystallographic data have been collected at 1.1 Å resolution for protonated RpDf and for deuterated RpDf. In addition, X-ray data have been collected to 0.75 Å resolution from a crystal of H-RpDf cooled to 100 K. Anisotropic refinement is being performed and is expected to be completed in the coming months. Similarly, the deuterated is also expected to be completed in the coming months.

SYSTEMS BIOLOGY FOR ENERGY, WATER, AND CARBON CYCLES INITIATIVE

00003

Systems Biology of the Mammalian Cilium: A Cellular Organelle Essential for Human Health and Development

Edward J. Michaud III and Carmen M. Foster

Project Description

Primary cilia are microtubule-based organelles that project from the surface of cells in organisms as diverse as green algae and humans. Primary cilia function as biochemical and mechanical sensors for the cell, receiving information from neighboring cells and from the environment. Cilia play critical roles in human development and physiology, as evident from numerous genetic disease syndromes arising from defects in cilia. Symptoms of these diseases include abnormalities in left-right sidedness, retinal degeneration, hydrocephaly, infertility, obesity, respiratory distress, and cystic lesions in the kidney, liver, and pancreas. Recent comparative genomics and proteomics studies revealed that the primary cilium is composed of about 1000 proteins, but most of their functions are unknown. We are using *Caenorhabditis elegans* (worms) and *Mus musculus* (mice) as model organisms to determine the biological functions and interactions of highly conserved cilia proteins. The major focus of this project is on generating mutations in orthologous mouse cilia genes with a state-of-the-art, high-throughput, and cost-effective mutagenesis strategy developed at ORNL. The phenotypes of mutant mice will be examined at the molecular, cellular, and whole-animal levels, which will provide insights into the assembly and function of cilia. This work may also facilitate the development of new methods for the diagnosis, treatment, and prevention of cilia diseases.

Mission Relevance

DOE initiated the Human Genome Project and played a major role in the completion of the human genome sequence. DOE, through the Joint Genome Institute, continues to provide the scientific community with DNA sequences of many other prokaryotic and eukaryotic organisms. These sequenced genomes are facilitating innumerable comparative genomics and proteomics approaches, including the identification of the “cilia proteome,” which would otherwise have been impossible without these sequences. This project will help annotate the conserved cilia proteome in humans by initiating a systems-biology-based understanding of cilia assembly and function through mutagenesis of the homologous genes in mice. This work also benefits the National Institutes of Health. Cilia dysfunction causes human diseases, including Meckel syndrome, Kartagener syndrome, polycystic kidney disease, primary ciliary dyskinesia, nephronophthisis, Bardet-Biedl syndrome, Alstrom syndrome, Joubert syndrome, and orofaciodigital syndrome.

Results and Accomplishments

In FY 2008 phenotypic investigations of mutant mouse models of cilia disease generated at ORNL were studied as well as the primary cilia on murine skin and hair follicles in mutant mice. The phenotypic investigations or mutant mice are under way in the laboratory of Dr. Brad Yoder at the University of Alabama, Birmingham. The study of the primary cilia on murine skin and hair follicles was accomplished at ORNL. The following mutant mice were shipped to Dr. Yoder:

- CMMB 3415: Mutation in the transmembrane protein 67 (*Tmem67*).
- CMMB 931: Mutation in the echinoderm microtubule associated protein like 2 (*Eml2*).
- CMMB 564: Contains a mutation in dynein, axonemal, heavy chain 3 (*Dnahc3*), which may act as a motor for the movement of organelles and vesicles along microtubules and involved in the movement of cilia and flagella.
- Ift140flox: These mice are a conditional knockout of a gene (*Ift140*) involved in cilia assembly and maintenance, and a component of the intraflagellar transport machinery, which coordinates rapid, bidirectional transport between the cell body and the distal tip of the cilium.
- TNF receptor-associated factor 3 interacting protein 1 (*Traf3ip1*): Mice have null mutations in *Traf3*. They die by 10 days of age with progressive runting, hypoglycemia, and depletion of peripheral white blood cells.

Using the Cre-lox system, cilia assembly in the dermis was disrupted and the effects on hair follicle development evaluated. Mice with disrupted dermal cilia have severe lack of hair. Histological analyses reveal that most follicles arrest at stage 2 of hair development and have small or absent dermal condensates. This phenotype is similar to skin of mice lacking sonic hedgehog or Gli2, proteins involved in the sonic hedgehog pathway, which may suggest that this pathway is down-regulated in the dermis of the cilia mutant hair follicles.

Publications

Lehman J. M., E. Laag, E. J. Michaud, and B. K. Yoder. 2008. "An Essential Role for Dermal Primary Cilia in Hair Follicle Morphogenesis." *Journal of Investigative Dermatology*. November 6, ahead of publication.

Lehman J. M., E. J. Michaud, T. R. Schoeb, Y. Aydin-Son, M. Miller, and B. K. Yoder. 2008. "The Oak Ridge Polycystic Kidney Mouse: Modeling Ciliopathies of Mice and Men." *Developmental Dynamics* **237**(8), 1960–71.

Williams, C. L., M. E. Winkelbauer, J. C. Schafer, E. J. Michaud, and B. K. Yoder. 2008. "Functional Redundancy of the B9 Proteins and Nephrocystins in *C. elegans* Ciliogenesis." *Molecular Biology of the Cell* **19**, 2154–2168.

00007

Novel Approaches for Uncovering Total Environmental Gene Expression Patterns

Martin Keller, Zamin K. Yang, Amudhan Venkateswaran, Mircea Podar, and Christopher W. Schadt

Project Description

Tremendous progress has been made in studying total transcriptional activity in microorganisms, due to the emergence of genomics-based technologies such as reverse transcription polymerase chain reaction and microarrays. However, none of these approaches can be applied routinely for comprehensive understanding of environmental microbial communities and uncultured bacterial cells, since both methods require background genomic information to allow for design of specific primers and/or microarray probes. The purpose of this project is to circumvent this limitation by developing a method involving direct sequencing of cDNA from the environmental samples utilizing a high-throughput sequence analysis system such as the Roche 454. These methods will allow total transcriptome sequencing and analysis from environmental samples, unknown bacteria, or uncultured cells. We developed these novel methods using *Desulfovibrio vulgaris* as the test organism.

Mission Relevance

Our goals were to develop and demonstrate methods in microbial communities that have direct application to DOE mission areas in bioenergy (e.g., selection of strains and consortia efficient in the conversion of cellulose to ethanol), environmental stewardship (e.g., reduction of uranium and other contaminants), and climate change science (e.g., understanding the storage and cycling of carbon through soils). By providing methods for understanding how microorganisms respond directly to perturbations and manipulation of these environments through gene expression patterns, we hope to provide fundamental new insights into the functioning of these communities.

Results and Accomplishments

Our primary goal was to develop and implement methods for high-sensitivity, high-throughput, and high-content analysis of global gene expression patterns useful for studing environmental microbial communities or small numbers (a few cells) of uncultured bacteria. Our efforts focused along three primary tasks that were pursued simultaneously. In Task 1 (optimizing methods for efficient removal of ribosomal and other structural RNAs), we adapted and tested three distinct techniques for rRNA removal. None of these techniques alone were found to be adequate for our intended end-use applications, and we optimized a combinatorial two-step method, which was able to remove approximately 50% of ribosomal rRNAs. In Task 2 (developing and testing methods for unbiased amplification of cDNA from low biomass/low activity environments), we implemented a protocol based on phi29 polymerase amplification and tested the sensitivity and bias associated with these new methods. This method achieves over 10,000-fold amplification of target cDNAs when combined with rRNA removal protocols in Task 1. The results from these first two tasks form the basis for two papers in draft form for the *Journal of Bacteriology*. In Task 3 (enrichment and amplification of an uncultured thermophilic ammonia oxidizing archaea [AOA] as a test for next-generation sequencers), we completed the amplification of DNA from as few as 1−20 cells. Sequence analysis showed issues with non-target contamination, and the time and funding of the project did not allow us to repeat the task.

00020

Systemic Approaches in Recombinant *Zymomonas mobilis* to the Regulation of Ethanol Fermentation

Steven D. Brown, Shihui Yang, Timothy J. Tschaplinski, Dale A. Pelletier, Gregory B. Hurst, and Yunfeng Yang

Project Description

Ethanol is currently blended as an oxygenate in transportation fuel. Its expanded use has great potential to reduce fuel imports, to create American jobs, and to improve our nation's energy security. However, there are barriers and challenges to a rapid expansion of cellulosic-ethanol production. Robust process-tolerant and inhibitor-resistant microbes are recognized as key short-term technological goals. In this project, we utilized systems biology tools, the recently completed genome sequence, an inhibitor tolerant strain, and physiological studies to elucidate the molecular basis of process inhibitor tolerance and stress responses in *Zymomonas mobilis*. Understanding the molecular basis for inhibitor tolerance and stress in a genetically tractable organism will provide rapid and fundamental insight into important fermentation attributes and potential improvements for applied ethanol production. This study provides baseline data useful for other opportunities involving systems biology database construction, modeling, and simulating microbial systems. The techniques, systems, and data also have broader implications for bioenergy and other mission-related microbes.

Mission Relevance

The *Z. mobilis* stress responses characterized in this project were aligned with key science research milestones outlined in the joint DOE Office of Science and Office of Energy Efficiency and Renewable Energy Biomass to Bioethanol roadmap report. Our systems biology approach has delineated important loci, regulators, and key metabolites in stress response and inhibitor tolerance pathways. These studies will likely lead to identification of useful biomarkers and targets for strain improvement and potentially provide broader insight into other ethanol-producing microorganisms. The study will demonstrate and expand ORNL's expertise in the application of a systems-level approach to the study of *Z. mobilis*, which could be readily adapted to other microorganisms of importance to the DOE Office of Science Genomics: GTL program and the Office of Energy Efficiency and Renewable Energy Biomass programs. The fundamental and applied outcomes of our research will assist DOE with the goals outlined in the President's Advanced Energy Initiative to help break America's dependence on foreign sources of energy and develop cleaner, cheaper, and more reliable alternative energy sources.

Results and Accomplishments

Our first manuscript from the project has been accepted for peer-reviewed publication (see details below). This is one of the first papers where transcriptomic and metabolomic profiling studies have been combined for microorganisms. These studies also help identify transcripts for genes not predicted in the primary annotation of the organism's genome and enhance our current understanding of *Z. mobilis* physiology. We have vastly improved the *Z. mobilis* ZM4 gene models and annotation using comparative genomics, proteomics, and newly developed bioinformatic approaches and are preparing a manuscript and website to disseminate our findings. We have genetic and physiological data that supports the role of a *Z. mobilis* locus for increased acetate tolerance and are presently preparing an invention disclosure and manuscript describing these findings. We also characterized *Z. mobilis* growth in the presence or absence of ethanol and have tested a novel bacterial mRNA amplification kit to access bacterial transcript profiles via pyrosequencing techniques. We demonstrated proof-of-principle detection of sRNA via microarray and 454 sequencing. These techniques and proof-of-principle studies will be integrated into future projects and proposals. A number of manuscripts are in preparation to disseminate our studies.

Publication

Yang, S., T. J. Tschaplinski, N. L. Engle, S. L. Carroll, S. L. Martin, B. H. Davison, A. V. Palumbo, M. Rodriguez, Jr., and S. D. Brown. 2008. “Transcriptomic and Metabolomic Profiling of *Zymomonas mobilis* During Aerobic and Anaerobic Fermentations.” *BMC Genomics,* accepted for publication.

00021

Unraveling the Regulatory and Biosynthetic Genes that Control Cellulose Production in the Model Bioenergy Crop *Populus*

Udaya Kalluri, Timothy McKnight, Dale Pelletier, Jennifer Morrell-Falvey, Gregory Hurst, Patricia Lankford, and Sara Jawdy

Project Description

The percentage of usable substrate per unit feedstock biomass is one of the prime factors affecting efficiency of conversion to ethanol. The long-term goal of this project is to unravel novel biosynthetic and regulatory genes that control plant cell wall composition, specifically cellulose, in *Populus*. A twofold approach is proposed towards this goal. Task 1 will develop carbon nanofiber–based transient expression system as a rapid screen to divulge roles of candidate genes in wall biosynthesis. Development of such a system will circumvent the current impediment of long turnaround times in generation of stable transgenic plants for evaluation of gene function in *Populus.* Task 2 will develop and apply protein interaction assays such as chromatin immunoprecipitation and pull-down assays to cell wall biosynthesis studies. Progress made through this project will add new technological and scientific capabilities to ORNL, which will propel not only the pursuit for a comprehensive understanding of cellulose biosynthetic pathway in bioenergy crops but also the pursuit of plant systems biology–based solutions in support of other DOE missions.

Mission Relevance

A better understanding of the molecular controls on plant cell wall composition will lead to warranted applications towards improving the efficiency of biomass conversion to ethanol. The protocols being developed through this project can find direct applications in the current and future projects sponsored by Office of Science, Basic Energy Sciences, such as Plant Feedstock Genomics for Bioenergy and large bioenergy research efforts, specifically, the BioEnergy Science Center. Moreover, owing to the potential broad applicability of the approaches developed through this project, we also anticipate future funding opportunities to exist with DOE (scientific focus areas such as GTL: Fundamental Science), the Department of Agriculture, and the National Science Foundation (such as NSF Plant Genome Research Program). These approaches will also be relevant to the anticipated DOE large science solicitations in the areas of GTL: Bioremediation and GTL: Carbon Cycling.

Results and Accomplishments

Culture conditions for cell wall formation were standardized. A new confocal microscopy–based technique was successfully developed as a chemical imaging technique to study plant cell wall formation. Immunolocalization of monoclonal wall antibodies was demonstrated using *Populus* protoplasts that are actively regenerating cell walls. This technique had already formed the basis of a larger-scale wall antibody screen under a distinct DOE project. The carbon nanofiber–based transient expression is working better for tissue samples compared to single cells. The plant proteomics method developed during the first year was successfully applied to further evaluate the *Populus* developing xylem proteome. Crude, membrane, and nuclear fractions of wild-type xylem samples were shotgun profiled. The initial DBDigger-based data analysis approach was developed to a SeQuest-based approach. Monoclonal antibodies raised against peptide sequences submitted in the first year became available in the second. These antibodies, specific to sucrose synthase and cellulose synthase proteins, have been successfully used in western hybridizations. This approach was used to experimentally confirm the presence of sucrose synthase in membrane as well as crude fractions, as first observed through the shotgun proteomics approach. Both coorthologs of full-length *Populus* sucrose synthase gene have been cloned. The aforementioned research progress is significant because further application of these proteomics methods will inform the system biology models of not only cell wall biosynthesis but also of other plant developmental and physiological pathways. Overall, this work has directly resulted in three oral presentations and contributed towards at least five other presentations at various workshops and conferences as well as in preparation of two research publications.

00033

Aberration-Corrected, Three-Dimensional Scanning Transmission Electron Microscopy for Studying Microbiological Systems

Niels De Jonge

Description of Project

Aberration-corrected, three-dimensional (3-D) scanning transmission electron microscopy (STEM) is capable of high-resolution 3-D imaging of specimens without a tilt stage. In a manner similar to confocal light microscopy, the sample is scanned layer by layer by changing the objective lens focus so that a focal series is recorded. Optimized 3-D STEM is expected to exhibit significant advantages over tilt-series transmission electron microscopy (TEM) for conventional thin sections, such as (1) better resolution, (2) absence of mechanical tilt, (3) capability of imaging large-area thin sections, and (4) faster 3-D data collection. Our goals are to fully understand the image formation mechanisms, evaluate the feasibility of 3-D STEM with respect to radiation damage, and optimize the performance of 3-D STEM for the imaging of thin sections of biomedical relevance.

Mission Relevance

Three-dimensional STEM can be used to study the complex organization of the nanoscale assemblies of macromolecules and compartments (e.g., ribosomes, proteasomes, Golgi apparatus, and mitochondria) within eukaryotic cells. Understanding how these structures are organized, and thereby function, within the crowded 3-D volume of the cell can be applied, for example, to aid the development of new therapeutics or to improve existing ones. By establishing this new structural analysis tool and demonstrating its power on relevant biological samples, we expect to be in a good position to (1) support the Genomics: GTL program and initiatives in bioenergy (e.g., by setting up a user facility), (2) pursue applications to the National Institutes of Health (NIH), and (3) pursue National Center for Research Resources funding including 3-D STEM for biology.

Results and Accomplishments

In FY 2007 we obtained 3-D images of conventional thin sections containing 3T3 cells with a lateral resolution of 0.6 nm (the grains of the stain are resolved) and an axial resolution of 60 nm. The images were recorded with a STEM (JEOL 2200 FS 200 kV STEM/TEM equipped with CEOS aberration corrector) with a beam semi-angle of 26.5 mrad. Conventional thin sections containing mammalian cells (NIH 3T3, mouse fibroblast cell line) were prepared at NIH and optimized for 3-D STEM imaging. We also developed the framework of a theoretical model for 3-D STEM imaging and, in particular, of the radiation-dose-limited resolution.

In FY 2008 we obtained a new type of sample from NIH containing the cytoskeleton network of a 3T3 cell, prepared with the so-called platinum shadow evaporation method. This sample is not sensitive to beam damage. High-quality 3-D data sets were recorded with a lateral resolution of 0.6 nm and an axial resolution of 60 nm. This data set had a noise level sufficiently low to allow a deconvolution procedure to work. The deconvolution procedure was developed together with a software engineer from Media Cybernetics Inc. Deconvolution improved the axial resolution by maximal a factor of 5, depending on the particular size of a platinum particle. The 3-D STEM modality was implemented in commercially available software. We have made progress in the theoretical model of the 3-D STEM imaging, resulting in an analytic model of the resolution. Furthermore, STEM was implemented in a Monte Carlo software package for electron beam imaging in collaboration with the University of Sherbrooke, Canada. The latest models for the electron-sample interaction were implemented. The calculations were tested on experimental results and found to agree. Finally, an R01 project proposal was submitted to NIH on the investigation of 3-D STEM imaging for biological specimens involving a consortium of scientists from ORNL, Vanderbilt University, NIH, and the University of Sherbrooke. Latest data was provided in time to be included in the second round of review. The proposal was granted funding for 4 years in support of three scientists, one postdoctoral researcher, two graduate students, one undergraduate student, and other required costs.

Publication

De Jonge, N., R. Sougrat, D. B. Peckys, A. R. Lupini, and S. J. Pennycook. 2007. "Three-Dimensional Aberration-Corrected Scanning Transmission Electron Microscopy for Biology." In *Nanotechnology in Biology and Medicine*, T. Vo-Dinh, ed., CRC Press.

00040

Electricity and Biohydrogen Production via a Systems-Level Understanding of Microbial Fuel Cells

A. P. Borole

Project Description

Power output from microbial fuel cells (MFCs) is a limiting factor impeding application of these devices for energy production. In the first year, acidophilic MFCs were investigated. Electricity production was demonstrated at low pH, using an H-type MFC. To improve power density of MFCs, a two-pronged approach was taken. Engineering and biological factors limiting the power density were identified and modified to yield MFC power densities higher than those reported in the literature. Novel enrichment strategies employed resulted in identification of new exoelectrogenic families. This project was targeted for development of expertise in two areas: microbial communities and energy production. Electrogenic microbial communities were tracked over time with different carbon sources via 16S r RNA and DGGE analysis. Application of the MFCs to energy production was studied for two industrial processes, biorefinery-based ethanol production and food industry processes. Electricity production with simultaneous removal of biorefinery by-products was demonstrated, enabling water recycle in biorefinery. Electricity production from a milk dairy farm wastewater was also demonstrated.

Mission Relevance

The project addresses the DOE mission to obtain energy independence, while improving environmental quality. The project deals with energy production in the form of electricity and hydrogen from renewable resources such as sugars, organic acids, and waste materials. The ability to effectively produce electricity from cheap renewable resources is an important goal for DOE. Specific programs likely to benefit from this research are Hydrogen, Fuel Cells and Infrstructure Technologies (of the DOE Office of Energy Efficiency and Renewable Energy), Genomics: GTL (of the DOE Office of Science, Basic Energy Sciences) and clean coal technology (of the DOE Office of Fossil Energy). The Department of Defense (DOD) needs remote and portable energy sources to power transmitters, receivers, sensors, monitors, etc. MFCs are very stable, although low-energy, devices that could be used in such applications. This project can potentially help improve power yield from MFCs to enable use in other DOD applications requiring greater energy needs.

Results and Accomplishments

Novel electrode designs for MFCs were created and implemented to demonstrate power densities up to 490 W/m^3. Materials and electron mediator issues associated with operating MFCs at low pH conditions were investigated. Electricity production with *A. cryptum* as a biocatalyst was demonstrated (work published in *Biot. Lett.,* 2008).

The overall accomplishments are listed here.

1. Designed MFCs with reduced ohmic resistance and compact design to enable enrichment of biofilm-forming exoelectrogenic organisms.
2. Developed a novel enrichment strategy to improve selection of electrogenic biocatalytic microbial consortium (patent application submitted).
3. Improved anode performance and obtained power densities higher than those reported in the literature (>5000 mW/m^2) (manuscript in review).
4. Developed electrochemical impedance spectroscopy techniques to study limitations of MFCs.
5. Identified path forward to develop sustainable MFCs using air as the oxidant.
6. Obtained proof of principle for application of MFCs in biorefinery.
7. Sutmitted four invention disclosures (first patent already filed).
8. Published one article, two manuscripts in review, three others in preparation.

Publications

Borole, A. P., C. Y. Hamilton, D. S. Aaron, and C. Tsouris. 2008. "Demonstrating Cathode as a Limiting Factor in Achieving High Power Densities in Microbial Fuel Cells with Improved Anode." *Environ. Sci. Technol.,* submitted.

Borole, A. P., C. Y. Hamilton, T. A. Vishnivetskaya, D. Leak, C. Andras, J. Morrell-Falvey, M. Keller, and B. H. Davison. 2008. "Fusing Biology with Engineering to Improve Power Density of Microbial Fuel Cells." *PLoS One,* submitted.

Borole, A. P., H. O'Neill, C. Tsouris, and S. Cesar. 2008. "A Microbial Fuel Cell Operating at Low pH, Using an Acidophile, *Acidiphilium cryptum.*" *Biot. Lett.* **30**, 1367–1372.

Borole, A. P., et al. 2008. "Electricity from Food and Bioindustry Wastewaters Using Microbial Fuel Cells." *Proceedings of the American Chemical Society Annual Meeting*, Philadelphia.

00043

Microfluidic Platform for Individual Microbe Capture, Cultivation, and Selective Release

Martin Keller, Anthony Palumbo, Mircea Podar, Tim McKnight, Nance Ericson, and Mitch Doktycz

Project Description

The recent application of molecular phylogeny to environmental samples has resulted in the discovery of an abundance of unique and previously unrecognized microorganisms. The vast majority of this microbial diversity has proved refractory to cultivation with traditional methods; thus, little is know of their physiology or capabilities. We are (1) developing a microfluidic platform that will allow the site-specific capture of individual bacteria, cultivation with controlled doubling cycles, and selective release for downstream collection and further analysis and (2) applying flow cytometry to isolation and subsequent manual cultivation of single cells. The microfluidic platform will incorporate encapsulation of cells in gel microdroplets. This cultivation under low nutrient flux conditions will be followed by further characterization and analysis of microbial microcolonies through "lab-on-a-chip" concepts. The subsequent analysis will include the implementation of multiple displacement amplification (a linear type of DNA amplification) for subsequent analysis by genome sequencing. This approach will ultimately replace the flow cytometry approach, leading to higher throughput and reduced costs. The flow cytometry approach is being developed further by applying the method to anaerobic bacteria. We are exploring methods to handle anaerobic bacteria in the flow cytometry.

Mission Relevance

The ability to grow and study previously uncultured organisms will enhance our understanding of microbial physiology and metabolic adaptation and will provide new sources of microbial metabolites. These capabilities are applicable to DOE programs involved in bioenergy, bioremediation, and carbon sequestration. In all these applications use of novel microorganisms may lead to more efficient processes relevant to DOE missions. For example, DOE is interested in isolation of more efficient bacteria for the degradation of cellulose to sugars and the processing of sugars to alcohol. In addition, these capabilities will have applications to the National Institutes of Health (NIH) and potentially the Department of Homeland Security. NIH applications could come from areas such as isolation of novel pathogens and characterization of gut microorganisms.

Results and Accomplishments

Flow cytometry–based approaches to isolate novel bacteria from groundwater samples at the DOE field research center at ORNL have been developed. These bacteria were sorted into liquid culture media and isolated from a low-pH site where no previous isolates were obtained. We have also modified the sorting chamber to hold a standard agar plate so that bacteria that prefer growth on solid media can be isolated. We also tested and demonstrated the survival after sorting of bluegreen algae (the dominant carbon-fixing organisms in the ocean) in the flow cytometer, and sorting of poplar chloroplasts for study of effects of genetic changes in poplar that could result in better growth characteristics for biofuels production. Rapid prototyping approaches have been developed and implemented to provide fast turnaround and in-house replica production of microfluidic structures capable of generating segmented flow and alginate encapsulation of microbial populations. Using these platforms, we have successfully generated and cultured GFP-expressing *E. coli* in alginate microbeads ranging from approximately 20 to 100 μm in diameter, uniformly sized dependent upon the flow rate in the bead generation section of the fluidic platform. A downstream cultivation chamber has also been implemented, which provides containment and media exchange of upwards to one million microbeads per device. The cultivation chamber provides visual inspection of microbial growth within the alginate microbeads in a single-layer, arrayed-bead format. We will continue with implementation of downstream processing of the cells.

During FY 2008 significant progress was made towards designing and fabricating microfluidic structures capable of generating alginate microdroplets. These microdroplets were used successfully for containing and culturing individual microbial cells. Multiple designs were fabricated and tested. To facilitate these efforts, a complementary approach to developing alginate microdroplets also was developed. This approach used a piezoelectric droplet generator. This "ink-jet" based technique was capable of generating millions of microdroplets and facilitated the identification of effective experimental conditions for droplet formation and cell culture. Significantly, it facilitated the integration and development of the flow cytometry technique for bead sorting. Identification and selection of individual alginate microdroplets by flow cytometry have been accomplished. The flow cytometer has also been used to facilitate the analysis of unclassified microorganisms from mercury contaminated and uncontaminated reference creeks located on the Oak Ridge reservation. Phylogenetic characterizations of this site have been performed. These samples will be used for demonstrating the efficacy of the developed technology in the upcoming year.

00044

Methodological Development of Computer Simulation in Molecular Biophysics

Jeremy C. Smith

Project Description

Motions in proteins play a key role in their function. Here we establish a program developing methodological aspects of combining computer simulation with neutron scattering experiments with a view to characterizing correlated dynamics in proteins relevant to bioenergy in different functional states and environments. Work is also performed aimed at understanding the functional mechanisms of cellulase activity.

Mission Relevance

Progress made through this project will place ORNL in an advantageous position to secure funding from anticipated solicitations from the DOE Office of Science, Basic Energy Sciences and Biological and Environmental Research programs over the next several years. The results from the proposed work will, moreover, add new technological as well as scientific capabilities to ORNL, which in turn will strengthen ORNL's position as a leader in biophysical bioenergy research.

Results and Accomplishments

Coarse-grained biomolecular simulation with the REACH (Realistic Extension Algorithm via Covariance Hessian) algorithm was developed and shown to be transferable. A coarse-grained force field for the nucleosome was derived using self-consistent multiscaling. The distribution of atomic fluctuations in thermophilic and mesophilic dihydrofolate reductase was derived using elastic incoherent neutron scattering. A hydration-dependent dynamical transition in protein:protein interactions was found at ~240 K**.** Subdiffusion in peptides was found to originate from the fractal-like structure of configuration space. Solvent electrostriction-driven peptide folding was revealed by quasi Gaussian entropy theory. The dual function of the hydration layer around an antifreeze protein was revealed by atomistic molecular dynamics simulations. Partitioning of amino-acid analogues in a five-slab membrane model was explored. Charge-based interactions between peptides were observed as the dominant force for association in aqueous solution. The key role of water molecules in bacteriorhodopsin proton transfer reactions was determined. Instantaneous normal modes were calculated from molecular dynamics trajectories and were found to describe the protein glass transiton. A molecular dynamics study of G-actin showed instability of the open state and suggests the existence of a superclosed state.

05055

Host Genetic Diversity as a Variable Selection Environment for the Gut Microbiome

Elissa J. Chesler, Anthony V. Palumbo, and Mircea Podar

Project Description

Specific host genetic factors that influence the composition of the gut microbial community and its correlations or causal relationships with chronic diseases are poorly understood. A colony of standard inbred and hybrid mice will be used to study the connection between mammalian genetic variation and gut microbial ecology. Using genomic approaches in both gut microbial communities and the mouse intestine, we will identify variation in gut microbiomes and establish the heritability and pleiotropic effects of genetic variation on interactions of host and normal flora. These studies will lay important foundations for an integrative and interdisciplinary research program that will allow us to map the interface between the mouse genome and the gut microbiome. We will approach this by analyzing the association of the abundance of specific microorganisms with the steady-state abundance of mouse mRNAs. This will allow us to identify networks involving host and microbe for causal studies. The goals of using mouse models are to identify predictive biomarkers and polymorphic loci that determine susceptibility to a number of human diseases that result from the interplay of gut microbes, genetic susceptibility factors, and environmental exposure including celiac disease, irritable bowel syndrome, and Crohn's disease.

Mission Relevance

The techniques developed here in rapid screening of community composition of environmental samples are applicable to DOE programs. Community composition has implications in key mission areas such as biofuels, bioremediation, and carbon sequestration. This project is of interest to the DOE Office of Biological and Environmental Research in studies of biological complexity and health effects of radiation. It is also of tremendous interest to the National Institutes of Health, and there are likely to be calls for proposals in this area over the next few years. There are several human diseases that this work would allow ORNL to address in future proposals. The Environmental Protection Agency has shown an interest in tracking sources of enteric contamination in streams, lakes, and rivers. Thus, there is an interest in studies of domesticated and wild animals as potential sources of contamination to water bodies. The techniques developed in this project will be applicable to this area.

Results and Accomplishments

We have collected samples of intestinal RNA and cecal content DNA from a panel of genetically diverse mice, the Collaborative Cross. Primers have been designed for isolation of rare uncultured microbes using in situ hybridization labeling and flow cytometry. Heritability analysis of gut microbial phenotypes was performed in the eight progenitor strains of the Collaborative Cross. Between 7000 and 25,000 sequences were obtained from each intestinal microbe sample. Seventy-seven sequence clusters had significant strain by sex effects on their abundance in the mouse intestine. We found that most of the differentially abundant microbial clusters were elevated in a single strain of mouse, though the organism was present in all strains. The sequence clusters were entered into a terrain mapping analysis, which confirmed that gut microbial community composition is a strong classifier of mouse strains. This classification was used to group the mouse strains into three classes to compare gene expression results among them. Specific examples of differential expression were found for each class. We were also able to demonstrate that overall there was heritable variation in intestinal expression of metabolizing enzymes and intestinal immune processes. Combinatorial applications for the analysis of gut microbes and their association to intestinal mRNA species at the level of microbial taxa have been devised and will be implemented upon complete collection of project data.

05063

Scale-Dependent Metrics for Bioenergy: Land-Nutrient-Water Interactions Under Future Energy Scenarios

Virginia Dale, Latha Baskaran, Budhendra Bhaduri, Robin Graham, Richard Middleton, Patrick Mulholland, Esther Parish, Alexandre Sorokine, and Amy Wolfe

Project Description

The proposed vast increase in bioenergy use and production certainly will have interdependent environmental and socioeconomic impacts. Several technological pathways connect the various biomass sources to diverse forms of bioenergy (fuels, heat, and power). Currently, the complexity and scale dependency of such decisions and their impacts are not understood, defined, or described with adequate clarity to enable policy makers to develop strategies to ensure a sustainable bioenergy future with acceptable environmental and socioeconomic consequences, particularly under a changing climate. This project will develop scientifically rigorous, practically useful, scale-dependent metrics and an approach that will help policy makers understand environmental and socioeconomic consequences of alternative bioenergy regimes and policies. We will use a specific policy goal to develop a spatially explicit conceptual model of the complex interactions that constitute the bioenergy system. Through use of a stepwise spatial optimization approach, the sensitivity of the economic, social, and environmental constraints in the model will be deployed at two scales of resolution in watersheds in east Tennessee within the Tennessee Valley Authority (TVA) region. This model will provide a foundation for developing scale-dependent metrics to gauge environmental and socioeconomic effects of alternative methods for achieving specific bioenergy goals.

Mission Relevance

This research effort is directly relevance to the Biomass program of the DOE Office of Energy Efficiency and Renewable Energy. The Biomass program needs an integrated strategy for bioenergy implementation that allows the agency to address environmental concerns in view of farming practices, energy pressures, economic constraints, and changing climate conditions. The effort is also relevant to the DOE Office of Science's new Carbon Mitigation Science Focus Area in the Office of Biological and Environmental Research, which encompasses not only terrestrial carbon sequestration but also bioenergy. Other federal agencies (e.g., Department of Agriculture, Environmental Protection Agency, National Aeronautics and Space Administration, and Department of Transportation), the private sector (e.g., Southern Alliance for Clean Energy), and international organizations will be keenly interested in these research results, for they are the implementers and monitors of the sustainable biofuel plan. The Department of Defense also has a strong interest in the next phase of this research, for it is the largest user of biofuels in the United States and recognizes the opportunities of developing this strategic resource. States, such as Florida, are actively engaged in finding ways to pursue the next steps in implementing biofuel alternatives (personal communication, Don McConnell, UT-Battelle).

Results and Accomplishments

During the project's first year, our interdisciplinary team all contributed to the development of the conceptual framework by investigating and contributing information about social and behavioral factors and well as ecological conditions. The geospatial information system was created, and the Soil and Water Assessment Tool (SWAT) was parameterized and set up to provide results to feed into the optimization model. Strategies for parallelizing SWAT runs and setting up optimization environment were investigated. Our current strategy is to perform paired sub-watershed runs with alternative SWAT simulation parameter Business Sensitive 2 sets. We have developed a spatial optimization model (SOM) that optimizes land-use decisions within a watershed. The SOM efficiently distributes where dedicated energy crops should be grown while maximizing profits (or minimizing costs) and maintaining water quality limits (nitrogen, phosphorous, and sediment concentrations) and acceptable land-use displacement (e.g., area of forest, cropland, and pastured converted to energy crops). These metrics were selected from the conceptual model to represent sustainability issues and farmer choices. The SOM is parameterized using SWAT; this integration combines the decision-making power of an optimization model (i.e., SOM) with an advanced nonlinear watershed simulation tool (i.e., SWAT). We believe that SOM will make a significant impact on watershed modeling and sustainability research in the near future.

Publication

Kline, K. L., and V. H. Dale. 2008. "Biofuels: Effects on Land and Fire." *Science* **321**, 199–200.

05064

Possible Impacts of Relatively Severe Climate Change

Thomas J. Wilbanks, Auroop Ganguly, Anthony King, David Erickson, Keith Kline, and Sherry B. Wright

Project Description

This project is focused on the development of proof-of-principle scientific advances for the regional analysis of severe rates and levels of climate change, because observations in recent years have suggested that climate change is likely to be more severe than previously expected and analytical tools for such analyses are lacking. It involves innovative integration of knowledge from diverse fields of science, focused on advances in the ability to consider variance/extremes within projections of average climate changes, the ability to relate climate change projections to socioeconomic scenarios and story lines, and innovative visualization approaches for research heuristics and communicating meaning. Its "laboratories" are two regions, one in the United States (the Southeast) and one in a developing country (Northern India), in which impact analyses for key sectors are conducted, including ranges of possible impacts, possible impact thresholds, and uncertainties.

Mission Relevance

The DOE Office of Science strategic plan calls for predicting and assessing "the effects of climate change based on models of human actions and costs and benefits of alternatives for mitigation and adaptation." A key indicator of success is "progress in delivering improved climate data and models for policy makers to determine safe levels of greenhouse gases." This project specifically benefits this indicator by improving capabilities to determine how relatively severe climate change might relate to judgments about safe levels of greenhouse gases.

Results and Accomplishments

The project is focused on two regions utilizing two climate change scenarios and an impact assessment team. In the first of the two years of the project, the two regions for the impact assessment work were selected (and a local partner for the Northern India case study was arranged), the climate change scenario was selected (A1fi, with A2 as the backup), projections and visualizations were developed at appropriate scales (a capability already used by other ORNL projects), and progress was made in three areas of regional impact assessment science advancement, especially analyses of variance/extremes and innovative visualization. For example, examining monthly and weekly temperature and precipitation projections gives a different picture of implications of climate change than simply using decadal averages of annual means. The main challenges were knitting together scenario development, visualization, and impact concerns; mobilizing a diverse project team with limited resources; and considering how to address the fact that some of the most important regional impact issues cannot be fully informed by available climate change scenarios (e.g., storm impact concerns for the U.S. Southeast and glacier melt and socioeconomic change for Northern India).

05133

Carbon Drivers of the Microbe-Switchgrass Rhizosphere Interface

Christopher W. Schadt, Hector F. Castro-Gonzalez, Marie Anne De Graaff, Charles T. Garten III, and Aimee T. Classen

Project Description

Plants allocate a significant proportion of their carbon belowground as roots and root exudates. These often-labile carbon substrates serve as the energy source for complex microbial communities that inhabit the rhizosphere and stimulate ecosystem nutrient processes. In spite of its ecological importance, root exudation is poorly understood, and even less is known about how changes in the amount and type of root exudate might alter the functions of the soil microbial community. Microbial functional group composition in the rhizosphere is likely influenced directly and indirectly by a number of complex factors, including interactions with the dominant plant species and interactions with other microorganisms. Studies of the feedbacks between root exudation and microbial community function will enable better understanding of how shifts in plant genetics (e.g., bioenergy crops) may alter soil carbon cycles, crop sustainability, and carbon sequestration. In laboratory and greenhouse studies, we will merge the power of two technologies—^{13}C stable isotope probing (SIP) and DNA analysis—to link root exudate quality and quantity with microbial community structure and function in the rhizosphere using switchgrass as a model system.

Mission Relevance

Understanding of the rhizosphere interface supports DOE objectives in carbon cycling and the role of soils in bioenergy crop sustainability. This project proposes an approach that could be used in several ecosystems by further development of genomic tools for ecosystem research. This will benefit research programs in the DOE Office of Science, DOE Office of Energy Efficiency and Renewable Energy, other federal agencies such as the Environmental Protection Agency and the Departnment of Agriculture, and state extension progams. Within the Biological and Environmental Research Program of the DOE Office of Science, this proposal will enhance the goals of the Program for Ecosystem Research (PER) to understand and predict effects of environmental changes associated with energy production on terrestrial ecosystems. PER has encouraged explorations across levels of biological organization and the use of genomics in ecology. This project will also fit the Genomes-to-Life (GTL) program goals to characterize the functional repertoire of microbial communities in natural environments and position ORNL to compete for DOE's planned investment in GTL centers that focus on carbon cycling and climate change research.

Results and Accomplishments

Thus far we have successfully (1) designed microcosms enabling us to semi-hydroponically grow plants under anexic conditions to collect, and accurately identify, root exudates; (2) identified some of the major root exudates derived from the switchgrass cultivar "Alamo" using high-performance liquid chromatography and gas chromatography–mass spectrometry (GC-MS) methods; (3) set up microcosms to identify exudates from three different switchgrass cultivars exhibiting distinct root architectures to look at genotypic variation; (4) designed and initiated labeling of plant material using an airtight, closed circulation CO_2 chamber for producing ^{13}C-labeled plant biomass and exudates for soil incubations; (5) begun initial soil incubations using synthetic exudate analogs; and (6) developed the initial simple compartment model of microbial community dynamics. During FY 2009 we will continue identification of exudates in laboratory systems using GC-MS. Laboratory studies employing stable isotope probing using ^{13}C-labeled materials will continue towards conclusion of the molecular work to define the microbial phylotypes responsible.

05169

Design, Simulate, and Prototype Facilities for Macroscale Experiments of Ecosystem Response to Climate Change

Paul J. Hanson, Stan D. Wullschleger, Richard J. Norby, Kenneth W. Childs, and Warren K. Thomas

Project Description

New advanced facilities are urgently needed for rigorous scientific evaluations of the responses of complex ecosystems to unique climate conditions not observable in current natural settings or through the use of climate gradients. We will design the next-generation, state-of-the-art experimental systems needed to evaluate and understand responses of terrestrial ecosystems and their components to simultaneous aboveground and belowground warming expected for a range of future climate scenarios. We envision a long-term, follow-on research program using new experimental systems that will address uncertainties in process-level responses of microbial, plant, and animal communities in whole, intact ecosystems. The proposed effort includes a physical (heat and mass flow) and biological (scaling plant and microbial function) modeling phase to establish performance criteria for the facilities, engineering design studies to optimize specific plans, and the development of physical prototypes to generate proof-of-concept data sets for peer-reviewable summaries of the new methods. The manipulative systems will be designed for application to a wide range of important vegetation types.

Mission Relevance

This project seeks to design, simulate, and prototype facilities for macroscale experiments of ecosystem responses to climate change and to evaluate the magnitude of biological responses associated with this new approach. Such facilities are needed because projected terrestrial environments under climatic change may be 4 to 8°C warmer than today depending on their location on Earth. These experimental systems are needed by the DOE Office of Science, Biological and Environmental Research program and other agencies contributing to the U.S. Climate Change Science Program to provide a capacity to measure terrestrial ecosystem responses to climate conditions not observable today.

Results and Accomplishments

Several belowground warming systems were conceptualized and modeled with a general-purpose heat conduction code to arrive at a suitable design. The original concept of a deep soil warming system accessed from an excavated trench was plausible, but it proved impractical to build and cost prohibitive. Infrared heating of the ground surface by itself was also simulated, but it did not achieve the desired temperature differentials throughout the soil test volume. The original concept was ultimately replaced by an elegant deep-circumferential heating design. The deep-circumferential heating concept requires the installation of a ring of vertically oriented guard heaters just outside the perimeter of the test volume to supply the energy to heat the target soil volume. The number and spacing of the heaters were varied, the depth to which the heaters extended was varied, and the heater power and power distribution within the heater were varied. A design with 12 heaters that are 3 m long and equally spaced around a 3.5 m diam circle produced satisfactory uniformity of target temperatures within the test volume over a 30 day warm-up period. A design with 24 heaters gave better temperature uniformity and offered some redundancy in case of failure of individual heating elements. A concept for the warming of a larger experimental warming area was also conceived. Having accomplished the conceptualization and simulation of an optimized experimental design for deep-circumferential soil warming, project personnel produced and completed working drawings for the translation of the theoretical concepts into a workable design for prototyping and testing. An appropriate site for the location of the prototype plots was identified, evaluated, and approved by ORNL and DOE land use committees in early March 2008; National Environmental Policy Act documents were filed, reviewed, and approved on April 18, 2008; and prototype infrastructure installations were completed by September 30, 2008.

05370

Stable Isotope Approach to Nitrogen Cycling Analysis

Richard J. Norby

Project Description

Understanding how the biological nitrogen cycle responds to environmental conditions is a critical component of assessments of ecosystem response to atmospheric and climatic change. Nitrogen cycling in ecosystems is characterized by fluxes through plant and soil pools with a wide range in turnover times, which makes evaluation using traditional allometric approaches difficult. We will develop methods for using stable isotope labeling of a forest stand to track nitrogen accumulation in various ecosystem pools and measure the fluxes between those pools. Ammonium sulfate labeled with ^{15}N will be applied to a forest stand, and the fluxes of nitrogen into different ecosystem pools (tree and soil) will be quantified directly from isotopic mass balance. A critical test of the approach will be evidence that the ^{15}N label enters the biological cycle without resulting in a measurable increase in total nitrogen concentration. The isotope-labeling approach will be evaluated for application in new experiments being developed under the leadership of ORNL's scientific focus areas on Climate Response and Climate Forcing Feedback research.

Mission Relevance

The Climate Change Research Division of the DOE Office of Science, Biological and Environmental Research supports research on the responses of ecosystems to atmospheric and climatic change. Predictions of the impacts of atmospheric and climatic change can be highly dependent on accurate assessments of nitrogen uptake and soil nitrogen availability, and future ecosystem warming and CO_2 enrichment experiments must include more sensitive evaluations of nitrogen cycling. By developing ^{15}N isotopic tracing as an ecological research tool at larger scales than it is generally applied, we will be better positioned in our planning for next-generation field experiments, which we expect to be supported by DOE through the Climate Response Scientific Focus Area. We also will be able to use this tool for gaining process-level understanding that is needed for continued development of ecosystem and global models within the Climate Forcing scientific focus area.

Results and Accomplishments

Applications of ^{15}N were made to one-quarter of each of four forested plots at the beginning of the growing season in 2008. The application provided 0.19 g ^{15}N m^{-2}, which is approximately half the amount of annual nitrogen deposition; therefore, no fertilization effects were expected to occur in conjunction with the tracer addition. This expectation was confirmed by analysis of leaves of understory trees in May and canopy sweetgum trees in June 2008. Total leaf nitrogen concentrations did not differ between labeled and unlabeled plots, but the samples from labeled plots were enriched in ^{15}N, indicating that the label had entered the biological cycle without causing a fertilization effect. Additional samples of canopy foliage, understory leaves, and soil samples were obtained in early to mid-August 2008 from both ^{15}N labeled and unlabeled portions of the plots. Coarse and fine roots were removed from the soil samples at four different depths (0–5, 5–10, 10–15, and 15–20 cm). Soil samples were separated into particulate and mineral-associated organic matter to determine associations of the ^{15}N tracer in the mineral soil. There was a strong difference in the ^{15}N content of the forest floor in unlabeled (mean = 0.378 at. %) and labeled (mean = 1.778 at. %) areas. Grasses and other small plants that were rooted in the surface soil of the labeled portion of each plot were highly enriched in ^{15}N (mean = 2.277 at. %) relative to those growing in unlabeled areas (mean = 0.382 at. %).

05371

Investigation of Unique ORNL Resources and Methodologies for Biomedical Applications

Brynn Voy, Ram H. Datar, and Gary Van Berkel

Project Description

Recent developments at ORNL in mammalian-based methodologies and characterization techniques have the potential for biomedical applications that would be of interest to the National Institutes of Health. In this project we will investigate, in collaboration with researchers at Georgetown University Medical Center, this potential for two specific technologies.

1. Every medical institution in the country has a repository of pathological material that consists of aldehyde-fixed paraffin embedded human tissue. In many cases these samples are linked to clinical records, making these repositories a vast storehouse of pathological and, potentially, molecular data that can be retrospectively analyzed and linked to patient outcome. In this task we will investigate whether ambient surface sampling/ionization and imaging sources coupled with mass spectrometry–

based detection (SSIMS) in conjunction with modern metabolomic analyses have the potential to overcome the restrictions on measuring genomic and proteomic parameters of these data.

2. Much of the worldwide rise in obesity is blamed on the spread of a Western lifestyle, in particular an obesigenic, high fat diet. A less recognized but also significant risk factor is chronic stress. Yet not everyone consuming a high fat diet or under chronic stress becomes fat, highlighting the critical role of gene-environment interactions in the risk for obesity. We will employ the resources of the Collaborative Cross (CC) to determine the genetic and mechanistic interactions between adverse responses to stress and risk for obesity. The CC is a novel mouse population–based model system that enables the relationships between complex traits like obesity and stress response to be uncoupled genetically and mechanistically. In this task, we will (1) define the spectrum of stress-responsive phenotypes across a panel of CC lines and perform an initial quantitative trait locus mapping study; (2) determine if stress alone is sufficient to induce obesity in genetically susceptible CC lines; and (3) construct an initial network between metabolic and biochemical stress phenotypes, adipokine levels, and genetic variants.

Mission Relevance

The technologies to be developed in this project will be broadly useful to DOE programs, especially for application to other organisms. Application of these technologies to issues of human health will be of great interest to the National Institutes of Health (NIH). In particular, NIH will be interested in genetic susceptibility to stress and obesity. Because of concerns about post-traumatic stress disorder, the Department of Defense may also be interested in the stress-obesity project. We will approach both DOE and NIH to explore follow-on funding opportunities.

Results and Accomplishments

We planned initial experiments to be carried out using animal models in which we have access to fresh, frozen, and fixed embedded normal and tumor material from the same individual. The actual experiments completed showed that the surface sampling probe experiments could not be used in a straightforward manner to directly analyze the paraffin embedded tissue. This was because of difficulty in penetrating the wax with conventional solvents used in the mass spectrometry portion of the experiments. However, simple dewaxing procedures offline from the sampling experiments were found to provide a surface that could be sampled successfully. Initial results are now being processed to determine is any identifiable markers are present in the spectra obtained. Once completed, if results look promising, we will expand our studies to sections of human tumor material. If successful, SSIMS-based molecular profiling will revolutionize molecular pathology.

We implemented a social stress protocol used previously in mice by the Zukowska lab. Mice from approximately 25 lines from the CC (one control and one stressed line) entered the stress paradigm, and a battery of tissues were collected from each mouse. In addition, nuclear magnetic resonance–based measures of whole body composition were made prior to euthanasia. Basic data (body and fat pad weights, plasma glucose levels) were recorded from each mouse. The Zukowska lab completed analysis of neuropeptide Y levels in adipose tissue and brain of the sample collection, and additional assays from both the Zukowska and Voy labs are ongoing.

ULTRASCALE COMPUTING INITIATIVE

00006

Exploring Reconfigurable Computing Programming Models to Accelerate High-Performance Computing Applications

Olaf O. Storaasli

Project Description

High-performance computer (HPC) vendors see field-programmable gate array (FPGA) accelerators as a next major performance advance. Silicon Graphics Inc. (SGI) predicts FPGAs will "accelerate mission-critical applications by over 100 times." Cray selected DRC FPGA coprocessors for future XT supercomputers, as they offer "the greatest opportunity for application acceleration," enabling new scientific breakthroughs to solve hitherto intractable problems. New algorithms are needed to effectively harness FPGAs for large science codes, a challenge requiring bottom-up FPGA expertise and a top-down HPC application developer/user perspective. This research proposes a computational framework to speed DOE science codes by placing their compute-intensive kernels (floating point, fast Fourier transforms, matrix and linear algebra, etc.) on FPGAs via appropriate tools/languages, demonstrating computation speedup via selected "pathfinder" applications charting a way others may follow. This research leverages close collaboration with Xilinx's HPC group, Cray, SGI, Mitrion, University of Tennessee (UT), the National Science Foundation (NSF) Center for High-Performance Reconfigurable Computing (CHREC) at the University of Florida, OpenFPGA.org, and others.

Mission Relevance

This research supports DOE's Office of Science Ultrascale Computing Initiative and the President's Information Technology Advisory Committee (PITAC) as being "critical to scientific leadership, economic competitiveness, and national security." It is anticipated to grow into a broader program impacting diverse technologies supporting the Defense Advanced Research Projects Agency, Air Force, Army, Department of Homeland Security, National Security Agency, NSF, and National Aeronautics and Space Administration. This research should demonstrate how key DOE codes (bioinformatics, climate/weather, molecular dynamics, and matrix equation solution) can achieve major performance gains (up to 100× speedup) by harnessing FPGAs, leading the way for other codes to follow. FPGA acceleration may prove attractive for ORNL supercomputer performance to exceed 1 petaflop, enabling major application speedups and scientific breakthroughs.

Results and Accomplishments

Significant progress was made on all tasks with 50× and 100× speedups (over a 2.2 GHz Opteron) achieved for human-genome DNA matching on Cray XD1s with Virtex-II and Virtex-4 FPGAs, respectively. These computation speedups were observed to scale (increase) with both the number of FPGAs used and the database query size. Tasks were expanded/accelerated via no-cost additions

(CHiMPS/Xilinx's HPC team, a UT professor and full-time Ph.D. student, Cray and Mitrion programmers, SGI FPGA system and software). Development tools, ranging from VHDL to C-to-FPGA (CHiMPS, DSPlogic, Viva, and Mitrion-C), were evaluated for performance and ease of use. Bioinformatics, molecular dynamics, and weather/meteorology codes were successfully ported to FPGAs with up to two orders of magnitude performance achieved and published. The molecular dynamics code, ported to both Xilinx and Altera FPGA systems, achieved 7× overall speedup. The mixed-precision matrix solver was coded, and initial Cray XD1 FPGA results are expected soon. Results from this project have been reviewed favorably by and included on the OpenFPGA.org web site. They have extended to the biology community by their inclusion in a tutorial entitled "The Promise of FPGA-Acceleration Processors to Bioinformatics Research." With access to the Naval Research Laboratoy's 150 FPGA Cray supercomputer, a human genome sequence (155,000,000 characters) was compared with that of a mouse (165,000,000), a process involving 51×10^{15} cell updates/second (CUPS). The solution (which would require 20 years for one 2.2 GHz Opteron), took 5 months on one FPGA, 6 weeks on 150 Opterons, and one day on 150 FPGAs for a measured rate of 46 teraCUPS. This corresponds to 605 teraCUPS had all FPGAs run simultaneously (dedicated mode), a 7,350× speedup for Virtex-2 FPGAs over one Opteron (14,700× speedup had Virtex-4 FPGAs been used).

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00008

Predictive Simulation and Virtual Design of High-Speed, High-Density Molecular and Nanoscale Sensors and Devices

Vincent Meunier, Edoardo Apra, Jerzy Bernholc, Robert Harrison, William Shelton, and Bobby Sumpter

Project Description

Theoretical methods have recently evolved to a point where the properties of materials can be successfully predicted based solely on their atomic structure and without any experimental input. Furthermore, simulation can provide a "theoretical microscope," by identifying the origins of the various properties of a given structure and by uncovering principles that can be used to systematically enhance the desired characteristics, or to suppress the unwanted ones. Unfortunately, current first-principle methods and software can handle only a few hundred atoms. Developing scalable methods, able to fully utilize petascale systems, would enable predictive simulations of entire device structures from first principles, thereby revolutionizing the design of molecular and nanoscale sensors and electronic devices. Our expertise in quantum methods, applied mathematics, and large-scale computing uniquely positions us to establish ORNL as a leader in the emerging field of predictive design of nanodevices.

Mission Relevance

Developing scalable methods that can fully utilize petascale systems would enable predictive simulations of entire device structures from first principles, thereby revolutionizing the design of molecular and nanoscale sensors and electronic devices. This virtual design would impact many areas critical to DOE needs, such as the development of specific biosensors with nearly single-molecule detection limit, and of ultradense, ultrafast, molecular-sized electronic components, with very small power requirements and persistent, reprogrammable memories. The proposed work will also benefit other agencies. The National Science Foundation is expecting multiple program calls in the development of petascale software and its applications in several of its directorates. We also expect additional calls for proposals in areas of strategic Department of Defense interests. The National Institutes of Health is already soliciting proposals for its Centers in Nanomedicine.

Results and Accomplishments

We have used the codes optimized during the first year of this project to make a number of important predictions and undertake theoretical work in various areas of materials sciences, mainly in the area relevant to energy and energy storage. We studied how modification of the chemistry of the graphitic layer making up a carbon nanotube can help increase energy storage and how it affects the electronic transport properties of the chemically modified system. This is important for an energy storage device that hinges on the storage of electrons, as the matrix forming the device should display good conductivity to ensure fast release and subsequent uptake of charges. Our work has been published in several journals. A detailed description of our achievements can be found in the papers whose references are given below.

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00009

Storage Virtualization: An Integrated Approach to Machine-Room Storage Management

Sudharshan S. Vazhkudai, John W. Cobb, and Xiaosong Ma

Project Description

A renewed national priority is procurement and optimized utilization of petascale supercomputers and centers. Sustained performance and availability of such large centers is a key technical challenge that will significantly impact their usability. As recent research shows, storage system faults, data unavailability, and input/output (I/O) bandwidth bottlenecks can cause even today's supercomputers to fail. These problems significantly impact common supercomputing I/O operations such as data staging, offloading, checkpointing, and prefetching, leading to suboptimal high-performance computing (HPC) center performance, increased job turnaround time, frequent resubmissions, and poor use of precious center resources as well as users' allocated time. Solving these issues is highly critical for scaling to petascale systems. Modern HPC centers and users' job workflow offer numerous opportunities for significant improvements along the storage hierarchy that have gone unnoticed. To this end, we propose a fresh look at the HPC storage crisis with an eye toward virtualizing the entire center as a system. In this setting, we propose to perform the following: (1) global coordination and scheduling of data and computational activities, (2) construction of novel storage abstractions using untapped storage resources available in the machine room, and (3) their conjoined use with each other and traditional storage elements.

Mission Relevance

DOE is building a leadership-class computing facility (LCF) at ORNL, which is expected scale to a petaflop in the coming years. LCF is expected to be a national user facility running significant applications. Successful delivery of petaflop capability is dependent on robust computing, storage, and networking environments. The success of this project will enable the delivery of robust storage solutions for LCF. This can significantly improve the usability, performance, and uptime of LCF, all of which are of high importance to DOE. In addition to DOE, the National Science Foundation and the Defense Advanced Research Projects Agency are soliciting proposals for large-scale HPC acquisitions. Machine uptime and productivity (percentage of user jobs successfully completed with resubmissions) are key metrics when it comes to measuring the success of these high-end petascale machines. I/O and storage problems addressed by this project are of significant importance to the HPC solicitations from these agencies.

Results and Accomplishments

On-the-Fly Data Reconstruction. We have developed an online, staged-data reconstruction technique in the Lustre parallel file system to recover from data unavailability during job execution. Our reconstruction technique can trap an I/O error and seamlessly recover a running job's data from remote data sources. Our simulation results indicate a significant reduction in job resubmission rates due to this technique.

Just-in-Time Staging. We have developed a just-in-time staging framework that uses a combination of batch-queue predictions, user-specified intermediate nodes, and decentralized data delivery to coincide input data staging with job start-up. Timely staging of input data optimizes space use and also avoids delays due to storage failures. Our preliminary prototype has been integrated with the Portable Batch System job submission system, BitTorrent data delivery, and Network Weather Service network monitoring facility.

Timely Offloading of Result Data. We have adapted the same framework for the timely, decentralized offload of result data, addressing gaps in extant direct-transfer-based offloading. The decentralized offload maximizes bandwidth, provides fail-over capabilities for the offload, and meets center-user Service Level Agreements.

Memory-Based Storage for Checkpointing. We have built a checkpoint storage device, built from memory resources, that acts as an intermediary to the central parallel file system. Our system comprises a dedicated manager that aggregates memory resources from processors (benefactors) and makes it available as a collective space for checkpointing clients, using a standard POSIX file system interface, thereby alleviating the I/O bandwidth bottleneck for checkpointing I/O.

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00010

Virtualized Systems Environment for Petascale Computing and Beyond

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Project Description

DOE is deploying petaflop computing. In order for systems this size to run "out of the box," several challenges in petascale system software and application runtime environments have to be addressed to ensure day-one operation. Efficiently exploiting tens of thousands to hundreds of thousands of processor cores using thousands similar number of interdependent computational tasks requires appropriate scalability, manageability, and ease of use at the system software and application runtime environment level. Furthermore, the expected system upgrade interval demands an incremental strategy for scientific application development and deployment that avoids excessive porting. This project addresses these issues at the system software level through the development of a virtual system environment (VSE). In addition to providing a scalable and reliable "sandbox" environment for scientific application development on desktops and clusters, the VSE will offer an identical production environment for scientific application deployment on terascale and petascale high-end computing (HEC) systems. The proposed VSE concept enables "plug-and-play" supercomputing through desktop-to-cluster-to-petaflop computer system-level virtualization based on recent advances in hypervisor virtualization technologies. The goal of the proposed effort is to advance the race for scientific discovery through computation by enabling day-one operation capability of newly installed systems and by improving productivity of scientific application development and deployment.

Mission Relevance

This work is relevant to the DOE Office of Science program for operating/runtime systems for extreme-scale scientific computing. More specifically, it deals with the issues of (1) developing scalable, fault tolerant system software and runtime technologies to enable the efficient utilization of petaflop computers; and (2) developing tools that increase the productivity of the application development environment for petascale systems. It also benefits the National Science Foundation (NSF) Directorate for Computer and Information Science and Engineering program for software and tools for HEC and the Defense Advanced Research Projects Agency's Information Processing Technology Office. We have successfully secured follow-on funding for the resilience aspect of this work from a Department of Defense agency.

Results and Accomplishments

We focused on the following topics: tools, a Virtual Machine Monitor (VMM) for High Performance Computing (HPC), performance analysis of VMM-bypass techniques, and fault tolerance. Based on this project, NSF funded the following two related projects that are associated with our team: (1) virtualization in education, led by our partners from University of New Mexico and Northwestern University (Stephen L. Scott is member of the scientific board), and (2) storage and I/O virtualization, led by our partner from Tennessee Technological University with Stephen L. Scott as a co-principal investigator. We also initiated the very successful Association for Computing Machinery workshop on virtualization for HPC (HPCVirt 2008) with plans to continue the series in the future.

Tools. This effort focused on the OSCAR-V integration, which implements the concept of VSE directly into OSCAR, making it available to the cluster computing community.

VMM for HPC. This effort led to the implementation of a module mechanism for Xen which allows one to decrease the system footprint of VMM and to extend its capabilities on demand. This mechanism is a requirement for fine-grain performance analysis since current profiling tools do not allow the profiling of the overall application life cycle when running within VMs (i.e., the implementation of instrumentation mechanisms).

VMM-Bypass. This effort focused on the evaluation of existing VMM-bypass mechanisms developed during the past year by all major virtualization solutions. We specifically evaluated the KVM I/O bypass mechanism (virtualization solution of the Linux kernel) and the Xen networking bypass mechanism. Both show good performance and could be reused without modifications in an HPC context.

Fault Tolerance. This effort led to the use of the fault tolerance framework initiated in the context of the MOLAR FastOS project. This framework enables the implementation of efficient pro-active fault tolerance policies, validated by simulation. However, there are still limitations imposed by the failure prediction mechanism accuracy (not specific to virtualization but to the nature of proactive fault tolerance).

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00011

Petascale Computing in Nanoscience on ≥100,000 Cores

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Project Description

The overarching goal of this project is to implement a general methodology for computing thermodynamic quantities in nanoscale systems that can make effective use of petascale computing systems with 10^5 or more cores. Thermodynamics in nanoscale systems present new challenges that cannot be met with conventional techniques. Atomic-scale interactions change drastically even over short distances; indeed the mechanisms governing stability can differ between surface and interior of a nanostructure and are often dominated by entropic effects. In this milieu, the physics can be unraveled only at the first-principles level and combined with statistical methods to include entropy. Our approach combines a novel stochastic sampling scheme, the generalized Wang-Landau (gWL) method, to compute the density of states (and hence the entropy and free energy) of a nanoscale system with accelerated density functional theory (DFT) methods that have previously been scaled to thousands of processors. Unlike metropolis Monte Carlo, the gWL is not embarrassingly parallel, but we nevertheless anticipate that the combined gWL/DFT codes will scale to 10^5 or more processors.

Mission Relevance

The application codes, along with the methods and experience we develop in this project, will be part of the computational nanoscience endstation at ORNL. With this, the Center for Nanophase Materials Science (CNMS) and the National Center for Computational Sciences (NCCS) user programs will gain a unique aspect and a competitive advantage over comparable facilities and efforts in the nation. This will allow us to enhance the programs in the DOE Basic Energy Sciences user facilities and ensure the scientific success of the next-generations NCCS machines through plug-and-play petascale computing applications. In particular, this project will allow us to take on new staff scientists who will be available for programs in support CNMS and NCCS.

Results and Accomplishments

1. We have developed a hybrid parallel programming model for the gWL method that will naturally scale to ~10^5 cores when combined with DFT codes.
2. We have implemented a prototype implementation of the gWL/DFT code with LSMS (the locally self-consistent multiple scattering method) at its core and have demonstrated strong scaling to up to 20,000 cores on Jaguar.
3. We demonstrated that the gWL/DFT codes will have similar performance as the underlying DFT code—in the case of gWL/LSMS, the sustained performance we reached is 70–80% of peak.
4. We showed that fast and nonetheless accurate computations of the magnetic energy of magnetic nanoparticles are possible with the LSMS code.
5. By studying simpler models of magnetic nanoparticles, we demonstrated that free energy barriers for switching can be effectively computed with the gWL method.
6. We found that nontrivial nanoscale effects require investigation with ab initio techniques.
7. We demonstrated that the magnetic force theorem holds for magnetic systems in the presence of charge transfer and strong inhomogeneity such as near vacancies or surfaces.
8. We developed a tool for interpreting energy differences strictly of the one electron density of states that is more reliable than previous methods.
9. The specific heat and curie temperature of a small iron cluster was calculated from the density of spin states calculated with the gWL-LSMS code.
10. Petaflop performance was exceeded with the gWL-LSMS on Jaguar as described in http://www.hpcwire.com/features/The_Search_for_Stable_Storage.html.

00012

Modeling Cellular Mechanisms for Efficient Bioethanol Production Through Petascale Comparative Analysis of Biological Networks

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Project Description

The project aims to characterize biochemical and regulatory machineries of ethanol-producing biological systems by scaling algorithms and advancing underlying theory in the area of graph analysis. Graph theory naturally forms the mathematical language to formulate and solve problems on biological networks (of genes, interacting proteins, coexpressed gene products). Biological networks tend to be extremely large (up to millions of nodes) and complex (connectivity is nonuniform). This presents a significant computational challenge and motivates development of parallel algorithms, efficiently scalable to thousands of processors on high-performance competing architectures—one of the ultimate objectives of this project. Our approach to the Library of Parallel Graph Algorithms is centered around very efficient and highly parallelizable implementations for a few core algorithms (e.g., maximum clique enumeration, vertex cover) used as building blocks for more complex algorithms with dozens of applications to bionetwork analysis and reconstruction. At this early stage the acquired graph analysis capabilities were demonstrated to be crucial for the success of the three different biological applications.

Mission Relevance

The 2005 Energy Bill and DOE initiatives aim to replace 75% of our oil imports with renewable alternatives by 2025. The primary approach seeks to produce ethanol from plant biomass using microbial and fungal systems. This process involves degradation of lignocellulose to sugars and their fermentation to ethanol via biochemical pathways that are poorly understood. We propose to investigate mechanisms for efficient functioning of these pathways and their regulation through computational modeling that will require petascale data analytics. The DOE Office of Biological and Environmental Research and the DOE Office of Advanced Scientific Computing Research will benefit from advances proposed in this project. In addition to benefitting DOE, comparative network analysis tools such as those proposed here will have an impact akin to BLAST-like comparative genomics tools in the Human Genome era. As such, National Institutes of Health and National Science Foundation programs dealing with systems-level understanding of complex biological systems, especially comparative evolutionary analysis of metabolic, regulatory, and signaling pathways, will benefit from our innovations.

Results and Accomplishments

Maximal clique enumeration and maximum common subgraph are fundamentally important in graph theory and serve as core elements for more complex graph algorithms. We demonstrated significant acceleration (up to 1000 times) and near perfect scalability (only ~30% loss of peak capacity on thousands of CPUs) for several core algorithms. The following results were obtained on the computer science side of the project: (1) obtained analytically proven estimates for the maximum common subgraph problem and common subgraph problem for multiple graphs, opening new opportunities for applications in alignments of gene sequences, metabolic pathways, and protein-protein interaction networks; (2) proposed a novel load balancing approach to search-tree based optimization algorithms; and (3) developed a novel algorithmic solution for the clique enumeration search problem with almost perfect parallelization scalability.

The acquired graph analysis capabilities were deployed in three types of bioenergy related projects: (1) conducted analysis of protein co-expression in *Rhodopseudonomas palustris* (a microbe capable of degrading aromatic compounds and releasing H_2) that revealed a new conceptual mechanism balancing activity of its crosscutting biochemical pathways; (2) developed novel algorithms for accelerated protein folding and detection of the native folds in such simulations, an important task for achieving more complete reconstruction of the intercellular network mechanics in targeted organisms; and (3) applied novel algorithmic frameworks for protein identification and inferring protein functional modules to (a) quantify changes in cellulosomal proteins in response to various carbon sources (cellobiose, amorphous cellulose, and crystalline cellulose) and (b) identify and categorize regulatory proteins in *Zymomonas mobilis*—a promising ethanogenic bacterium.

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00014

An Evolutionary Framework for Porting Applications to Petascale Platforms

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Project Description

This project investigates a fundamentally new approach to petascale computing that addresses the severe synchronization overheads inherently associated with large numbers of processors. Inherent tight coupling among processors is relaxed by incrementally and semitransparently enabling speculative computing using novel synchronization mechanisms such as reverse computation. The envisioned framework attempts to move beyond traditional checkpointing-based approaches to newer directions in reversible computing, thereby freeing applications from tight global coupling. This framework enables easy porting of existing message passing model (MPI)–based applications and moving them in a backward-compatible, evolutionary fashion to petascale computing platforms, without having to restructure existing codes. The overall effort offers significant benefits along multiple directions, including new scientific techniques such as reverse computation–based relaxed parallel execution, new petascale extensions to existing message passing standards, and least-effort paradigms to porting existing applications for potentially significant productivity and efficiency improvements.

Mission Relevance

The project will benefit supercomputing applications, such as large-scale scientific computing/simulations that are critical to DOE and other agencies. It is intended to improve the utilization of high-performance computing platforms and also facilitate gains in productivity by reducing model redevelopment and/or porting efforts for execution on larger numbers of processors. In addition to DOE, the technology developed as part of this project potentially could be applied to scalable scientific computing efforts in other agencies, such as the Defense Advanced Research Projects Agency's High Productivity Computing Systems (HPCS) program.

Results and Accomplishments

We have made progress on all the four tasks originally planned. We have an initial, backward compatible framework for a subset of the MPI interface extended to support asynchronous, speculative execution. We have demonstrated the feasibility of scalable, asynchronous collective communications and have shown runtime performance that is very competitive with native synchronous MPI implementations on Cray XT4 up to 16,384 cores. We also have demonstrated the significance of performance gains of reverse computation vs checkpointing in reversing basic linear algebra services (BLAS), especially due to caching effects. We have demonstrated scalability of our Time Warp–based speculative engine with synthetic benchmarks on up to 8,192 cores, which, to our knowledge, is the first of its kind in the world. We have studied the fundamental aspects of reversibility in various scientific simulations, including molecular dynamics and electromagnetism. We have uncovered new fundamental modeling aspects that seem to underlie reversibility of models. Interesting relationships have been obtained between the trace size of simulation and entropy of the simulated phenomenon. These findings have strong bearing on the use of asynchronous speculative execution methods for porting applications to petascale platforms. We developed new models of vehicular traffic using a novel reversible formulation and executed them in parallel using speculative execution. On these models, we have achieved a 65% increase in speedup compared with a traditional nonspeculative execution on as few as 32 processors. We have now added support for level 2 primitives in our reversible version of the BLAS library. Our results and findings are being documented in technical reports, and we are preparing to publish them in reputed conferences for wider dissemination.

Publications

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00016

Development of a Global Advanced Nuclear Fuel Rod Model

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Project Description

Advanced nuclear fuel is the primary technology required for the realization of new nuclear reactor technologies, including transmutation fuel designed to consume spent fuel and nuclear weapons material. Central to the development of advanced nuclear fuels with enhanced reliability and accident performance, extended burnup, ease of fabrication, capability to contain significant fractions of minor actinides, and reprocessing is the need to develop a fundamental understanding of the materials involved. The objective of the research is to develop the computational framework needed for fine-scale simulation of nuclear fuel, thereby incorporating the relevant multi-physics and chemistry occurring within a fuel pellet/rod during operational conditions. Such a computational framework should be capable of simulating a large-scale, fully three-dimensional model of nuclear fuel elements to the desired resolution dictated by underlying fuel physics and chemistry. The developed model will provide interfaces and mechanisms for coupling reactor fluid thermodynamics, thermomechanics, neutronics, fuel chemistry, chemical species transport, and more detailed multiscale physics models. Due to the physical complexity of the problem and the need for high spatial and temporal resolution of the model, scalable computing algorithms and approaches that target relevant phenomena at appropriate time and length scales will be developed. The nuclear fuel modeling computational framework will be implemented on the ORNL leadership computing systems.

Mission Relevance

Comprehensive, fully three-dimensional computer models of a nuclear fuel rod do not exist. Current "legacy" fuel performance tools are entirely empirical; hence they are not predictive for processes outside existing design space and databases. Execution of this program will therefore be groundbreaking work in the area of fuel performance modeling. This work is directly relevant to the DOE Global Nuclear Energy Partnership Program, specifically for the development and modeling of advanced reactor fuel systems. The development strategy is to build on ORNL's existing capabilities in fuel performance modeling and to leverage advanced computing tools developed under the DOE projects Scientific Discovery Through Advanced Computing, and Advanced Simulation and Computing. The detailed multi-scale model of the nuclear fuel rod will provide the framework for incorporating atomistic and electronic fuel models funded by the DOE Office of Science, Basic Energy Sciences program.

Results and Accomplishments

During FY 2008, the project's second year, we extended capability to the nuclear fuel model by incorporating additional physics modules and improving on the existing ones. The model developed during FY 2007 combined neutronics, thermal, and mechanical solvers, where neutronics was implemented as an internal heat source for the thermal solver and the effect of fluid flow was modeled as a convection boundary condition with prescribed fluid temperature and velocity. All the material properties and heat sources were assumed constant. During FY 2008 we developed and implemented separate modules for neutronics, isotope composition, chemistry, and material properties that allow for modeling of nonlinear variation of properties based on temperature, material composition, power generation history, etc.

The scalability of the Finite Element Method (FEM) solver on ORNL's Cray XT3 was demonstrated during the first year of the project by solving the solid mechanics problems of 330 million and 1.1 billion degrees of freedom on up to 8000 processor cores. The models used regular, rectangular meshes that were generated through node connectivity maps. The FEM models with spatial resolution capable of resolving the microstructural heterogeneity and geometry of the nuclear fuel pellets require large unstructured FEM meshes and, accordingly, result into very large models that cannot be generated using simple spatial connectivity relations. During the second year, we developed computer programs, partly based on publicly available software, that can generate large-scale models of nuclear fuel and can map discrete microscale models onto large-scale FEM models.

For the remainder of the project in FY 2009 we plan to implement the transport solver that will add capabilities to model the effect of transport of fission products, effect of the transport on material properties and composition, and the overall time evolution of the nuclear fuel.

00026

Waveguide Entangled Photon Sources for Quantum Information

Warren P. Grice, Ryan S. Bennink, Philip G. Evans, and Travis S. Humble

Project Description

The rapidly emerging field of quantum information science (QIS) exploits novel features of quantum physics to open up new possibilities in computing and information management. One of the most exciting prospects is the quantum computer, which would simultaneously process superpositions of different bit states and perform tasks intractable on any classical computer. The creation and manipulation of physical quantum bits is the first step in implementing a quantum computer and represents the current frontier of QIS and the ultimate technical goal of this project. Photonic quantum computing is one of the leading proposals for quantum computing, drawing on decades of experimental techniques for encoding information in the properties of individual photons. Yet current sources for single and entangled photons are unwieldy and often ill suited for quantum computing. This project addresses these shortcomings with the development of an entangled photon source integrated into an optical waveguide device. A quantum optical "chip" provides the ability to engineer a photon source with the requisite properties while providing the integrability and scalability necessary for a functional quantum computer. Characterization and performance testing will complement the design and, ultimately, the fabrication of the proposed device.

Mission Relevance

QIS is a multidisciplinary endeavor, and significant overlap already exists between QIS needs and the missions of DOE, particularly as reflected in ORNL capabilities (computing, quantum optics, quantum dots, nanoscience, materials science, etc.). This was recently brought to light in the American Competitiveness Initiative (ACI), in which QIS was highlighted as a national priority and DOE was given the task of "overcoming technological barriers to the practical use of quantum information processing." The development of a waveguide entangled photon source clearly addresses the ACI challenge. The Department of Homeland Security (DTO, NSA, CIA) and the Department of Defense (ARO) are currently funding projects in quantum computing and quantum communication. The development of a compact entangled photon source with spectral and spatial characteristics perfectly tailored for these applications will directly benefit these programs.

Results and Accomplishments

This project has yielded a number of significant accomplishments. First, we have established a connection between transverse momentum entanglement and the spatial mode composition of emitted photons. This result is relevant to the quantum computing community because photonic quantum computing involves interference of photons from independent sources, a process that is impacted directly by the spatial quality of the interfering photons. A second group of results is related to the spectral properties of photon pairs generated in waveguides. Starting from first principles, we have developed the theoretical framework for down-conversion in structured environments. Using this theory, we have obtained theoretical proof that a waveguide can be more efficient at producing spatially unentangled photons than a bulk crystal and have derived the conditions under which this is the case. In addition, we have analyzed the effect that simple optical resonators (i.e., cavities formed by external or internal reflectors) have on the joint spectrum of photon pairs and on the total pair production efficiency. These theoretical results guided the design process, which yielded a number of proposed configurations, each with its advantages and disadvantages. In the laboratory, our fabrication efforts led to a wealth of practical information regarding micro-machining of potassium titanyl phosphate (KTP) using a focused ion beam. The project culminated with the successful fabrication of ninth-order surface Bragg gratings in periodically poled KTP.

Publication

Evans, P. G., R. S. Bennink, and W. P. Grice. 2008. "Modeling Resonant Cavities for Single-Photon Waveguide Sources." *Proceedings of SPIE 7092,* 709202.

05038

Preparing for New Programming Languages for Ultrascale Applications

David E. Bernholdt, Valmor F. de Almeida, Richard F. Barrett, Wael R. Elwasif,
Robert J. Harrison, and Aniruddha G. Shet

Project Description

The languages developed under the High-Productivity Computing Systems (HPCS) program (Chapel, Fortress, and X10) offer a significant number of new features aimed at improving the productivity of scientific application developers and users. Traditional programming approaches (sequential language + message passing library + thread library) will face increasing challenges for scale to petaflop and exaflop performance levels, as well as scaling of the codes themselves. The HPCS languages currently offer the best path to providing computational scientists with qualitatively new tools that have the potential to scale to meet the challenges of the coming decade. However, these languages are significantly different from the traditional approach to parallel programming, and developers will require help and guidance to rapidly and effectively adapt their applications to fully realize the capabilities of coming systems. The objective of this project is to develop local expertise in these new languages in the context of applications of strategic interest to ORNL and DOE and to interact with the language developers to ensure the best possible support for these applications. This work will give ORNL applications and facilities a strong strategic advantage in bringing these new programming environments into production when they reach the appropriate level of maturity.

Mission Relevance

This work is focused on developing expertise and experience with next-generation parallel programming environments for coming petaflop and exaflop computer systems. These environments are central to computational science and other simulation applications of interest to DOE, the Defense Advanced Research Projects Agency, and other Department of Defense agencies. The target applications are directly related to key DOE mission areas: computational chemistry and materials, fusion modeling, climate modeling, and nuclear energy. There are direct ties to planned DOE programs such as the Fusion Simulation Project, the Global Nuclear Energy Partnership, and Simulation and Modeling at the Exascale for Energy, Ecological Sustainability, and Global Security.

Results and Accomplishments

During FY 2008 we investigated four of the five proposed mini-applications. We made significant progress in understanding the languages and how they can be used in the target applications. Our work on the Fock Matrix Builder (quantum chemistry) focused on the various approaches of these languages, all to the dynamic load balancing this application requires, as well as distributed array operations. Both global shared counters and task pool mechanisms were implemented to provide dynamic load balancing, exploiting operations, syncronization variables, futures, and other language concepts available in the traditional Fortran+MPI+OpenMP approach. Through the MADNESS Tree Walking application (quantum chemistry), we investigated the role language features, including global address space, object-iterators, dynamic parallelism, and locality control, in separating managing parallel programming concerns like data concurrency, and algorithm for this application. With the AORSA application (fusion), we explored a global view of distributed data structures. For example, AORSA operates on Fourier space as well as an irregular subset of it, specified using Chapel domains, distributions and traits, and X10 regions. Such data structures are combined with syntax for iterating over the distributed data to assemble the linear system. For the Sn Sweep application (neutronics), we implemented simple generic containers in Chapel that distribute the data over locales natively. This approach has the potential to circumvent the time-consuming, error-prone distribution/reconstruction of mesh data on multiple processors. Therefore, it is of great interest to users/developers. We also exploited distributed containers to implement a generic sweeping algorithm that operates on the distributed data in parallel.

Publications

Barrett, Richard F., Sadaf Alam, and Stephen W. Poole. 2008. "Exploring the Performance Potential of Chapel in Scientific Computations." *Proc. 50th Cray User Group Meeting*.

Barrett, Richard F., Sadaf R. Alam, Valmor F. de Almeida, David E. Bernholdt, Wael R. Elwasif, Jeffery A. Kuehn, Stephen W. Poole, and Aniruddha G. Shet. 2008. "Exploring HPCS Languages in Scientific Computing." *SciDAC 2008,* July 14–17, Seattle, Rick Stevens, ed., *Journal of Physics: Conference Series,* Institute of Physics.

Shet, Aniruddha G., Wael R. Elwasif, Robert J. Harrison, and David E. Bernholdt. 2008. "Programmability of the HPCS Languages: A Case Study with a Quantum Chemistry Kernel." *2008 IEEE International Parallel and Distributed Processing Symposium.*

Shet, Aniruddha G., Wael R. Elwasif, Robert J. Harrison, and David E. Bernholdt. 2008. *Programmability of the HPCS Languages: A Case Study with a Quantum Chemistry Kernel (Extended Version).* Technical Report ORNL/TM-2008/011, Oak Ridge National Laboratory.

05040

A Petascale Parallel Programming Environment for Scientific Software

Edoardo Aprà, Robert J. Harrison, and William A. Shelton

Project Description

Next-generation computers composed of ≥100,000 processors, multiple cores per node, and complex memory hierarchies (e.g., the CRAY petaflop computer to be installed at ORNL in 2008) present formidable challenges to the development of highly scalable scientific software. These challenges, pervasive in all computational scientific disciplines (e.g., energy, climate), require the development of novel software tools capable of exploiting the aggregate hardware resources of petascale computers. Our solution to these problems is a latency-tolerant, multi-paradigm environment that insulates the developer of scientific codes from the intricacies of hybrid software (i.e., that effectively treat multithreads and distributed network resources). This represents a significant advance over the current state of the art, which mostly uses message passage interface (MPI) constructs. We aim to reach maximum computational efficiency by developing a parallel execution environment based on the Global Arrays toolkits and built directly on top of the fastest communication protocol available. Other significant outcomes will be the development of in-house expertise in the low-level capabilities of the petascale hardware, and a much reduced and fully understood software stack. We will work with Cray and the ORNL Center for Computational Sciences staff to integrate this software and its requirements into the Cray development and deployment test suites to ensure productive use as soon as the hardware becomes available. These tools will be tested by applying them to NWChem and MADNESS.

Mission Relevance

Our project will have a significant impact on the larger software effort that aims to provide computationally efficient software tools for petascale infrastructure (DOE, National Science Foundation, and Defense Advanced Research Projects Agency all have activities in this direction). While the roadmaps of several current DOE energy-related initiatives (e.g., Global Nuclear Energy Partnership, solar energy) contain a significant simulation component, none of the major DOE Office of Science chemistry and material science simulation codes can yet run reliably and efficiently on the Cray XT4. This is despite significant effort being made by various groups to address software and system issues. We have identified the major causes of this problem as being overly complex and poorly understood software and lack of in-house control over the critical software components. Our proposed activities address these issues by developing a smaller software stack that is fully controlled and understood, and by working to eliminate problems very early in the product life cycle.

Results and Accomplishments

A major first-year achievement was enabling a subset of the NWChem methods to run at scale on the Cray XT4. This was achieved both by modifying the parallelization approach in NWChem and by working closely with Cray to fix some major stability problems that GA/ARMCI were encountering on the CRAY XT4. The modifications at the application level resulted in increasing data locality of distributed data structures (to avoid some show-stopping Cray XT bugs); this has allowed users of the “An Integrated Approach to the Rational Design of Chemical Catalysts” CHM022 INCITE allocation to run density functional theory (DFT) energy and gradient calculations (the workhorse of current quantum chemistry). Work in collaboration with Cray required (1) identification of problematic sections of the NWChem software and (2) coding of a self-contained “reproducer” that has the same behavior as the problems isolated in point 1 so that Cray could easily debug the issue; this has allowed Cray to narrow the root causes of the bugs.

The fixes then deployed at the Cray system software level have been a critical component in improving the stability of NWChem runs so that users of the CHM022 allocation could effectively use the DFT method.

We established the goals for a brand new implementation of ARMCI to overcome both performance and stability issues. This work has led to identifying four more bugs in the Cray Portals software layer; fixes have yet to be deployed. Once these fixes are deployed and the new ARMCI reaches maturity, we expect NWChem to perform near the peak performances expected on Cray XT computers.

The MADNESS active messages layer has been used to motivate additional functionality for ARMCI, the OpenMPI runtime, and has been discussed during the meetings of the MPI3 Forum. The new design of ARMCI (event queue, buffer management layer and task pool) should replace most of the current MADNESS active messages layer.

05043

Global Climate Feedbacks and the Development of Biofuel Climate Scenarios

John B. Drake

Project Description

The attraction of developing renewable energy sources is that biomass production removes as much CO_2 from the atmosphere as the biorefinery and subsequent fuel use emit. The carbon neutral aspect, though attractive, must be considered carefully in the context of land-use change and possible effects on climate and the environment. This project will test the hypothesis that significant feedbacks between the land use of bioenergy crop production, the hydrological cycle, the ocean thermohaline circulation, and climate exist and are a key element of climate change in the next century. We will test this hypothesis by developing a biofuels scenario and simulating the climate under this ORNL-defined biofuels scenario. Our methodology uses the Community Climate System Model to simulate an ORNL-defined biofuels scenario and to elucidate and quantify new feedbacks in the climate system. The novelty of our method will be in the use of a very high resolution land model in conjunction with the coupled climate system model. This is required for two reasons: (1) to capture the land use changes that may be predicted as a result of increased biofuel production and consequent destruction of ecosystems and (2) to represent the multiscale heterogeneous forcing of the climate system by hydrological, biogeochemical, and energy fluxes from the land. Development of the ability to define and evaluate our own scenarios in this important area of climate science will position ORNL as the leading DOE laboratory in climate science and is central to plans for climate modeling initiatives.

Mission Relevance

The growing importance of climate change in the DOE research portfolio should lead to new opportunities for climate simulations that target energy supply and carbon mitigation scenarios. The Climate Change Research Division of the DOE Office of Science, Biological and Environment Research program has as part of its mission to determine the safe levels of atmospheric CO_2 and to improve climate models by making them more comprehensive and reliable. The activities of this project are relevant to these DOE missions in several ways: (1) by implementing a highly resolved land model into a coupled climate system simulation; (2) by developing datasets, methodologies, and conceptual framework to define the land use change associated with increased biomass production; (3) by discovering climate feedbacks associated with biofuel energy strategies; and (4) by assessing the level of impact that biofuels could have on the global carbon budget and temperature and precipitation patterns of future climates.

Results and Accomplishments

Milestones for the first year of the project have been met with a definition of a climate change scenario. This ORNL scenario for bioenergy branches from the A1FI scenario from the Special Report on Emissions Scenarios. We analyzed the climate simulation results of the base case recently run on the National Center for Computational Sciences Leadership Computing Facility. The biofuels extension of this fossil energy–dominated scenario assumes that cropland is allocated first to meet population demands for food, and as a result, the biofuels are grown in the Business Sensitive 2 leftover and marginal land. This scenario has been vetted with several groups, including a team from Brazil.

Crop allocation and bioenergy land use based on clustering algorithms have been mapped to a 4 km land-use grid. We are finalizing these maps, which form the basis of the boundary condition data set that will be used to force the climate model. A few additional variables that indicate length of growing season and more information about the physical climate variables have been added to the clustering in order to gain more realistic coverage of agricultural crops. The clustering technique is being used for these plant functional types as well as biofuel crops under changing climatic conditions.

A revision of the A1FI population scenario has also been suggested and calculated. The standard scenario shows too rapid a decrease in population after 2050, given national and international projections. The model configuration with high-resolution land components is beginning to come together.

05046

Overcoming the Barrier to Ultrascale Climate Simulation

J. B. White III, R. K. Archibald, J. B. Drake, K. J. Evans, D. B. Kothe, and P. H. Worley

Project Description

Climate simulation will not grow to the ultrascale without new algorithms to overcome the scalability barriers blocking existing implementations. Until recently, climate simulations concentrated on the question of whether the climate is changing. The emphasis is now shifting to impact assessments, mitigation and adaptation strategies, and regional details. Such studies will require significant increases in spatial resolution and model complexity while maintaining adequate throughput. The barrier to progress is the resulting decrease in time step without increasing single-process performance. In an attempt to overcome this time barrier, we will implement and test fully implicit, parallel-in-time, and multi-resolution methods. We will use standard tests defined for numerical climate simulations and benchmark solutions to the shallow-water equations on a sphere. We will then be poised to incorporate the best algorithms in full climate models, thus lifting climate simulation to the ultrascale and clearing the way for new predictive skill in climate simulation.

Mission Relevance

This project could revolutionize the scalability of climate simulation, enabling breakthrough scientific progress within the DOE Office of Biological and Environmental Research, Climate Change Prediction

Program (CCPP). Because CCPP funds modeling efforts jointly with the National Science Foundation, that agency's climate science stands to gain from this project as well. The various modeling efforts among U.S. agencies regularly share ideas and implementations, so improved algorithms would be of equal interest to the modeling programs within the National Aeronautics and Space Administration and the National Oceanic and Atmospheric Administration. The methods we propose to develop hold great promise for climate simulation, but they are also applicable to other areas within the DOE Office of Science, particularly those that target ultrascale computing, such as the Advanced Scientific Computing Research program. The applied mathematics program of the DOE Mathematical, Information, and Computational Sciences Division is similarly a natural beneficiary of the numerical algorithms to be developed by this project.

Results and Accomplishments

In the first year of the project we accomplished the following. We developed a fully implicit implementation using the spectral-element formulation in the high-order method modeling environment (HOMME) from NCAR. We are using Trilinos as a solver framework, because the Trilinos project, in collaboration with the PETSc TOPS project, was eager to use our application as a target for a Fortran interface for Trilinos components. We now have results for Test Cases 1 and 2 from Williamson, Drake, Hack et al., results that demonstrate stability for time steps well beyond the stability limit for the analogous explicit method. Despite limited preconditioning (the target of next year’s work), the increased time step for Test Case 2 allowed comparable run time to the explicit, faster for higher resolution, with similar accuracy. We recently completed a parallel-in-time solver for Burgers' equation and got favorable results for the Burgers’ test case of Example 4 from “Adaptive Solution of Partial Differential Equations in Multiwavelet Bases,” by Alpert, Beylkin, Gines, and Vozovoi. For up to 128-way parallelism on this small problem, the parareal algorithm converges to the high-resolution serial solution in just two iterations. In developing the Burgers’equation solver, we developed a new time-integration method and a new linear solver, both complementary to parareal. We have developed a complete curvelet-based shallow-water formulation, using a periodic longitude-latitude mapping of the sphere, and we have preliminary results of Test Cases 1 and 2. This curvelet formulation allows acceleration of time integration by performing multiple steps of integration in a single step while maintaining sparsity. We are now implementing this time acceleration and optimizing the sparsity of the curvelet operators to maximize performance.

05047

Cost and Effectiveness of Fault Tolerance in Quantum Computing

Ryan Bennink, Jim Kohl, Doug Lepro, and Dude Neergaard

Project Description

Quantum computing (QC) is a future technology that has the potential to radically alter the computing landscape by making feasible certain kinds of important, but currently intractable, computations. The true potential of QC will depend critically on the effectiveness and cost (hardware and operational burden) of methods to overcome the ubiquitous imperfections in real devices and environments. Such methods call for a large amount of physical redundancy, making QC far too large to be simulated using known methods. In this project, we are developing a groundbreaking simulator of quantum computers that have a large fault-tolerant redundancy. This simulator will lead to pioneering studies that go beyond existing studies of error codes and generic estimates of critical error thresholds in several ways: (1) by predicting the start-to-finish performance of “killer app” quantum algorithms in realistic settings, (2) by determining trade-offs between cost and performance, and (3) by identifying performance barriers and possible solutions. The knowledge to be gained from such numerical studies is essential for the development of robust quantum algorithms and architectures.

Mission Relevance

QC has been identified as a national research priority and a strategic priority for ORNL. It is of great interest to military and intelligence communities around the world because of its potential to render current encryption technologies insecure and to solve certain intractable computational problems. U.S. agencies including DARPA, IARPA, ARO, NRO, DTO, and NSA currently fund research on QC. At present it is uncertain which of the many proposed QC technologies may be successful. By realistically modeling a hypothetical quantum computer, we hope to firmly establish the feasibility of quantum computing and identify technological opportunities, as well as critical challenges. Such work will bring QC a step closer to reality and benefit the aforementioned agencies. Furthermore, it will strengthen ORNL's position as a leader in high-performance computing and establish the Laboratory as a "go-to" player in the development of a potentially game-changing technology.

Results and Accomplishments

During this project's first year, our work had three major thrusts: (1) development of an efficient simulation method; (2) explicit specification of Shor's quantum factoring algorithm, including error-correction, as a case study for simulation; and (3) development of the software infrastructure. Our major scientific achievement was the development of a multifaceted method for substantially reducing the memory and computational steps needed to simulate a fault-tolerant quantum computer on a conventional (nonquantum) computer. This method is based on the identification of a basis (coordinate system) in which the state of the quantum computer can be expressed in highly compact form and on an approximation technique that identifies and discards negligible terms. In the second thrust, a literature review was conducted to identify the most efficient implementation of Shor's algorithm currently available. Various parts of the algorithm were gleaned from several papers and assembled into a complete implementation, specified in the form of pseudocode. Third, a preliminary simulation infrastructure was implemented, providing quantum circuit specification, data structure generation, and simulation of quantum operations. The specification semantics provide sufficient flexibility for designing hierarchical/nested quantum circuits, as will be required for complete quantum computers with multiple levels of error protection. Combining these efforts, we performed mock simulations of a quantum computer, estimating the memory and flops (floating point operations) involved at each step of the simulation. According to these mock simulations, a full simulation of a 20×7 qubit computer using our novel method is predicted to require ~10 GB of memory and $\sim 10^{10}$ flops per simulation step, which is tremendously less than the $\sim 10^{34}$ GB and $\sim 10^{42}$ flops of existing simulation methods.

05095

A Knowledge Discovery Framework for America's Transportation System

Budhendra Bhaduri, Raymond Boeman, Frank Southworth, Cheng Liu, James Nutaro, Stanton Hadley, Glen Harrison, Oscar Franzese, and Amy Wolfe

Project Description

America's ground transportation system has helped ensure economic prosperity and high quality of life through efficient movement of people and freight. It is also one of the primary forces behind the two major global crises of today's world—namely, energy scarcity and climate change. To reduce U.S. oil dependence, environmental impacts, and congestion, a number of alternative energy supply, distribution, and end-use transportation systems, technologies, and policies are being explored. However, it is still unclear when and in what precise combination these sources and technologies will emerge as successful and sustainable solutions. Ideally, future plausible development and implementation strategies for alternative energy resources and technologies will secure and support a societal system in which energy, environment, and mobility interests are simultaneously optimized. Given the intertwined nature of such a system across wide geographic scales, assessing the effectiveness of possible planning strategies and discovering their unanticipated consequences require data collection, modeling, and simulation at the finest data, process, and societal response levels *coupled* with the system's behavior over large spatial and temporal scales. The primary goal of the project is to design, develop, and test a simulation-based knowledge discovery framework that enables scenario-based analysis leading to identification and visualization of the consequences of alternative energy use scenarios.

Mission Relevance

ORNL, with internationally recognized experience and expertise in geospatial data sciences, high-performance discrete event simulations, transportation planning, and vehicle and energy technology development, is strategically positioned to develop such a capability. This project is proposed to support ORNL's commitment to transportation initiatives that help address the nation's increasing challenges over energy use and dependency, climate change, and economic vitality. The proposed high-resolution, simulation-driven framework will clearly fill a critical need for decision makers at all levels—local, state, regional, and federal.

Results and Accomplishments

To establish a framework in which the interdependencies within the transportation system can be assessed relative to various scenarios, we have developed high-level metrics from a functional standpoint. The most fundamental function is the movement of people and freight. Metrics have been developed with simultaneous consideration of energy, infrastructure, vehicle, and societal requirements. We have compiled a list of the modeling and simulation approaches available to address the interdependency elements of the transportation systems at different levels of granularity and geographic scales. An initial analysis was performed to assess the requirements for developing new algorithms and models to capture both transportation engineering as well as social and behavioral dimensions necessary for the proposed knowledge discovery framework. These were further evaluated for their suitability to be scaled geographically and integrated within high-resolution and high-performance modeling and simulation. Three major transportation knowledge discovery framework components are data, traffic simulation engines, and analysis tools. We have collected, processed, and analyzed the geographic information system data, such as street networks, business locations, and population distributions. The transportation data includes National Household Travel Survey and workers flow among census tracks. We selected an open-source, agent-based traffic simulation model, TRANSIMS, as the basic development platform. TRANSIMS has two major parts: Router, a trip assignment model, and Micro-simulator, a microscopic cell-and-agent based traffic simulation model. Both modules were modified for this effort. To evaluate an alternate approach, a new event-based mesoscopic traffic simulation model was also developed to compare with Micro-simulator. The ORNL Meso-simulator is an implementation of a discrete event model of traffic moving on a network of roads, the development of which was completed this year. This model is closely based on Burghout's Mezzo model. The simulation was tested using high-resolution data for, and daily commuting patterns of, 173,000 workers residing in of Knox County, Tennessee.

Publications

Bhaduri, B., C. Liu, J. Nutaro, and T. Zacharia. 2008. "Ultrascale Computing for Emergency Evacuation." In J. Voller (ed.), *Wiley Handbook of Science and Technology for Homeland Security,* in press.

Dalal, P., C. Lui, and B. Bhaduri. 2008. "Developing Trip Chain Sequence Probabilities for a National Household Travel Behavior Model." *Proceedings of the 71st American Pacific Coast Geographers Conference,* Fairbanks, Alaska.

05109

Joining Ultrascale Computing and Neutron Scattering Studies to Enable Revolutionary New Materials Development

Thomas A. Maier, Gonzalo Alvarez, Jeremy Meredith, Michael S. Summers, and
Thomas C. Schulthess

Project Description

The goal of our combined modeling/simulation and characterization project is to develop a capability for the deliberate design of complex materials with applications in the energy sector. Our immediate aim is to develop simulation tools with predictive power that will enable computation of emergent properties of strongly correlated electron materials. Additionally, we propose to perform neutron scattering characterization experiments along with the simulations in order to verify predictions, validate the models, and further refine properties. On the computing side, we will focus our efforts on the development of algorithms and computer codes that make effective use of ultrascale computing infrastructure, which will be needed to perform simulations that can predict physical properties of realistic, materials-specific models. The aim of the neutron scattering measurements will be to test, confirm, or reject the hypotheses made with the simulations, and, if necessary, in an iterative process improve the models and computational predictions. As proof of principle, we will study cuprate high-transition-temperature (high-Tc) superconductors, focusing on the pairing mechanism, where we have high hopes in solving one of the most important problems at the forefront of condensed matter science. The tools and procedures we develop in this project will be applicable to a range of new materials systems that will be part of the solutions to the energy challenge.

Mission Relevance

This project is relevant to several DOE initiatives. It is consistent with the vision for computational science beyond the petaflop limit that is being discussed at the highest levels at DOE. Specifically, the DOE Office of Science, Advanced Scientific Computing Research, Mathematical, Information, and Computational Sciences program will greatly benefit from the computational capability developed in this project. The new tools will also be beneficial to the Center for Nanophase Material Sciences (CNMS) by providing a new capability that will enable growth of its user community, an important goal of the CNMS. The project is also in line with DOE's basic research needs for superconductivity. In a recent report, it was stated that "bridging the gaps in practical superconductor performance requires not only empirical exploration of new materials and the factors affecting their performance but also a fundamental understanding of the microscopic origins of superconducting behavior." In addition, this project will help establish ORNL as a leader in the use of neutron scattering in nanoscience and technology, fulfilling an expectation of DOE.

Results and Accomplishments

Our work in FY 2008 focused on extending, optimizing, and accelerating the DCA++ code that implements a dynamic cluster approximation for models of correlated electron systems. Our scientific/technical accomplishments during FY 2008 can be summarized as follows:

1. We completely rewrote the DCA++ code base using generic programming techniques that build on the model of the C++ Standard Template Library.
2. We extended the scope of the DCA++ code to cover models with disorder in the interaction strength.
3. We developed a hybrid parallel programming model for the DCA++ code that naturally scales to O(100,000) cores when applied to disordered Hubbard models.
4. We demonstrated weak scaling of the DCA++ code to up to 31,000 cores on Jaguar with a sustained performance that routinely achieves near 100 teraflops.
5. We increased the speed of the calculations by running the quantum Monte Carlo (QMC) parts of the code in single precision without significant reduction in accuracy.
6. We accelerated the DCA++ code using graphics processing units, resulting in significant speedups (up to 19 times faster) while retaining the accuracy required for scientifically meaningful results.
7. We implemented a Lanczos-based exact diagonalization solver to replace the QMC solver for models with complex interactions.
8. These advances have allowed us to study the effects of disorder on superconductivity in the Hubbard model of cuprate superconductors.

GENERAL CATEGORY

05104

Imaging of Molecular Structure and Electron-Driven Dynamics

Mark E. Bannister, Robert L. Hettich, Charles R. Vane, Douglas E. Goeringer, Charles C. Havener, Gary J. Van Berkel, Herbert F. Krause, Michael R. Fogle, Jr., David R. Schultz, Robert E. Continetti, Mats Larsson, and Richard D. Thomas

Project Description

A large range of energy-relevant science and technology requires the development of new tools to understand the dynamics of chemical, atomic, and physical structure and change on the molecular scale. In this project, we are developing novel techniques based on creating and storing molecular ions in an electrostatic storage trap long enough that they cool to a well-defined state or range of states, initiating a reaction via interaction with another particle such as an electron, molecule, or material surface (simulating the relevant environment or as a tool to probe molecular structure and dynamics), and finally imaging the resultant fragments. Proof-of-principle experiments will demonstrate these steps for both a relatively small molecular ion of relevance to atmospheric chemistry and several larger molecular ions important in biological science, utilizing an electrostatic ion beam trap, part of the recently upgraded ion research facility in the Physics Division. These electron-induced fragmentation experiments will involve interfacing an electrospray ion source and low-energy electron gun to the trap and will probe the dependence of the fragmentation process on the internal state of the molecular ions by varying the cooling parameters of the trap. The work will be carried out by an interdisciplinary team from the Chemical Sciences and Physics divisions and universities with expertise in molecular ion chemistry and molecular ion production and storage technologies.

Mission Relevance

Many of the most important challenges facing society today are related to energy production, use, and impact and are central themes in DOE's mission. To answer some of the most basic and pivotal scientific questions underpinning these challenges requires development of new tools to probe structure and dynamics at the molecular level. Of interest to the DOE Office of Science, Basic Energy Sciences, insight into new methods for dissociation of large ions produced by electrospray ionization sources afforded by the unique capabilities of a molecular ion storage ring facility can make tandem mass spectrometry an even more powerful analytical technique. In support of the DOE Office of Science, Fusion Energy Sciences, the tools developed in this project will enable research aimed at answering key questions that underpin successful operation of the International Thermonuclear Experimental Reactor and other next-step reactors regarding edge and divertor plasma operation and issues such as tritium retention in the walls. Within the DOE Office of Science, Biological and Environmental Research, there is substantial interest in improving the capabilities of mass spectrometry to more comprehensively probe microbial proteomes and protein complexes. A key element of these studies is better understanding and control of ion fragmentation.

Results and Accomplishments

During FY 2008 a number of tasks were completed as we integrated key experimental components in order to perform the proposed proof-of-principle experiments during the second year of the project. The electrostatic ion trap was modified with an increased length to accommodate an electron gun and optics for side-injection of molecular ions. Extensive simulations were performed which led to the addition of trim electrodes to correct for any misalignment. Molecular oxygen ions were injected into the trap, and simultaneous detection of two oxygen atoms from dissociative charge exchange on the residual gas were observed on the two-dimensional neutral fragment imaging detector.

An electron gun was designed and constructed; it features nonmagnetic copper electrodes to produce high currents using only electrostatics to minimize perturbations on the ion orbits in the trap. Gun side shields prevent stray electrons from reaching the mirror regions of the trap. A control system for powering the cathode heater and gun electrodes was constructed and tested. The cathode was activated over a period of 10 days to achieve sufficient emission. Initial optimization of the electron extraction and acceleration voltages was performed, and the perveance of the gun was measured.

Preliminary studies on the production of O^{3+} ions using an electron cyclotron resonance ion source yielded beam currents of 15 nA; further optimization of the source extraction optics should yield at least a factor of 2 more. Imaging experiments on fragmentation of O^{2+} and O^{3+} ions will be completed in the first part of FY 2009.

An Analytica-type electrospray ion (ESI) source has been obtained and assembled. High-voltage isolation components have been procured in order to bias the ESI system for optimum ion extraction. Preliminary mass spectra were measured to optimize the molecular ion production for the protonated and metalyated oligonucleotide dGMP and make an initial assessment of electron-induced fragmentation needed to plan fragmentation experiments in the electrostatic trap in the second year of this project.

Summaries of Projects Supported Through the Seed Money Fund

BIOSCIENCES DIVISION

00442

Destroying Pathogenic Bacteria Using Targeted Nanoparticles

Mitchel Doktycz, David Allison, Thomas Thundat, Baohua Gu, Wei Wang, and Christopher Rey

Project Description

Bacteria are a primary cause of human disease and infection. They can adapt, through mutation, to major changes in their environment, such as to exposure to toxic compounds. Consequently, an increasing number of pathogens have developed a resistance to antibiotics. Alternative therapies are needed. Ideally, these therapies should be generally applicable, targeting multiple components, such that naturally selected mutants in the pathogen cannot avoid destruction. In this project, we are pursuing the development of functionalized nanoparticles for the specific targeting and destruction of pathogenic bacteria. This approach targets magnetic nanoparticles to the cell walls of specified bacteria. After targeting, an alternating magnetic field can be used to inductively heat the attached nanoparticles, destroying the pathogen. The use of nanoparticles should result in localized heating, such that only the pathogen in contact with the nanoparticle, and not the surrounding area, would be destroyed. This should minimize or eliminate tissue damage, making this technology suitable for medical applications. Additional advantages are the versatility of the technique and its ability to work in any medium. It should be capable of targeting any selected pathogen through the choice of binding agent and should be capable of destroying pathogens anywhere within the human body due to the depth of penetration of the magnetic field. This technology can be developed as an alternative to antibiotic therapy and can find diverse biomedical uses. Establishing the proof of principle of this technology is the goal of the project.

Mission Relevance

This work is relevant to the Medical Sciences Research program within the DOE Office of Science, Biological and Environmental Research. Further, it is pertinent to DOE programs related to nanoscience and to efforts related to understanding the fate and transport of nanomaterials in the environment. This technology also addresses research needs in national security as a countermeasure to pathogens that are specifically designed to evade antibiotics. Also, the biomedical focus of this work fits the research needs of the National Institutes of Health (NIH). NIH funds both fundamental and applied studies in interfacing nanomaterials to biological systems and to extending research in nanotechnologies for probing and understanding biological processes. Additionally, this research is relevant to several agencies that fund research on biological countermeasures, including the Department of Defense, the Defense Advanced Research Projects Agency, and the Department of Homeland Security.

Results and Accomplishments

The project involved three aims. With regard to Aim 1, synthesis of superparamagnetic nanoparticles, and Aim 2, characterization of magnetic induction heating of nanoparticles, a variety of nanoparticles were synthesized, and magnetic induction heating was assessed. A variety of magnetite and hematite core particles were prepared and clad with silica. An inductive heating apparatus was set up, and assessment of heating of the bulk solution by the various nanoparticles was performed. Additionally, an induction heating system from Induction Atmospheres (Rochester, New York) was tested on five samples of magnetite nanoparticles by the instrument manufacturer. Optimal frequency and power settings for specifically heating the materials were identified. At a nanoparticle concentration of 50 mg/mL, the solution could be brought to boil within 5 minutes. A concentration-dependent temperature effect was demonstrated. These studies indicate that significant heating of the bulk solution can be accomplished. Further, these studies have revealed the importance of using the proper induction frequency. With regard to Aim 3, the targeting and killing of bacteria using nanoparticle and inductive heating, progress was made towards bioconjugation of the nanoparticles, and a demonstration of specific targeting was accomplished.

00451

Nanostructured Three-Dimensional Electrodes for Enzyme Fuel Cells

Abhijeet P. Borole

Project Description

New and clean sources of enegy are needed as fossil fuel–based resources are depleting and resulting in environmental problems such as global warming. Use of renewable resources for energy production can also improve national security by decreasing dependence on oil. Fuel cells using hydrogen as a fuel constitute a potential source of clean energy. These cells, however, use platinum as the catalyst, which has limited availability and is expensive. Enzymes have been used to replace platinum as the catalyst, but their power density is low. The aim of this study was to develop a novel enzyme-biofuel cell architecture exhibiting high electron transfer capability, high enzyme loading and activity, and improved catalyst stability enabling a stable power output and a high power density. Enzyme fuel cells (EFCs) were designed using a biological anode or cathode. The opposite electrode in each case was a platinum-based electrode to demonstrate the proof of principle. This project was also used to promote the undergraduate education and training of two Oak Ridge Institute for Science and Education students who worked on the project. A publication resulted from their work, and one of them was selected for the DOE Science and Energy Research Challenge competition.

Mission Relevance

This project, which focuses on developing alternative energy production devices and, specifically, electricity production from hydrogen and renewable resources using biofuel cells, is relevant to the Hydrogen, Fuel Cells, and Infrastructure Technologies program and the Biomass program, both of the DOE Office of Energy Efficiency and Renewable Energy. Department of Defense programs also have an interest in biofuel cells due to the potential to develop energy production devices that can be portable and, thus, suitable for field and remote applications.

Results and Accomplishments

The enzyme electrodes were prepared using laccase and hydrogenase as the electrocatalysts. The EFCs were designed to enable improved mass transfer of the fuel and/or the oxidant to the electrode as well as to improve the rate of proton and electron transport. The improved design resulted in an increase in the power density to 2.9 kW/m^3 (9.3 W/m^2) using a laccase biocathode coupled to a platinum anode using hydrogen as a fuel. For development of a bioanode, an oxygen-tolerant hydrogenase was isolated from

R. eutropha. The bioanode with hydrogenase as the catalyst was also demonstrated but exhibited low power densities, potentially due to use of partially purified hydrogenase. The biological catalysts have an added advantage of minimal catalyst poisoning and short-circuiting, experienced in conventional fuel cells. The bioelectrode concept was also applied to enable use of alternative fuel sources, such as ethanol and methanol, in a fuel cell with a laccase biocathode. Such fuel cells have applications in the emerging biorefineries and bioproducts industries. The use of nanomaterials such as carbon nanotubes was investigated. It was found that pure enzyme preparations are required to take advantage of the high surface area provided by nanomaterials. This is an avenue for future work. The resistances in EFCs were assessed in detail using electrochemical impedance spectroscopy. This has enabled identification of the individual internal resistances and an insight into the proton and electron transfer limitations. This will be used to further improve design and, therefore, power density.

00470

Systems Neurogenetics of Methyl Mercury Exposure

Elissa J. Chesler and Carmen M. Foster

Project Description

In both humans and animal models, polymorphisms of multiple genes confer either a predisposition to or protection from any particular consequences of exposure to environmental contaminants. By identifying genetic factors that modify response to these substances, novel mechanisms of action can also be discovered, leading to development of exposure assays, susceptibility and individual risk assessment, and remedial measures for exposed individuals. Acute methyl mercury (MeHg) exposure causes neurodevelopmental problems, brain malformations, cerebral palsy, and seizures. We exposed a subset of recombinant inbred (RI) mice to MeHg perinatally to evaluate the genetic sensitivity to behavioral effects and brain gene expression changes in the cerebellum, a site of MeHg's neurological effects. This will allow us to identify gene-environment interactions involving MeHg exposure, especially during development.

Mission Relevance

Methyl mercury is one of the top three environmental contaminants at superfund sites, including the Oak Ridge Reservation. The Superfund Basic Research Program (SBRP) is a collaborative program of the National Institute of Environmental Health Sciences and the Environmental Protection Agency aimed at addressing the health and environmental issues that arise from the multimedia nature of hazardous waste sites. A critical factor underlying the physiological consequences of exposure to most hazardous substances is the genetic variability inherent in the population. Based on our research, we, along with scientists from the ORNL Biological and Environmental Sciences Directorate and Vanderbilt University, have applied for two National Institutes of Health–funded SBRP components for a study on genetic variability in the neurological and behavioral effects of MeHg to complement studies in the role of microbial communities and effects on aquatic populations to be performed at ORNL.

Results and Accomplishments

MeHg offspring and controls were tested at 4 weeks of age on common assays of anxiety, activity, and ataxia, using the light/dark box, open field and Rota-rod apparatuses. The cerebella from a separate group of mice treated with the same MeHg exposure regimen were dissected for gene expression analysis at 4 weeks of age. A total of 193 offspring from the 4 BXD RI strains were tested. Strain-specific effects on both anxiety and ataxia were found. RNA samples were prepared from cerebella of 4 week old mice and hybridized to Illumina Mouse Sentrix 6 mRNA expression arrays. Transcript abundance measured on these arrays was analyzed to detect gene-environment interactions regulating transcriptional changes in response to MeHg. The affected transcripts were further analyzed for gene ontology and KEGG pathway category overrepresentation and were compared to other cerebellar gene expression experimental results. This analysis was performed using our own software, the Ontological Discovery Environment. These results reveal genetic variation in MeHg effects on neural tube development, Wnt signaling, MAP kinase, developing GABAergic systems, and similarity to genes related to fissure development and other genetic studies of ataxia. Non-strain-specific effects were found on the glutathione S-transferase pathway, widely appreciated to be the focus of MeHg effects. Our results show that some individuals may be more susceptible to MeHg, and possibly a broader group of neurological teratogens. Based on our results a presentation abstract for the Society of Toxicology Annual Meeting was accepted, and a manuscript is being prepared.

00472

An All-Optical Plasmonic Pump for Integrated Applications

Ali Passian

Project Description

Based upon the thermal states of nanostructures, we propose a nanopump that will enable a reversible nanoscale pumping action. The proposed process can occur only at the nanoscale in a unique approach that utilizes Knudsen-like forces induced by nonradiative decay of optically excited surface plasmons. Potential applications include integration with micro- and nano-electromechanical systems and a lab-on-a-chip. The proposed plasmonic approach to inducing a nanoscale pumping action is unique and has not been exploited previously. No integrated system is currently capable of establishing a pressure drop across nanostructures by a noninvasive all-optical method. A very powerful feature of plasmonic systems is the ability of confining electromagnetic energy in nanoscale domains. Pumping energy into nanostructures over such length scales is not easily achievable with other means, and even harder to compete with is the superior (almost instant) rate at which plasmonic systems are capable of delivering the needed energy.

Mission Relevance

An integrated pump for small-scale operation will aid the development of compact sensors and on-chip laboratories that are particularly relevant to national security. The proposed approach is of tremendous potential for harvesting and managing energy (e.g., solar radiation, heat waste). The proposed system will be attractive to the Defense Advanced Research Projects Agency and other defense-related agencies. Applications are numerous as providing microscale and nanoscale pressure regulation and control are widespread needs.

Results and Accomplishments

Design parameters were established from the complementary surface modes of a cylindrical nanorod. This yielded the modes of a single nanohole. Computational codes were developed to obtain the optical response for an array of nanoholes. We can compute the field inside, as well as outside, the nanohole. The mode decay can be obtained if we neglect the coupling at the top and bottom of the film and whether there is a surface plasmon coupling. The modes propagating in the holes appear independent of the periodicity as long as there is enough metal between the holes. Porous silicon was manufactured and was characterized using a variation of an AFM (scanning ultrasonic subsurface microscopy) and SEM (scanning electron microscope). The pore diameters have been measured to be in the range 20–100 nanometers (with most holes around 100 nm). From the developed computational codes, the nanohole axial thermal gradient was determined. This determines the optimum laser power and wavelength used for the excitation of the surface plasmons. The manufactured porous silicon will be metalized by vacuum evaporation and characterized for integrity and uniformity. After establishing a successful excitation and coupling of the surface plasmons, measurements of the molecular transport through the nanoholes will be carried out using helium as a working gas, and the results will be used to determine the efficiency of the system as a pump and the potential for separation of various molecular species.

00479

Mapping Quantitative Trait Loci that Regulate Telomere Length Using Collaborative Cross Mice

Yisong Wang, Elissa Chesler, and Yie Liu

Project Description

The ORNL Systems Genetics Group is developing a critical biological resource for systems genetics by generating a large panel of recombinant inbred (RI) mouse strains derived from a genetically diverse set of eight existing founder strains called Collaborative Cross. About 1000 inbred strains will be produced in ORNL. Since the mechanisms that underlie disease susceptibility and progression are commonly influenced by numerous genetic/environmental factors, the random recombination of genetic material from the eight founder strains will result in variation in disease susceptibility, allowing us to map candidate genes that underlie genetic susceptibility to chromosomal instability. In support of this promising resource, we have carried out a proof-of-concept experiment for the use of the Collaborative Cross to study genetic modifiers of chromatin structure. We have explored the available Collaborative Cross mice to map quantitative trait loci (QTL) that control the length of telomeres, the ends of eukaryotic chromosomes known to be critical in the regulation of genome stability, aging process, and cancer development. Our proposed work may serve as a pioneer experiment to demonstrate the utility of the Collaborative Cross for the identification of genetic networks that determine genetic susceptibility to human diseases and aging.

Mission Relevance

The data generated in this study will be beneficial to DOE-sponsored systems biology as well as the mouse user facility programs. In particular, our proof-of-concept data for use of the Collaborative Cross will establish mouse models for the study of the effects of biohazardous or bioterror materials for DOE-sponsored national security programs. The Collaborative Cross is the unique and valuable resource currently under development in ORNL for high-resolution and high-power mapping of QTL for systems genetics studies. Identification and characterization of the genetic basis that control the telomere length will be beneficial to aging-related programs of the National Institute on Aging, systems genetics and cancer programs of the National Cancer Institute, and genomes and biomolecule cluster programs of the National Science Foundation.

Results and Accomplishments

In this study, we show that the telomere length varies significantly among the eight founder strains of the Collaborative Cross, with CAST/Ei being the shortest and A/J, the longest—indicating that genetic factors indeed play important roles in telomere length regulation and/or maintenance. Since random recombination of genetic material from the eight founder strains will result in segregation of modifiers of telomere length regulation and/or maintenance, we are exploring Collaborative Cross G2:F7-G2:F9 mice to map QTL that influence the length of telomeres. We have determined the telomere lengths of more than 50 G2:F7-F9 mice and are currently analyzing samples collected from more than 200 mice of the same generations. In addition, supported partially by this Seed Money, we identified a potentially significant QTL on chromosome 15 for telomere length regulation using BXD (C57BL/6J x DBA/2J) RI mice. Two BXD strains that have potentially the shortest telomeres among so-far explored experimental mice were identified. In parallel, we developed a dual-tag affinity purification system to isolate and identify, via mass spectrometry, novel interacting proteins of shelterin, a multi-subunit protein complex that binds to and helps maintain the telomeres. Several novel interacting proteins that may participate in the regulation of shelterin and its related functions have been identified. The significance of these interactions and their relationship with the QTLs identified in BXD studies are under investigation.

Publication

Giannone, R., J. Wu, L. Branstetter, D. Miller, E. Chesler, Y. Liu, and Y. Wang. 2008. "Exploration of the Genetic Basis and Protein Networks That Regulate Telomere Length Using Collaborative Cross and Mass Spectrometry Approaches." *7th Annual Meeting of the Complex Trait Consortium,* May 31–June 3, Montreal.

00492

Development of a Microfluidic Device to Mimic Vasculature for Studying the Mechanism of Tumor Metastasis

Henry K. Lin, Ram H. Datar, Boyd Evans, Thomas Thundat, and Siyang Zheng

Project Description

We are developing a microfluidic device that mimics the vasculature system to (1) understand the mechanism of circulating tumor cells (CTC) extravasation under controlled environment and (2) distinguish the underlying factors within a subpopulation of CTC that have the ability to form malignant masses at secondary sites. The proposed device consists of a parylene membrane, functionalized with layers of Matrigel to mimic basement membrane, type I collagen, and endothelial cells, sandwiched between two microfluidic channels formed in a transparent elastomer material. Such an in vitro microfluidic system will allow real-time monitoring of the extravasation process via imaging, followed by molecular characterization of endothelial cells and CTC to understand the molecules involved in extravasation, which can lead to discovery of novel drug targets.

Mission Relevance

Development of this microfluidic platform falls under DOE's scientific discovery mission that directly leads to improving the quality of life. This project will enable researchers to further understand the mechanism of tumor cell extravasation from blood vessels, which may lead to novel drug development for better cancer patient management. Moreover, this platform has the potential to become a clinical assay for testing the invasiveness of captured circulating tumor cells in blood withdrawn from cancer patients. The project directly benefits the mission of the National Cancer Institute within the National Institutes of Health. The development of this platform enables cancer researchers to better understand the intricate process of tumor cell extravasation from blood vessels. This in vivo microfluidic platform can also serve as an ideal screening tool for novel drug development for cancer patient management. Specifically, this project responds to the Innovative Molecular Analysis Technologies program for development of a tool for cancer research.

Results and Accomplishments

The first phase of this project is dedicated to manufacturing the microfluidic device using a simple single-channel fluidic design with protocol optimization for an associated fluorescence microscopic detection capability and functionalization of channel walls with blood vessel-like environment using type I collagen, Matrigel, and endothelial cells. Three months into the project, we have worked towards accomplishing the first phase by designing the microfluidic channels, and the fabrication process is in progress. A fluorescence microscope has been acquired with an appropriate image capturing device and software for monitoring tumor cell extravasation; moreover, relevant cell cultures are currently in culture. Progress also has been made in determining the necessary fluid flow to mimic biological blood flow characteristics.

CENTER FOR NANOPHASE MATERIALS SCIENCE

00426

Mapping Carrier Distributions and Photovoltaic Activity in Nanophase Materials by Electrical Dissipation Microscopy

Sergei V. Kalinin

Project Description

Understanding the fundamental mechanisms linking the operation of photovoltaic devices to their microstructure can open pathways to technological advances that will circumvent bottlenecks that currently limit device efficiency. Progress requires the development of capabilities to image the operation of photovoltaic devices, specifically the spatial and electronic structure and photoinduced carrier dynamics, in real space. We propose a novel approach for noninvasive measurements of carrier concentration on the nanoscale using electrical dissipation detection in scanning probe microscopy (SPM). This approach is based on the recently developed band excitation method—a paradigm shift in SPM technology based on nonsinusoidal excitation signals which have a specified spectral density in a given frequency range. The spatial resolution, sensitivity, and calibration of the electrical dissipation SPM will be ascertained using a semiconductor sample with different dopant densities (dopant grating). The method will be used to probe the photovoltaic activity of nanotube-based devices, in particular the identification of individual single-walled carbon nanotubes (SWNTs), determination of their electronic structure, and probing their photovoltaic behavior. This data will provide the guidelines for nanotube-based organic photovoltaic (OPV) optimization.

Mission Relevance

Fundamental and applied research in photovoltaic energy generation is one of the highest priorities for DOE and is a central component of the President's "Solar America" initiative. A novel tool capable of probing carrier distribution in photovoltaic devices in operandi will provide a key characterization capability for programs supported by the Office of Science, Basic Energy Sciences, and the DOE Office of Energy Efficiency and Renewable Energy. If successful, this method can be implemented on multiple SPM platforms, providing immediate and tangible benefit for energy-related programs. This work will have a wide-reaching impact on sensor technologies for aqueous or liquid environments and immediate benefit for the Defense Advanced Research Projects Agency (DARPA) and the Department of Homeland Security. The Homeland Security Advanced Research Projects Agency specifically has issued a call for bioagent sensors (Bioinformatics and Assays Development program). In addition, DARPA is considering a new program, "Instrumentation for Nanoscience," to which this research would be relevant. However, perhaps the most important aspect of band excitation is that it allows quantitative probing of energy dissipation on the nanoscale in all ambient and liquid dynamic SPMs and is thus ideally tailored for the DOE energy mission.

Results and Accomplishments

Probing energy dissipation on the nanoscale is crucial for areas ranging from information technologies to efficient energy production. SPM offers an approach for probing energy dissipation through detection of the quality factor of the cantilever interacting with the surface through the localized tip. Until recently, these measurements were hindered by the fundamental physics of SPM—namely, the dynamic behavior of the cantilever is described by three independent variables (amplitude, resonant frequency, Q-factor), while only two (amplitude and phase) are measured by conventional SPM at a single frequency. During FY 2007 we implemented our SPM technique in which the cantilever is excited and the response is recorded over a band of frequencies simultaneously. This band excitation (BE) SPM allows rapid acquisition of the frequency response at each point in an image and in particular enables the direct measurement of energy dissipation. The BE method was demonstrated for force-distance and voltage spectroscopies and for magnetic dissipation imaging. During FY 2008 the operation speed of the BE was optimized through the development of chirp and double-chirp excitation waveforms and improved synchronization between controller and microscope to achieve imaging at standard rates. This breakthrough extends the BE method to a full spectrum of ambient and liquid SPM techniques, including mechanical, electromechanical, electric, and magnetic, essentially creating a new family of SPMs.

The technology has been licensed by Asylum Research Corporation. The principal investigators have been recognized for this work, including (1) an R&D 100 Award, “Adaptive Band Excitation Method and Controller in Scanning Probe Microscopy” (S. Jesse, S. V. Kalinin, and R. Proksch, Asylum Research); (2) a Federal Laboratory Consortium Southwestern Technology Transfer Award; and (3) (in part) a 2008 Cosslett Award for Best Invited Paper of Microbeam Analysis Society (principal, S. Jesse). In addition, the results have been featured in *Physics Today* and web media.

Publications

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00487

Laser-Enhanced, Nanoscale-Focused, Electron Beam–Induced Processing

Jason D. Fowlkes and Philip D. Rack

Project Description

The directed assembly of nanoscale materials is essential for controlled nanofabrication. While standard lithographic techniques will continue to play an important role in nanofabrication, clearly the frontier of nanofabrication is the direct writing of nanoscale features with specified size, shape, location, orientation, and composition. Electron beam–induced deposition (EBID) is one such nanoscale, direct-write approach that has been successfully employed to deposit a diverse host of materials and structures. While EBID makes it possible to synthesize three-dimensional, nanoscale features on textured or complex surfaces, often the subsequent materials are amorphous or nanocrystalline. In addition, the final nanostructures are frequently contaminated with nonvolatile by-products resulting from the electron dissociation reaction sequence. These contaminants compromise material quality and ultimately the nanoscale functionality. We propose to use photon irradiation during EBID to remove adsorbed reaction by-products from the growing deposit to achieve deposits of high purity and controlled composition.

Mission Relevance

This research will benefit the DOE Office of Science, Basic Energy Science (BES) programs, particularly those related to nanoscale science, engineering, and technology. Specifically, this technique enables the direct-write deposition of two- and three-dimensional features on any substrate material and integrates fully with current nanofabrication approaches. Thus, the technique provides a new means to deposit unique nanoscale materials as well as prototype features to probe new material properties that are important for BES missions in areas such as solid-state lighting, photovoltaics, and energy storage. The capability to selectively and nanoscopically functionalize our synthetic biological interfaces using well-developed gold-thiol chemistries should benefit programs at the National Institutes of Health.

Results and Accomplishments

The electron beam–induced deposition of the gold-containing precursor gas first had to be characterized *without the laser beam assist* in order to determine deposit quality prior to the dual (electron + laser) beam process. Toward this end, gold deposits were characterized as a function of the electron beam energy, beam current, probe dwell time, and precursor gas refresh time. The deposit growth rate, composition, and precursor gas kinetics were determined from these data. Knowledge of the as-deposited gold composition (~20 at. %) must be known to evaluate the improvement anticipated from the dual irradiation process. The gas kinetics must be quantified in advance in order to later tailor the laser–electron–gas flux pulsing in the final experiments. Deposits were also annealed, following processing in inert and reducing atmospheres, to determine the effect of annealing on deposit gold composition. These gold features were deposited on micro, four-point probe electrodes to correlate gold deposit resistivity against the bulk value as well as dual beam.

In parallel, a light-coupling feed-through was installed on our electron microscope and qualified. This hardware contains the light-directing optics used to direct the pulsed laser light into the microscope as well as optical imaging capability for beam alignment. The hardware also contains precision translation to facilitate electron–laser beam coincidence. The complete dual electron–laser beam system is now being configured with the arrival of the 905 nm pulsed laser diode, power supply, and free space coupling optic.

00495

Nonlinear Nanomechanical Oscillators for Ultrasensitive Inertial Detection

Nickolay V. Lavrik and Panos G. Datskos

Project Description

This project seeks to combine unique features of nanoscale mechanical oscillators with advantages of nonlinear systems. To minimize parasitic effects of the ubiquitous noise sources, we propose to take advantage of stochastic resonance, the phenomenon characteristic of certain nonlinear systems in which synergistic action of deterministic and stochastic processes is observed. By pursuing this effort we will verify that intrinsically nonlinear nanomechanical oscillators can be operated in the stochastic resonance regime and that this regime would lead to dramatically improved ability of detecting mass changes very close to the fundamental limit imposed by thermal noise.

Mission Relevance

The proposed project is relevant to the Materials Science and Technology program within the DOE Office of Science. Several federal agencies expressed strong interest in technologies and devices that could enable ultrasensitive mass measurements. In particular, ultrasensitive mass detection is a critical component of advanced on-chip analytical systems of interest to the Defense Advanced Research Projects Agency, the National Institutes of Health, and the Department of Homeland Security. Such systems will have applications in detection of trace amounts of toxic chemicals or hazardous biological species. The potential broader area applications include accelerometers and inertial navigation devices. The project will benefit energy science and sensor technology with applications in environmental quality, nuclear security, and other related areas in which there is a need for detection of trace amounts of chemical or biological species using a highly portable platform. Currently, there is a consensus that future microminiaturized analytical systems will include a scaled-down preconcentrator, a microfabricated separation column, and an appropriately small detector with very high sensitivity. The objective of the proposed effort is to develop an innovative platform for the latter counterpart. An additional significant impact of the proposed approaches is expected in the broader area of sensing applications, in which minute forces need to be detected with high accuracy and reliability.

Results and Accomplishments

During FY 2008 we made progress in the initial part of the proposed effort that involved modeling, design, and fabrication of nanomechanical oscillator structures. More specifically, we designed targeted resonance structures using analytical models and finite element analysis and fabricated the initial batch of test devices using low-stress layers of silicon nitride and silicon oxide as structural materials. The fabricated devices have been inspected and characterized using scanning electron microscopy and down selected for further characterization using the optical methods we developed.

CHEMICAL SCIENCES DIVISION

00424

Taming Photosynthesis Regulation Through Genomics for Direct Synthesis of Ethanol from Carbon Dioxide and Water

James W. Lee, Barbara R. Evans, and Gary Van Berkel

Project Description

This project is designed to answer an important scientific question: Is it possible to tame the photosynthesis regulation mechanism by using the reducing power (NADPH) and energy (ATP) acquired from photosynthetic water splitting and proton gradient-coupled electron transport process for synthesis of ethanol (CH_3CH_2OH) from carbon dioxide (CO_2) and water (H_2O) immediately in the chloroplast? This hypothesis can be tested by accomplishing the following three tasks: (1) synthesis of designer genes to introduce phosphoglycerate mutase and enolase into algal chloroplast, (2) genetic transformation and screening of transformed cells, and (3) expression of the designer phosphoglycerate mutase and enolase genes to test the hypothesis. Successful accomplishment of this project would represent fundamental breakthroughs that could lead to new technology for photosynthetic production of ethanol directly from CO_2 and H_2O that will help ensure our nation's energy security.

Mission Relevance

This research is relevant to the DOE mission in two areas: energy independence and climate change mitigation. The objective of this project is to demonstrate proof of the concept that green algae can be used for ethanol production by evaluating a novel ethanol-production pathway by focusing on the first two enzymes (phosphoglycerate mutase and enolase) of the proposed recombinant pathway for photosynthetic production of ethanol directly from CO_2 and H_2O in the chloroplast. The project goal is clearly aligned with the President's Advanced Energy Initiative and the mission of the DOE bioenergy centers. The project could also benefit other federal agencies such as the Environmental Protection Agency and the Department of Commerce, since photosynthetic ethanol production could lead to a new clean-energy industry that could directly combine CO_2 fixation with ethanol production.

Results and Accomplishments

The green alga, *Chlamydomonas reinhardtii,* that was used as the model organism possesses a metabolism that combines features of green plants (photosynthesis) with those of bacteria (fermentative hydrogen production). The intrinsic *C. reinhardtii* mitochondrial alcohol-aldehyde dehydrogenase (ADHE) has been reported to produce low amounts of ethanol under dark, anaerobic conditions. However, similar ADHEs are bidirectional, enabling the related chlorophyte *Polytomella* to use ethanol as a carbon source under both aerobic and anaerobic conditions. A very low rate of ethanol production under anaerobic light-dark cycles was detected, but tolerance of ethanol added to the culture was fairly high, up to 3%. Addition of ethanol to the growth media during aerobic growth under photoautotrophic, photoheterotrophic, and heterotrophic conditions found tolerance to 2% ethanol but without an increase in growth rate.

Each of the genes for the proposed synthetic pathway was identified in Chlamy version 2.0, an initial draft assembly of the *C. reinhardtii* genome that has been made available on-line by the DOE Joint Genome Institute (JGI) and the *Chlamydomonas* Genome Consortium (http://www.jgi.doe.gov/). Gene identification was confirmed by homology search in the GenBank database (NCBI).

The set of five designer genes for expression of the ethanol pathway enzymes was designed and synthesized for the genetic insertion of designer-pathway enzymes into algal chloroplasts. The constructs were first cloned into a stable bacterial plasmid to ensure preservation of the constructs and to enable future subcloning into alternative expression vectors. Each of the constructs was then subcloned into a *Chlamydomonas* expression vector. Electroporation combined with gamete autolysin treatment was used to transform a *C. reinhardtii* recipient strain with the designer gene constructs. Following transformation, the algae were maintained on selective media for several passages to obtain stable transformants.

Publication

Lee, J. W. "Designer Organisms for Photosynthetic Production of Ethanol from Carbon Dioxide and Water." U.S. Patent Application No. 20080176304; International Publication No. WO 2008/039450.

00457

Turbopump Concentration of Heavy Atoms and Molecules

William B. Whitten and Peter T. A. Reilly

Project Description

The ratio of output to input pressure of a turbopump increases with the mass of the species being pumped. Our project is to explore this phenomenon for concentration of atoms or molecules with mass greater than nitrogen or oxygen at the input of an environmental mass spectrometer to increase the sensitivity for trace substances in the atmosphere. Substances of interest include the noble gases krypton and xenon, volatile organic compounds, chemical warfare agents, explosives, and drugs. The experiments will use a mass spectrometer at the exit of a turbopump to determine the concentration of heavy sample molecules in a carrier gas such as N_2. The concentration is expected to occur due to diffusion of the lighter carrier gas to the low-pressure inlet of the turbopump. This low-pressure environment will be maintained by a second turbopump.

Mission Relevance

Analysis of trace quantities of volatile organic compounds and atomic species in the atmosphere is important to DOE and other agencies. Detection of the noble gases is relevant to nuclear nonproliferation (DOE NA-22 and NA-24) since these substances are products of nuclear fission. Also, detection of substances in the atmosphere by environmental scientists studying climate change is relevant to the DOE mission. Other applications include detection of toxic substances in manned spacecraft by the National Aeronautics and Space Administration, and chemical warfare agents and explosives by the military. The ability to concentrate the substance of interest can enhance the sensitivity of the analysis and reduce the probability of false alarms.

Results and Accomplishments

Two Varian V70D turbopumps with separate roughing pumps were connected to a chamber so that one pump could be used to increase the concentration of the heavy species, and the other, to provide the low-pressure environment at the entrance of the concentration pump and remove the gas with lower concentration. The apparatus consisted of a sample inlet and two outlets, the foreline sides of the two turbopumps. The system was intrinsically symmetrical, in that either outlet could serve as the concentration outlet depending on the operating conditions of the two turbopumps. Relative concentrations of pairs of analyte molecules with different molecular weights were measured at the sample inlet and one of the outlets with a PolarisQ ion trap mass spectrometer. Choice of analyte molecules was complicated by charge exchange reactions between the ions in the trap and neutral species. These reactions precluded the use of N_2 or noble gases. The pair eventually studied was SF_6 and perfluorodimethylcyclohexane (PDMCH) in helium with molecular weights of 146 and 400, respectively. The pumps could be operated at either of two rotational speeds, 75,000 rpm or 50,000 rpm. Best results were obtained with the concentration turbopump operating at 75,000 rpm while the reduction turbopump was running at 50,000 rpm. Under these conditions, the concentration ratio of PDMCH to SF_6 at the concentration outlet was 2.4 ± 0.1 times the ratio at the sample inlet. These results show that there is a mass dependence to the pumping ability of a turbopump even at high mass.

00467

Development of a Novel Sensor System for Biomarkers of Physiological and Pathological Processes in Biomedicine

Elias Greenbaum and Ram H. Datar

Project Description

The goal of this project is to establish proof of principle for an original idea for the development of an assay system for biomarkers of physiological and pathological processes in humans without pretreatment of the sample. The gist of the project is the use of unicellular green algae or cyanobacteria as the biosensors and chlorophyll fluorescence induction as the readout in the presence of light scattering and attenuating biological components. It is known that fluorescence induction is a quantitative measure of the physiological health of photosynthetic systems. It is also known that human toxins such as cyanide, choline esterase inhibitors, electron transport chain blockers, bulk commodity agrochemicals, oxidants, etc. all alter fluorescence induction with unique signatures. If we could show corresponding effects for the molecular species involved in the onset of human disease, such as reactive oxygen species, using native human serum samples, we would have a simple and rapid early warning diagnostic assay for these disease biomarkers. Alternatively, our ability to screen and quantify the beneficial attributes of the dietary phenolics from fruit or plant extracts will provide an invaluable way to easily screen the dietary elements crucial in disease prevention.

Mission Relevance

This project is relevant to the DOE mission. In particular the Office of Science, Biological and Environmental Research program has an ongoing interest in biosensors and the development of advanced instrumentation. It is also of interest to the National Institutes of Health. Reactive oxygen species, such as hydrogen peroxide and superoxide anions, are produced in many physiological and pathological processes in humans, including aging, response to infections such as *Helicobacter pylori*, atheroma, asthma, joint diseases, chronic obstructive pulmonary disease, diabetes, and cancer. The superoxide anion, O_2^-, is the main reactive oxygen species (ROS). Increased ROS production leads to tissue damage associated with inflammation. Superoxide dismutases (SODs) convert superoxide to hydrogen peroxide, which is then removed by glutathione peroxidase or catalase. Thus, SODs prevent the formation of highly aggressive ROS, such as peroxynitrite or the hydroxyl radical. The production of ROS through either endogenous or exogenous insults is common for many types of cancers and is linked with altered redox regulation of cellular signaling pathways. The redox imbalance thus may be related to oncogenic stimulation. DNA mutation is a critical step in carcinogenesis, and elevated levels of oxidative DNA lesions (8-OH-G) have been noted in various tumors, strongly implicating such damage in the etiology of cancer. Measurement of ROS in human serum samples is therefore a method to assess the impact of pathological oxidative stress. It is known that altered redox regulation affects photosynthesis.

Results and Accomplishments

The pulsed amplitude modulated (PAM) fluorometer has been set up and is fully operational for fluorescence induction measurement. The protocol for measuring the change in fluorescence using PAM has been optimized: a formula to calculate the sample dilution based on chlorophyll density to give appropriate fluorescence intensity range has been developed, fluorescence induction curves were measured in 5 min increments in a 30 min period, and hydrogen peroxide or the same amount of water was introduced 30 s before the 15 min measurements. The marine algae strains *Chlamydomonas* sp. CCMP 222 and *C. parkeae* and the freshwater strain *C. kesseri* did not show expected drops of fluorescence upon peroxide treatments compared to the water controls. It was found that algae produce the enzyme catalase, which spontaneously converts peroxide to water. This self-protection mechanism resulted in the algae's ability to resist photosynthetic disruptions due to low concentration of peroxide. The freshwater algae mutant with catalase deficiency, NL-11, showed a peroxide threshold of 500 μM, at which NL-11 exhibited an obvious drop in fluorescence after peroxide treatment, while the wild types *Chlamydomons* sp. CCMP 222 and *C. parkeae* were still fluorescent normally in response to 500 μM peroxide. Linear regression analysis of 500 μM peroxide treated and untreated algae fluorescence data in NL-11 showed statistically different R^2: untreated, 0.97 ± 0.01; treated, 0.71 ± 0.07 ($n = 3$). These values can be used as quantitative measurements to define the significance of fluorescence changes in further experiments. The expected drop in fluorescence induction proved the feasibility of the concept of the project. The increased peroxide sensitivity of the mutant suggests a path forward for getting a sufficient sensitivity for large clinical screening of human serum with the algae strain that has a complete catalase deletion.

00477

A New Method for Controlling Densification during Chemical Vapor Deposition Production of Carbon Composites

Peter T. A. Reilly

Project Description

This project uses gas-phase pyrolysis of hydrocarbons under controlled conditions to create free radical condensates (FRCs). The idea is to measure and manipulate the chemistry of FRCs to more rapidly deposit pyrolytic carbon onto the surfaces of preforms and measure the kinetics and dynamics of deposition. This project takes advantage of the chemical equilibria between the FRC and the gas phase and the elemental carbon formed by controlled carbonization of the FRC. We plan to use hydrogen and thermal gradients to perturb the equilibria and cause controlled pyrolytic carbon deposition. Our goal is to precisely define the process in terms of the chemistry and the kinetics and then optimize it.

Mission Relevance

This project is not just about creating faster, better, cheaper carbon composites. It is really about understanding the chemistry of the FRC. FRCs can be used to reversibly abstract hydrogen from hydrocarbons to produce forms of elemental carbon or convert elemental carbon into hydrocarbons. This chemistry opens up a multitude of opportunities in DOE's hydrogen program. FRCs can be used to unlock hydrogen storage in hydrocarbons, produce hydrogen, convert coal into hydrocarbons, and convert biofuels like alcohols into diesel. They can also be used to create ultrastrong, lightweight materials faster, better, and cheaper. The Department of Defense program on Synthesis and Processing of Materials (W911NF-07-R-0003) focuses on the use of innovative approaches for processing high-performance structural materials reliably and at lower costs. Our project, if successful, would be directly applicable to this program. Successful demonstration of this technology would also create new opportunities at other agencies, such as National Aeronautics and Space Administration, and in industry.

Results and Accomplishments

Through FY 2008 this project is roughly one-third complete. It is based on the establishment of an equilibrium between FRCs and the production of carbon and hydrogen from them. To date, we have set up the reactor and demonstrated the equilibrium by reversing the carbonization process that forms pyrolytic carbon around carbon fibers. Segments of C/C rod were inserted into our reactor containing a white mist generated from the pyrolysis of acetylene at 1 atm pressure. After roughly 1 h in the reactor, the composite was reduced to a collection of carbon fibers. SEM images of the fibers as a function of time in the reactor show evidence of pitting and exfoliation of the fibers with increasing time. The rest of the project will demonstrate that the forward reaction also can be controlled to rapidly create carbon/carbon composites.

This work provides evidence that FRCs can be used to convert carbon into hydrocarbons through a reversible process. This single result has sweeping implications. It means that thermodynamically favorable forms of carbon can be preferentially produced. It suggests that carbon nanotubes can be created by the pound instead of the milligram. Hydrocarbons could be used to reversibly store hydrogen with better storage efficiency than believed possible. Oil could be extracted and refined from oil shale in a single step. Coal and natural gas could be combined to produce diesel fuel. Biological sources of carbon could be converted to fuel. The list goes on. Which of these processes is economically and environmentally feasible is a matter of intensive research; however, the chemistry of FRCs presents a vast number of new possibilities that could greatly change the course of society.

00478

Understanding Why and How Thiolate Groups Stabilize Gold Nanoparticles

De-en Jiang

Project Description

Gold nanoparticles have attracted tremendous research interest and found increasing use in catalysis, sensing, protein labeling, and drug delivery. The recently obtained single-crystal structure of a thiolate-functionalized gold nanoparticle challenges the conventional view that thiolate groups are either isolated or form gold-thiolate polymers on the particle surface. Here, we hypothesize that the newly observed structural motifs are the dominant structural unit that stabilizes thiolate-functionalized gold nanoparticles. In this project, we seek to understand the driving force for the formation of such new motifs on a gold nanoparticle by using first-principles density functional theory-based simulations. We will select a size of thiolate-protected gold nanoparticles that has been isolated in great yields but has not been structurally determined. We will use this undetermined system as a proof-of-principle system for testing our hypothesis. If our hypothesis is proved through this project, we will be uniquely positioned to propose better designs for gold nanoparticles.

Mission Relevance

Research on nanoparticles is of great importance to DOE's core missions. Nanoparticles are used widely as catalysts for energy conversion, materials for energy storage, and sensors for radiation detection. This project seeks to advance our understanding of the mechanism by which thiolate groups protect gold nanoparticles. The knowledge generated from this project will help design better nanoparticles, thereby benefitting the DOE Office of Science, Basic Energy Sciences program in catalysis, solar energy utilization, and separations.

Results and Accomplishments

The single-crystal structure of a thiolate-protected gold cluster shows that all thiolate groups form "staple" motifs on the cluster surface. We hypothesized that this staple motif is preferred on all gold clusters. To test our hypothesis and to determine the driving force for the staple motif, we used first-principles density functional theory simulations to model formation of staple motifs on an Au_{38} cluster from zero to full coverage. By geometry optimization, molecular dynamics, and simulated annealing, we showed that formation of staples is strongly preferred on a cluster surface and helps stabilize the cluster by pinning the gold surface atoms and increasing the gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. We devised a method to generate initial structural models for thiolate-protected gold clusters by adding staples to the cluster surface. Using this method, we obtained a staple-covered, low-energy structure for $Au_{38}(SCH_3)_{24}$, a much-studied cluster whose structure is not yet known. Optical band-edge energy computed from time-dependent DFT for our $Au_{38}(SCH_3)_{24}$ structure shows good agreement with experiment. Our results have been published in the *Journal of the American Chemical Society* and *Journal of Physical Chemistry C.*

Publications

Jiang, D. E. 2008. "In Search of a Structural Model for a Thiolate-protected Au_{38} Cluster." *J. Phys. Chem. C* **112**, 13905.

Jiang, D. E. 2008. "The 'Staple' Motif: A Key to Stability of Thiolate-Protected Gold Nanoclusters." *J. Am. Chem. Soc*. **130**, 2777.

00480

Hydration-Driven Processes in Bioenergy: Testing a Novel, Neutron-Scattering Approach

Hugh O'Neill, Sylvia E. McLain, and David C. Baker

Project Description

Water plays a vital role in the development of biofuels. Currently, the production of cellulosic ethanol is limited by the low solubility of cellulose in water and because natural cellulose contains appreciable amounts of lignin, which is also largely water insoluble. The structural barrier provided by lignocellulose to water hydration in potential biofuel feedstocks is an important factor determining the recalcitrance of biomass to undergo hydrolysis. In fact, studies concerning the economic potential of cellulosic ethanol as a potential biofuel cite lignocellulose pretreatment efficiency as a primary factor leading to increased profit and production capability. A microscopic understanding of hydration structure on the atomic length scale (0–10 Å) of lignocellulose and its constituents is critical to understanding fundamental processes of bioenergy production. Using neutron scattering techniques, we aim to synthesize isotopically labeled carbohydrate archetypes to determine the structural and the hydration properties of cellulose.

Mission Relevance

One of the DOE missions for the future is to increase the use of alternative fuel sources to help curb our dependence on a gasoline economy. The work for this project will lead to the greater physical understanding of hydration in cellulose-based materials, where the recalcitrance of cellulose to hydrolysis is currently a limiting factor to cellulosic ethanol production. This investigation is a step towards more efficient use of biofuel as a potential fuel source. DOE will benefit the most from this research, as it directly falls under one of the DOE directives of enhancing research in biofuels as an alternative fuel source.

Results and Accomplishments

To date, we have synthesized cellobioside from cellobiose and performed deuteration on the exchangeable hydrogen sites and methyl group of the cellobioside molecule. We also have performed neutron diffraction experiments on both cellobiose and cellbioside in aqueous solution using the SANDALS diffractometer located in the ISIS Facility at Rutherford Appleton Laboratory (RAL) in the United Kingdom. The data from this experiment is being modeled using standard neutron diffraction techniques and using computer simulation via empirical pair structural refinement, a reversed Monte Carlo method. The computations of two of the compounds are going well, and we expect to have definitive models in the near future. Additionally, we have performed inelastic neutron scattering experiments on these molecules on the MARI instrument also located at RAL, and the data analysis for these experiments also is under way. We are in the process of conducting nuclear magnetic resonance experiments on these same samples in the laboratory of David Baker at the University of Tennessee, Knoxville.

00481

Novel High-Power Cathodes for Lithium-Ion Rechargeable Batteries

Chengdu Liang, Jane Howe, Nancy Dudney, and Sheng Dai

Project Description

We propose to develop novel cathodes for lithium-ion rechargeable batteries based on a bimodal porous carbon material developed at ORNL. This carbon material possesses a bimodal pore-size distribution at 3 μm and 8 nm. The 8 nm pores will serve as host sites for $LiFePO_4$ particles, and the 3 μm pores will be employed as channels for the mass transport of electrolytes. The entire cathode will be synthesized as rods, 5 cm length and 1 cm diameter. Thin slices will be cut from the rods and assembled into batteries to demonstrate their performance advantages. The proposed cathodes are expected to have low resistances of both electrons and lithium ions because of their bimodal porous structures, which provide tight contact for electron transfer and fast mass transport for lithium ion migration. Therefore, these cathodes will have low electric resistance and high power density compared to traditional micron-sized particle-packed cathodes.

Mission Relevance

This project, which aims at the development of novel cathodes for lithium-ion batteries, is closely linked to DOE missions related to energy storage, including the Energy Frontier Research Centers, the DOE FreedomCar program, and DOE programs managed by the Office of Electricity Delivery and Energy Reliability. The Defense Advanced Research Projects Agency and the Department of Defense have great interest in high-power-density lithium-ion batteries, which are valuable to multiple defense applications.

Results and Accomplishments

During FY 2008, the first half of this project, we made considerable progress toward the synthesis of $LiFePO_4$ inside porous carbon substrates. We demonstrated that $FePO_4$ can be synthesized inside the mesoporous carbons through both electrochemical and chemical approaches. The electrochemical deposition resulted in an eggshell structure of $FePO_4$ on the porous carbon monolith, which had an outer layer of 1 μm thickness covered by $FePO_4$ and an inner core free of $FePO_4$. The chemical deposition gave a uniform deposition of $FePO_4$ on porous carbon through a two-step self-limiting reaction. In the chemical deposition approach, MnO_2 was deposited into carbons with pore sizes of 4 nm and 8.5 nm and then replaced by $FePO_4$ via an in situ displacement reaction. We found that the pore size significantly affects the displacement reaction. MnO_2 inside the carbon with 4 nm pores can only be partially displaced by $FePO_4$, while MnO_2 inside the carbon with 8.5 nm pores can be full replaced by $FePO_4$. The $FePO_4$ coatings were further converted to $LiFePO_4$ for a battery test. The $LiFePO_4$-coated carbon with 8.5 nm pores showed a hybrid electrochemical behavior of a capacitor and a battery. The capacitor behavior of the $LiFePO_4$-coated material has the potential for high-power-density electric energy storage. We also found that the coated materials have a limit of loading electroactive materials. This limit will be investigated in FY 2009. In addition, we found α-MnO_2 nanowires can be uniformly coated by $FePO_4$ as a composite material for possible applications in high-power lithium batteries. This was a serendipitous finding during the development of the chemical deposition of $LiFePO_4$ inside the porous carbon. An invention disclosure has been submitted to ORNL Technology Transfer for an evaluation of its commercial value and patentability.

00485

Molecularly Imprinted Ionogels as Optosensory Platforms

Gary A. Baker

Project Description

Our overall aim is to establish proof-of-principle for an ionic liquid (IL) template, molecularly imprinted polymer (MIP) sensor for the luminescent detection of naphthalene. By using a fluorescent probe tethered near the recognition site and having emission properties influenced by the analyte's presence, inherent advantages, such as very low detection limits and spectroscopic specificity, can be applied, reducing susceptibility to background interference and false positives. Moreover, the incorporation of an IL during MIP synthesis is expected to lead to sizeable improvements in sensitivity, stability, overall robustness, and selectivity beyond conventional imprinted materials.

Mission Relevance

By showing proof of principle for an MIP ionogel, we will introduce new chemoselective media with key potential in DOE missions, including environmental quality and fundamental science, underlying both energy and separations projects. The proposed research also has the potential to advance national security initiatives in the Department of Homeland Security, the Department of Defense, the Office of Naval Research, and the Defense Advanced Research Projects Agency (DARPA). For example, a recent DARPA solicitation (BAA 07-61) focused on the need for materials "optimized for future chemical and biochemical nanosensor technologies."

Results and Accomplishments

Excellent progress was made toward demonstrating ionogel-based MIPs. Specifically, to illustrate the ionogel-MIP scheme's potential, we demonstrated selective detection of the model compound 9-anthrol over structural analogues (anthracene, 9,10-anthracenediol, 2-naphthol). A full appreciation of how these materials fare compared to non-ionogel counterparts is still awaited; however, preliminary results bode well. We also determined semioptimized protocols for making rapid-gelling ionogels with excellent transparency (comparable to conventional sol-gels) that contain more than 50% (v/v) of an IL, while maintaining similar physical robustness. Most remarkably, using fluorescence recovery after photobleaching (FRAP) experiments, we successfully demonstrated "optical self-healing" for molecular diffusion within spin cast ionogel thin films. These results, which perhaps eclipse the aims set forth in the original proposal, suggest a continuous, interconnected liquid network entrapped within a silicate cage, with far-reaching consequences for the application of ionogels in various applications ranging from sensory elements to electrochemical devices and actuators.

00497

Ordered Nanoporous Hyperadsorptive Preconcentrators of Threat Agents

Jun Xu, Radu Custelcean, Steve Overbury, and Seth M. Cohen

Project Description

The Department of the Army's goal for the Joint Chemical Agent Detector is to have the minimum detection limits of ~1 part per trillion for chemical warfare agents. Current state-of-the-art detectors are unable to reach this goal due to lack of specificity and sensitivity. We plan to reach this goal by incorporating ordered nanoporous materials to our partners' differential mobility spectrometer (DMS). The objective of this project is to demonstrate proof of principle for sampling threat agents using ordered nanoporous materials. These novel materials include metal-organic frameworks (MOFs), ordered mesoporous carbons, and nanostructured zeolites. This project will be focused on MOF adsorbents and dimethylmethyl phosponate, a simulant for sarin (GB) as the adsorbate.

Mission Relevance

This research is focused on developing a new method for building a compact, but more sensitive, device for detection of threat agents, including chemicals associated with nuclear production, chemical warfare agents, and toxic industrial compounds. Recently, DOE NA-22 has stated the need for new sampling technologies. Our project is consistent with DOE's statements. The Defense Advanced Research Projects Agency, the Defense Threat Reduction Agency, and the Domestic Nuclear Detection Office have solicited proposals in novel sampling technologies. Successful demonstration of a novel preconcentrator would present a major breakthrough in sensitive detection of the threat agents and potentially allow us to develop a research program for the agencies.

Results and Accomplishments

In the last two months of FY 2008, four MOF materials were prepared with and without functional groups attached to ligands. The Sionex DMS sensor has been obtained and one investigator has been trained. In the next fiscal year, the overall tasks in this project are to (1) functionalize MOF pores so that sorption of the chemical threat agents is maximized and capture of background gas is minimized, (2) identify adsorption and desorption characteristics that will be used to completely extract the adsorbates into micro analyzers, (3) package the preconcentrators with micro DMS for detecting the chemical threat agents with approximate parts-per-trillion minimum detection limits.

COMPUTATIONAL SCIENCES AND ENGINEERING DIVISION

00435

A Hybrid Diffusion Model Driven by Chemoattractants

Richard C. Ward, Kara L. Kruse, James J. Nutaro, Barbara G. Beckerman, and Oscar Grandas

Project Description

A hybrid diffusion model (HDM) is being developed to predict complications associated with the treatment of vascular occlusive diseases (atherosclerosis) by balloon angioplasty. When complete, the model will simulate the main features of the complex intimal hyperplasia process that may lead to restenosis of the artery due to vascular remodeling. The model will include discrete simulation of changes in the state of a single cell type—vascular smooth muscle cells (VMSCs)—and their subsequent proliferation and/or migration within the artery wall. The model also will include continuous simulation of the production, diffusion, reaction, and degradation of a single chemoattractant—platelet-derived growth factor (PDGF). The code approach was developed in such a way (utilizing object-oriented programming) that expansion to more cell types and chemoattractants as well as incorporation of extracellular matrix–degrading enzymes is easily accomplished. This HDM is a novel combination of discrete-event simulation and continuous simulation. Ultimately, the objective is to predict the combination of mechanical and biochemical initial states and changes that push the system balance from a stable state to the potentially lethal unstable state. The team is collaborating with the University of Tennessee Graduate School of Medicine (UTGSM) to gather experimental data to estimate model parameters. The long-term goal is to help physicians predict appropriate treatments to effect desired outcomes in individual patients and provide a baseline model for use in determining the effects of hormone replacement therapy on the development of vascular remodeling after balloon angioplasty.

Mission Relevance

The HDM approach could be applied to a wide range of problems currently of concern to DOE. The problems, which are characterized by a high degree of nonlinearity and a mixture of continuous and discrete elements, include control and monitoring of the electric power grid, risk analysis for carbon sequestration, and optimization of advanced combustion systems and nuclear fuel cycles. The National Institutes of Health is supporting the development of computational, predictive models to anticipate the normal and disease responses of complex physiological processes, including vascular flow and remodeling.

Results and Accomplishments

A model of cell migration stimulated by a constant biochemical gradient was constructed and the model verified against established continuum models of cell population migration. The model was enhanced by incorporating a finite difference approximation of a varying biochemical diffusion gradient to simulate the Boyden chamber experiments being conducted at UTGSM. Two sets of experimental data were obtained from the Vascular Research Laboratory at UTGSM, and they are being used to calibrate the model and validate its predictions. Considerable interaction between ORNL and UTGSM was important to the development of the model and experimental protocols. A preliminary object-oriented design concept for modeling the larger intimal hyperplasia problem was created. The literature was searched for useful data that could be used in the model. Student interns helped with these tasks during the summers of 2007 and 2008.

The HDM was created using object-oriented C++ code. The HDM code models migration of VSMCs into the intima resulting from vascular injury (e.g., balloon angioplasty) to the vessel wall. Incorporated into this code, using a continuous approach, are the effects of the chemoattractant (PDGF) on the VSMCs. The parameters of the model, including the VSMC speed and persistence time, the random motility (diffusion confident in the absence of the chemoattractant), and the chemoattactic parameters that describe attraction of VSMCs by PDGF, have been obtained from the literature. This HDM code has been used to evaluate some of the Boyden Chamber experimental data provided by our partners at UTGSM. The object-oriented nature of the code will allow easy extension to additional cell types and other chemoattractants. Preliminary results of our studies were published in July 2007, and the final results will be published in an article to appear in the future.

Publication

Nutaro, J. J., K. L. Kruse, R. C. Ward, E. C. O'Quinn, M. M. Woerner, B. G. Beckerman, S. Kirkpatrick, D. Mountain, and O. Grandas. 2007. "A Discrete Cell Migration Model." *Proceedings of the Society of Modeling and Simulation International (SCS), SCSC'07,* July 15–18, San Diego.

00491

The Graphics Processing Unit–Enhanced Computer for Large-Scale Text Mining

Xiaohui Cui and Thomas E. Potok

Project Description

We are quickly reaching an age in which a capability is needed for text mining (TM) of terabyte-scale unstructured text corpora for prompt decision making. Analyzing large-scale text collections requires high-performance computing and various algorithmic changes to current TM approaches. The graphics processing unit (GPU) can solve some highly parallel problems much faster than the traditional sequential processor (CPU). Thus, a deployable system using a GPU to speed up large-scale TM processes would be a more effective choice (in terms of cost/performance ratio) than using a computer cluster. However, due to the GPU's application-specific architecture, harnessing the GPU's computational prowess for TM is a great challenge. The objective of this project is to prove the feasibility of utilizing the computational capabilities of GPUs to speed up TM on large-scale datasets.

Mission Relevance

In addition to the applications outlined for this project, our research result could be applied in intensive computer modeling, for supporting research such as climate change data processing, advanced computing architecture, risk analysis for national energy infrastructure, and confined plasma and high-energy particle beams problems currently of concern to DOE. The approach will provide general massive volume data analysis methods and advanced computing architecture that will be beneficial in many other research areas of interest. A successful result will enable us to demonstrate the use of much cheaper

GPU-enhanced systems to provide massive document processing capacities. This capability will benefit agencies such as the Department of Homeland Security, the Defense Advanced Research Projects Agency, and the intelligence communities, who have armies of analysts searching text on a daily basis in pursuit of the proverbial needle in a haystack.

Results and Accomplishments

During the project's first 3 months, we developed and presented a parallel latent semantic analysis (LSA) implementation on the GPU, using NVIDIA® Compute Unified Device Architecture and Compute Unified Basic Linear Algebra Subprograms. LSA aims to reduce the dimensions of large term-document datasets using singular value decomposition. Implementing LSA on a GPU is an important part of text mining a large-scale dataset on a GPU. With the ever-expanding size of data sets, current implementations are not fast enough to quickly and easily compute the results on a standard personal computer. The performance of this implementation is compared to traditional LSA implementation on a CPU using an optimized Basic Linear Algebra Subprograms library. The GPU version of the algorithm is five to six times faster than the CPU version for large matrices (1000×1000 and above) that had dimensions divisible by 16. By using this dimension-reduction technology, it is possible to fit 10^5 document vectors into a 1 GB graphic card for TM.

Part of this research is presented in an intern student research paper, "Massively Parallel Latent Semantic Analysis Using a Graphics Processing Unit." The paper has been selected for publication in DOE's *Journal of Undergraduate Research*, Vol. IX. The intern student has been invited by the DOE Office of Science to present this research at the annual meeting of the American Association for the Advancement of Science on February 12–16, 2009, in Chicago. An extended discussion of this research is being prepared and will be submitted to the 23rd IEEE International Parallel and Distributed Processing Symposium.

COMPUTER SCIENCE AND MATHEMATICS DIVISION

00471

Electron Transport at the Nanoscale: Grain Boundary Resistance in Interconnects

D. M. Nicholson, B. Radhakrishnan, X.-G. Zhang, An-Ping Li, and N. Kulkarni

Project Description

This project addresses the problem of the rapid increase in resistivity as copper interconnect lines in integrated circuits become narrower than 40 nm. Circumventing this problem is critical in maintaining Moore's Law growth in computer speed. A basic understanding of grain boundary (GB) resistance in interconnects will be obtained by phase-field crystal modeling of GB distribution and structure, first-principles calculation of the resistance of individual GBs, and the nanoscale measurement of resistance across individual GB of copper lines with carefully controlled geometry. The measurements will be done on copper lines that have been focused ion beam milled from blanket films that have been annealed to form large "bamboo" grains. The lines are 250 nm thick, 25,000 nm long, and 400–1200 nm wide. Electron backscattering diffraction is used to map the orientations of the grains in the line. The four-probe scanning tunneling microscope (STM) with cryogenic and ultrahigh-vacuum capability supplies current through two probes and measures voltage between two other probes that can be placed with nanometer precision. In this way the resistance of individual GBs is measured. First principles calculations of resistance of GBs are performed using multiple scattering theory within the Layer-Koringa-Kohn-Rostoker code. Understanding individual GB contributions to resistance will allow us to propose new microstructures and processes that may reduce resistance.

Mission Relevance

This project is important for the continued growth in computer speed needed to address DOE's energy and security problems, including basic energy science, climate modeling, and transportation. It is important to the Defense Advanced Research Projects Agency for military computing, sensors, control of manned and unmanned vehicles, missile guidance, implantable biodevices, and sensors. The National institutes of Health will benefit from the possible further miniaturization of biodevices and the reduction in power requirements, for example, for cochlear implants. The Department of Homeland Security will benefit from reduced power and size of explosive detectors.

Results and Accomplishments

We have extended a phase-field-crystal modeling method to run on parallel computers and used it to model microstructure evolution at the scale on interconnect lines. The electron transport codes based on multiple scattering theory have been modified and utilized to calculate resistance of grain boundaries in copper interconnects. We have analyzed the resistivity in terms of the effect of GB relaxation, electrostatic relaxation, and Fermi surface geometry. We have significantly improved our facility for making nanoscale wires suitable or investigation of interconnect resistance. Very small copper wires, 250 nm × 400 nm (less than a hundredth the size of a human hair) have been produced, and the orientation of each grain along the wire has been measured. The nano four-probe STM has successfully measured the resistance across line features including boundaries between grains. These measurements are the first of their kind.

Having demonstrated the ability to observe the resistivity of individual GBs, we will perform additional measurements as a function of wire width and thickness so that the relationship between surface scattering resistance and GB resistance can be quantitatively determined. Calculations will also be performed in support of these measurements. These two sources of information will be used as the basis for proposing solutions to the problem of high resistance in interconnect lines and the failure of lines due to electromigration.

ENVIRONMENTAL SCIENCES DIVISION

00429

Development of an Advanced Surface-Enhanced Raman Spectroscopy for the Identification and Characterization of Pollen

Shannon Mahurin, Meng-Dawn Cheng, and David Gossage

Project Description

The purpose of this project is to develop an advanced detection system utilizing the surface-enhanced Raman spectroscopy (SERS) technique for the identification and characterization of airborne, allergy-significant pollen. Raman spectroscopy provides chemical information through excitation of characteristic molecular vibrations. Raman signals of pollen are enhanced by attaching silver nanoparticles to the grains under flow conditions. This permits continuous in situ sampling and identification of the pollen grains as they flow through the system, resulting in a significant reduction in identification time as well as an increase in throughput. In addition to pollen identification, the chemical information provided by Raman spectroscopy allows us to characterize the chemical composition of the pollen grain and detect surface species attached to the grain. The effect of pollutants such as nitrogen dioxide on the pollen grain and attached surface species is explored using the SERS technique.

Mission Relevance

This project is relevant to the DOE mission of environmental quality through the reduction of the impact of energy production on the environment. Since the interaction of pollen with environmental pollutants has been suggested as one potential cause of the recent increase in allergy-related diseases in children, a reduction in pollutant concentration could reduce the number of respiratory problems in children and, potentially, the general population. This project also has significance to the Department of Homeland Security since the SERS technique can be used as a method for the identification and discrimination of pathogenic vs nonpathogenic bioaerosols, an area that has received focus primarily due to the recent national concern over bioterrorism. This project has significant potential to benefit other federal agencies such as the National Institute of Allergy and Infectious Diseases at the National Institutes of Health (NIH), whose mission is to better understand immunological and allergic diseases. The development of a technique to improve the characterization of a respiratory irritant such as pollen and to better understand the effect of environmental pollutants on the composition of pollen is ideally suited to the mission of NIH.

Results and Accomplishments

A microscope-based Raman system was successfully constructed and utilized for the simultaneous imaging and Raman spectroscopic measurements of pollen grains. Raman spectra from four different pollen grains (white pine, ragweed, tag alder, and velvet grass) were measured using the Raman instrument, and a unique Raman fingerprint for each pollen type was determined, verifying the application of Raman spectroscopy to the identification of pollen. SERS was used to increase the signal from the pollen grains with modest success, possibly due to weak silver-pollen interactions that result from surface charges on the pollen. Rhodamine 6g (R6g), a negatively charged organic molecule used as a Raman calibration standard, exhibited a strong SERS signal when attached only to the silver nanoparticles but a weak enhancement when combined with pollen then silver nanoparticles. Attempts to improve the silver-pollen interaction through modification of the surface charge on the pollen have produced limited gains in the SERS enhancement factors. Additionally, laser photobleaching was used to improve the signal-to-noise of the Raman spectra from the different pollen grains with good success. Modest Raman enhancements for antigens extracted from ragweed were observed using the colloidal silver and an evaporated silver island film. A manuscript detailing our results has been submitted to *Applied Spectroscopy*. In addition, a proposal based on this work is in preparation for submission to NIH.

00434

A Proof-of-Concept Implementation for a U.S.A. National Phenology Network Cyberinfrastructure

Bruce E. Wilson

Project Description

Phenology is the study of periodic plant and animal life cycle events, particularly those driven by changes in climate. Phenological measurements are extremely valuable indicators of local, regional, and global climate changes. Further, phenological variations have crucial environmental and socioeconomic implications for health, agriculture, and natural resource management. Despite this importance, broadly distributed phenological measurements are almost nonexistent in the United States. Over the last 3 years, substantial momentum has developed for a U.S.A. National Phenology Network (USA-NPN), with a variety of workshops, publications, and funding from several agencies. Given ORNL's existing expertise in environmental and biological informatics and our participation in USA-NPN planning activities, we have a leading position as a possible institution to be the cyberinfrastructure host for the proposed USA-NPN. The objective of this project is to maintain and enhance that position by developing proof-of-concept implementations of key informatics technologies needed for USA-NPN.

Mission Relevance

There are two areas of benefit to DOE. The first area is that phenological measurements are important to climate change research, particularly in terms of understanding ecosystem response and potential ecosystem disruption. Within this area, phenological measurements are particularly useful as inputs and validation measurements for climate model research funded by DOE. The second area is that the informatics technologies we will be developing in this project should be of use to other ecological research areas. It is possible, though far from certain, that these informatics technologies will have applicability to other data and information management needs within DOE.

Results and Accomplishments

During FY 2008 we extended the data model developed during FY 2007 and implemented it on servers provided by the U.S. Geological Survey and located at the University of Arizona. The USA-NPN website (http://www.usanpn.org) went live in early February, with a modest number of observers. Several improvements to the model and data entry codes have been made over the course of FY 2008, with these improvements expected to be in production use for the calendar 2009 growing season. We implemented a metadata harvesting, indexing, and searching tool for phenological data, based on the ORNL Mercury technology. Much of this work was done in FY 2007, with the tool going live in FY 2008. Based on our involvement with this work, Bruce Wilson was selected to be a part of the USA-NPN transitional Board of Directors for calendar 2008 and was elected to a two-year term on the full Board of Directors, with the term starting in January 2009. ORNL's involvement with USA-NPN has also resulted in Bruce Wilson being involved with two National Science Foundation workshops relating to cyberinfrastructure for environmental observing systems. To date, these workshops have not produced any substantive outputs, but they have served as a means for broadening our exposure in the environmental informatics community.

Publications

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00464

Linkage Disequilibrium as an Analytical Tool for Gene Discovery

T. M. Yin and L. E. Gunter

Project Description

In the post-genomic era for *Populus*, association studies based on linkage disequilibrium (LD) analysis will be one of the most promising genetic approaches for discovering genes underlying important economic and ecological traits. Although we have the capability to carry out most analyses essential to functional genomics studies, we lack this important LD association research tool, an approach that has proven successful in understanding human disease. With this project, our objective is to use gender determination in poplars as a proof of principle to develop LD capabilities and to test its power for novel gene discovery in *Populus* as well as in other outbred plant species. Building on this concept, we have carried out a research effort that includes (1) assembly of all the sequence scaffolds containing MADS-box genes (the expected result is to improve the overall sequence assembly for the poplar genome), (2) fine mapping of MADS-box genes linked to the gender determination locus (the expected result is to establish the capacity for genotyping coding genes and generate a list of candidate genes for LD analysis), and (3) identification of candidate genes for gender determination in *Populus* by LD analysis (the expected result is to create an LD association analysis pipeline at ORNL).

Mission Relevance

This work is relevant to the Bioenergy Center Program within the DOE Office of Science and supports the research programs relating to the nation's energy security. With the development of LD association as part of our genomics toolbox, our overall analytical capabilities will be strengthened. This type of resource is essential for the renewal of many ongoing genomics projects and for application of new funds that fall under the scope of DOE missions. By having developed this LD genetic tool, ORNL will be poised to offer a unique approach that will give us a distinct advantage in competitive funding opportunities.

Results and Accomplishments

During FY 2008 we fulfilled the three major goals by the following achievements: (1) generated a definitive list of MADS-box genes represented in the poplar genome and determined their distribution, (2) mapped the unmapped scaffolds that contained MADS-box genes with simple sequence repeat genotyping of 96 progeny of the sequenced individual Nisqually-1, (3) created better sequence coverage in the region of the gender locus on chromosome XIX and generated a candidate genes list for LD analysis, (4) sampled 40 female and 40 male poplars in Cumberland Plateau used for LD analysis, (5) sequenced the selected candidate genes and conducted LD association analysis with known gender phenotypes, (6) published two papers and have one manuscript in preparation relating to this project. We also established the LD analytical tool as proposed in this project.

Publications

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00466

Tracing Nanoparticle Transport in Porous Media by Neutron Radiography and SANS

Baohua Gu, Wei Wang, Ken Littrell, Hassina Z. Bilheux, and Xun-Li Wang

Project Description

We proposed to use thermal neutron radiography and small-angle neutron scattering (SANS) to probe the deposition and transport behavior of nanoparticles in sediment porous media because of growing concerns of potential environmental and health risks of engineered nanoparticles. Unlike the black-box approach used in early studies, this research represents the first-ever proof-of-principle measurements of the deposition and transport profiles of nanoparticles and particle aggregates in situ as a function of particle size and surface chemical characteristics. The transport behavior of titania (TiO_2) is investigated in packed columns under flow conditions. Both labeled and unlabeled TiO_2 nanoparticles with controlled sizes are synthesized to facilitate in situ, nondestructive analysis of the deposition and transport processes. This study will lay the foundation of using a neutron source to explore the fate and transport of nanoparticles in the environment and will benefit the development, management, and risk assessment of engineered nanomaterials.

Mission Relevance

Nanoparticles such as TiO_2, silica, and other metals or metal oxides are among the most widely used nanomaterials in advanced energy, catalysis, and commercial applications. Therefore, studies of the fate and transport of nanoparticles in the environment will benefit the development, management, and risk assessment of engineered nanomaterials and technologies. DOE programs that may benefit from the current research include biological and environmental research, basic energy sciences, and materials sciences.

Results and Accomplishments

In FY 2008 we performed both neutron thermal imaging and SANS experiments using different sizes of silica (SiO_2) and titanium oxide (TiO_2) nanoparticles. The neutron imaging experiment was performed at the Neutron Research Facility in Garching, Germany, and results provided the proof of principle for observing the particle transport through the porous quartz media. However, the image resolution and contrast were somewhat unsatisfactory, especially at relatively low particle concentrations (with doped cadmium or gadolinium). Additional proof-of-principle experiments are being planned in FY 2009 using relatively higher concentrations of particles and doping rates.

We also performed the SANS experiment at HIFR in July and October 2008. Results show clear patterns of particle interactions and aggregation behavior during the transport of either SiO_2 or TiO_2 nanoparticles through the quartz media under different pH and ionic compositions. In addition, we performed the breakthrough experiments of these nanoparticles using both gadolinium- and fluorescent-labeled SiO_2 or TiO_2 nanoparticles. Results indicate that the transport of TiO_2 nanoparticles in quartz media is significantly retarded and affected by the surface charge which, on the other hand, strongly depends on the pH of the medium. These results provide fundamental insights on how engineered nanoparticles behave and migrate in subsurface aqueous environments.

In FY 2009 we will continue studies by SANS of the interactions of particles, particle aggregation, and morphology within the porous media. Together with data obtained in FY 2008, we expect to elucidate the effect of particle size and geochemical properties on the deposition and transport of nanoparticles in situ, which would otherwise be impossible to obtain with conventional techniques. These studies will provide important information on the rates and geochemical controls on the fate and transport of engineered oxide nanoparticles in the environment.

00486

Analyzing Incentives Related to Patent Licensing and Technology Transfer for Large R&D Partnerships

D. J. Bjornstad and A. K. Wolfe

Project Description

This activity seeks to study the ability to adapt existing microeconomic models and related analysis that focus on current intellectual property (IP) topics to an emerging set of issues relevant to large R&D partnerships. In the past few years, ORNL developed a capability to study patenting issues related to gene sequencing topics through the DOE Ethical, Legal, and Social Implications (ELSI) program. The research identified important issues and investigated and tested microeconomic models dealing with patents for gene fragments. In this project, we investigated models that address a broader set of issues associated with patenting and licensing and examined their relevance to the outputs of R&D partnerships. We reviewed key pieces of relevant literature in which R&D firms look upstream to license tools of research and downstream to offer licenses to other firms that will make use of its IP in producing goods for final markets.

Mission Relevance

DOE is a major supporter of center-based R&D, within which teams composed of universities, other research centers, and the private sector collaborate to address basic and applied research objectives. By analyzing the impacts and consequences of alternative IP practices, DOE can better understand the forces that influence the speed with which the results of its research can be put into use. We anticipate that a variety of DOE research centers will benefit from the analysis demonstrated through this effort.

Results and Accomplishments

Our literature review and analysis indicates that the evolution of patenting issues and topics has continued since our earlier biomedical studies, with particular relevance evident in the nanotechnology research industry. We examined these topics for the nanotechnology industry and gathered together a range of publications describing the nanotechnology patenting situation. Our overall conclusion is that the set of topics relevant for nanotechnologies is much broader than those for biomedical topics, in part because the range of patentable subject matter has grown, the science and technology has proceeded incrementally, and the principal thrust of current nanotechnology studies is the development of enabling technologies with broad downstream applications. Our review of some of the technical models suggests this literature provides a basis for moving forward with the study of patenting issues for nanotechnology topics and should provide a starting point for bioenergy centers, a topic on which there has been done very little research. We document a portion of this work in the paper cited below.

00496

In Situ Neutron Imaging of Roots and Rhizosphere Water Exchange

Stan Wullschleger, Jeff Warren, and Hassina Bilheux

Project Description

Despite years of investigation, in situ imaging of roots and a dynamic evaluation of root water uptake from soil and transport within the plant has not been undertaken due to the lack of suitable techniques. In the past, root imaging and analysis of water exchange at the root-soil interface or rhizosphere has relied on isotope or dye tracers, or X-ray analysis. These approaches are labor intensive and either cause disturbance to the system or lack adequate spatial and temporal resolution to be informative. Our research explores the use of neutron imaging to create high-resolution images of plant roots and water dynamics in the root zone. Specifically, we are using the Spallation Neutron Source (SNS) and the High Flux Isotope Reactor (HFIR) facilities to determine temporal patterns of water exchange in a root system and transport through plant xylem. Our research will evaluate (1) whether or not neutron imaging can be used to determine physical and chemical boundaries between root, the root-soil interface, and soil; and (2) whether or not neutron imaging can resolve patterns of water flux to and from roots. Our research is directed at resolving basic biological principles regarding water, carbon, and nutrient flux dynamics within and between soil, plants, and fungi.

Mission Relevance

Our research is directly relevant to several areas of interest to DOE, especially as it relates to the integration of neutron facilities into areas of biological research, including bioenergy, carbon-cycle science, and global climate biology. This project attempts to address programmatic goals and objectives of the DOE Office of Science, Biological and Environmental Research through the GTL: Genomics Program, the Terrestrial Carbon Program, and the Program for Ecosystem Research. Many agencies support research that would benefit from new technology for the analysis of root images. Examples include evaluation of agricultural crops (Department of Agriculture, Agricultural Research Service), forest trees (Department of Agriculture, Forest Service), and basic research conducted by the National Science Foundation.

Results and Accomplishments

The goal of this research is to evaluate neutron imaging for nondestructive, quantitative analysis of root structure, and soil, root, stem, and foliar xylem water flux. Towards this goal, in FY 2008 we constructed small plant chambers that can be imaged using the SNS and HFIR facilities. Chambers were constructed from aluminum cylinders 1–20 cm in diameter or from aluminum plates welded into thin boxes, 1–3 cm thick. Switchgrass, maize, and poplar plants were successfully cultivated in sand using up to 50% deuterium with no visible side effects.

Initial neutron imaging of plants was successfully conducted at beam line 3 (SNAP) using a small 2 cm^2 experimental University of California, Berkeley detector system. The detector and stage size available limited imaging to small chambers (1 cm across) and plant stem and foliar tissue. Neutron imaging successfully distinguished between nondeuterated and deuterated poplar leaf samples. Fine leaf veins (<200 um) are readily visible in the nondeuterated sample, in comparison to the deuterated sample. This difference in contrast establishes the potential for tracking a pulse of water though plant xylem. A single switchgrass leaf blade, seed, and root system was also imaged through time following an injection of water; data are currently under analysis. Further work will be conducted at SNS and HFIR in summer 2009. We expect to have a 100 cm^2 detector available at HFIR and a much higher neutron flux, which will enhance imaging and enable expanded experiments well beyond this initial stage.

ENERGY AND TRANSPORTATION SCIENCE DIVISION

00462

Evanescent Power Transfer for Electric Vehicles

Timothy S. Bigelow, John B. Caughman, John W. McKeever, Philip M. Ryan, and Matthew B. Scudiere

Project Description

Electric vehicle applications will likely require power levels of 20 kW over half-meter distances for static transfer and over larger distances for dynamic transfer. This project, approved for FY 2009–2011, will employ models and hardware to extend the power level and transmission distance.The project objectives were to (1) apprehend the electromagnetic interactions identified in the literature as “evanescent power transfer,” (2) develop computer models to simulate the ability to transfer power from a stationary transmitter to both fixed and moving receivers, (3) check the models for consistency and compare with laboratory measurements using available coils, (4) use the simulators to quantify power transfer available to operate electric vehicles, (5) design and build large coils in a Faraday cage, and (6) measure their power transfer capacity. This enabling research addresses loosely inductively coupled power transfer, a favored power coupling option for guideways, to reduce pollution and oil use by supplying green power from renewable sources to a dedicated guideway or electrified highway. Three hundred watts was transferred between two large coils at an efficiency of 82% with full overlap at a separation of 0.17 m. Power was limited only by the available power source.

Mission Relevance

Two missions of the DOE Office of Vehicle Technology (OVT) are to reduce dependency on foreign oil and to reduce emissions. The plug-in electric vehicle, whose technology is being encouraged now by OVT, and electrified highways, whose power may be supplied in the near future by an existing utility source grid or by a special source grid created to use renewable power source, are two technologies that effectively support these missions. In both technologies power must be transferred from the source grid. Although the term *plug-in* in plug-in electric vehicle implies direct electrical grid contact to charge the batteries, power transfer also could be accomplished using a loosely inductively coupled system, which involves parking over a transmitting coil and eliminates the cord. For the electrified highway it may be possible to share a higher power transfer not only to charge the batteries but also to propel the traction drive.

Results and Accomplishments

The electromagnetic interaction labeled “evanescent power transfer” occurs in a loosely inductively coupled air-core transformer in which the primary is compensated to reduce the required VA rating, size, and cost of the power source, and the secondary is compensated to maximize the power transfer from the primary to the secondary. The phenomenon was modeled using software with several degrees of sophistication, including MathCAD™, PSim, and Microwave Studio (MWS). The MathCAD™ models were representations of a parallel double-tuned transformer circuit (Pieter L. D. Abrie, *The Design of Impedance-Matching Networks for Radio Frequency and Microwave Amplifiers*, Artech House, Inc., 1985, p. 109) and of an equivalent circuit modeled with a transformer coupling factor, k, whose variation described the effect of coil offset and separation. It revealed a bi-modal shape at 1.6 to 2.0 MHz with efficiency greater than 90%. Corresponding PSim models allowed fine tuning switching schemes for different loads and examination of corresponding efficiencies and peak power levels, indicating that precise source driving circuit control is necessary for high power transfer with antenna separations of 0.3 m at low to mid 90% efficiencies. The MWS electromagnetic solver characterized reflection coefficients and transmission coefficients for comparison with measurements on two small coils and on two large coils in a Faraday cage with one coil suspended on rollers. Measurements were made for large-coil separations of 0.17 and 0.3 m for lateral displacements from 0 to 1 m. Calculated and measured values agreed well, supporting use of these software tools in future research.

MEASUREMENT SCIENCE AND SYSTEMS ENGINEERING DIVISION

00436

Plasma Etching and Simulation of Electron Scattering in Nanoscale Copper Interconnects to Minimize Size Effects

Gary Alley, Nagraj Kulkarni, Boyd Evans, Hsin Wang, Harry Meyer, Bala Radhakrishnan, Don Nicholson, and Peter Todd

Project Description

This project aims to research and develop a low-temperature plasma etching process for copper interconnects for feature sizes ranging from 25 to 1000 nm having controlled anisotropy, surface roughness, and etch rates. Diffusion, plasma etching, characterization, and process monitoring studies in copper films will provide guidelines for the control of plasma etching in patterned features. Furthermore, an electron scattering simulation that can model the experimental resistivity in such features as a function of various microstructural properties in copper films will be developed with input from existing first principles, grain growth, and stochastic scattering models. Achievement of these objectives will provide for the first time a significant reduction of the size effect in the electrical resistivity of copper interconnects in semiconductor devices, which will meet the targets established by the International Technology Roadmap for Semiconductors (ITRS) for future generations of copper interconnects, and enable the continuation of Moore's law in the foreseeable future.

Mission Relevance

If adopted by industry, this project may provide significant energy and cost savings and productivity gains for interconnect manufacturing, which accounts for more than half of all the chip manufacturing steps in the semiconductor industry. In addition, significant environmental benefits due to minimization of process steps such as copper chemical mechanical planarization (CMP) and elimination of copper electroplating are expected. The modeling thrust in this project will investigate the scientific reasons for electron scattering in narrow interconnects that causes the size effect phenomenon in copper interconnects. These include factors such as the grain size and distribution, texture, geometry, and interfacial properties. Possible DOE programs benefitting from this research are programs in the DOE Office of Energy Efficiency and Renewable Energy on nanomanufacturing, nanotechnology, and power electronics packaging. Follow-on funding with the Defense Advanced Research Projects Agency is currently being pursued. Two user proposals (N. Kulkarni, B. Evans) related to this project were funded by the Center for Nanophase Materials Sciences (CNMS) and the Shared Research Equipment User Facility in FY 2008–2009. Collaboration between Intel and ORNL (X. Zhang, D. Nicholson) resulted in a successful CNMS user proposal in FY 2008–2009. Work for Others funding from Intel is currently being pursued.

Results and Accomplishments

The Trion plasma etch tool that is central to this project was not operational for the experimental work in FY 2007. An upgrade to install an electrostatic chuck permitting circulation of a low-temperature coolant (up to –80°C with a chiller) was completed in 2008. Preliminary experiments with the upgraded tool began in latter half of FY 2008. Plasma etching experiments were conducted on a sputtered 500 nm copper film on a 10 nm tantalum barrier layer that was sputter deposited on 10.2 cm thermally oxidized silicon wafers. Based on previous work, the two-step etching process for copper consisted of multiple chlorine and hydrogen cycles to etch copper films. Each cycle consisted of 15–30 s of chlorine plasma exposure followed by 30–60 s of hydrogen plasma exposure at different temperatures (below 25°C) and plasma operating parameters (e.g., pressure, inductively coupled plasma reactive ion etching power, flow rate, etc.). Profilometry was used to record the effective etched thickness that reflected both the copper thickness removed as well as the thickness increase due to the residual chlorine in the copper film after the last cycle. X-ray photoelectron spectroscopy was used to investigate the stoichiometry and bonding between copper and chlorine in films subjected to various plasma chlorination conditions. Initial plasma etching experiments were conducted, and the results illustrated the ability to convert copper to copper chloride in the chlorine plasma. Further work needs to be performed to obtain an etch rate as a function of plasma operating parameters. Unfortunately, work on copper patterns using lithography could not be performed due to the delay in the equipment upgrade; however, such studies are expected to continue through future funded programs in this area.

Preliminary first principles modeling of some special grain boundary (gb) resistivities in copper, such as Σ3 twin boundaries and Σ5 twist boundaries, was performed. The Σ5 resistivity (31×10^{-17} ohm-m^2) was found to be an order of magnitude larger than that of Σ3 (1.1×10^{-17} ohm-m^2), which confirms measurements in the literature. For mesoscale microstructure simulation, a Monte Carlo technique was used to simulate the evolution of grain structure when the growth dimension was constrained. The simulations also took into effect diffusion along the free surface of a thin film. All grain boundaries were assumed to be of the high-angle type with identical energies and mobilities. Surface diffusion led to the formation of a grain boundary groove. Various geometries involving confinement in one, two, and all three dimensions were studied to understand the influence of the constraint on grain morphology. The results indicated that in all cases the grain growth ceased after the mean grain size was roughly equal to the film thickness. A bamboo structure was obtained in all cases, and there was no evidence for the stagnation of an equiaxed grain structure for any of the geometries studied.

Publication

Nicholson, D. M., S. Namilae, B. Radhakrishnan, X. Zhang, and N. S. Kulkarni. 2008. “Modeling Electron Transport in Copper Interconnect Microstructures.” *Proceedings of the Advanced Metallization Conference (AMC2007)*, Oct. 9–11, 2007, Albany, N.Y. Published by the Materials Research Society, A. J. McKerrow, Y. S. Diamand, S. Shingubara, and Y. Shimogaki (eds.).

00459

Quantitative Imaging of Subcutaneous Veins with Multispectral Illumination and Three-Dimensional Modeling

Kenneth W. Tobin, Vincent C. Paquit, and Jeffery R. Price

Project Description

We aim to demonstrate that it is feasible to perform optical imaging of subcutaneous veins, including estimation of the relative vein depth and diameter. We approach the problem using (1) multispectral imaging, since the propagation of light in tissue has been characterized as a function of wavelength in previous research; (2) laboratory experiments on phantoms and human subjects in order to validate theoretical approaches and hypotheses regarding the skin structure selected and the optical phenomena to be considered; (3) three-dimensional Monte Carlo photon transport modeling to simulate light propagation in tissues (reflection, absorption, transmission) method used to link experimental results and theoretical formulations; and (4) investigate inverse imaging approaches, including parametric and pattern recognition techniques. If successful, we expect this project to enable the near-term development of devices to assist humans with venipuncture and catheterization procedures. In the longer term, we envision this technology as one component of a fully automated, robotic venipuncture device, a methodology for producing accurate biometric information using unique venous structures, and a methodology for surgical imaging to characterize blood reperfusion in transplant surgery.

Mission Relevance

This project can be associated with Strategic Theme 3 (Scientific Discovery and Innovation) of the DOE Strategic Plan: Strengthening U.S. scientific discovery, economic competitiveness, and improving quality of life through innovations in science and technology. With the potential applications in military health care, this project will be beneficial to national security needs as well. The project will benefit the program areas of several federal agencies, in particular the U.S. Army Telemedicine and Advanced Technologies Research Center (Medical Imaging Technologies, Hospital/Operating Room of the Future programs); the National Institute of Biomedical Imaging and Bioengineering (Image-Guided Interventions and Optical Imaging and Spectroscopy programs); and the National Institute of Justice (Biometric Technologies).

Results and Accomplishments

To demonstrate the feasibility of the proposed approach, we undertook three research tasks during FY 2008:

1. We constructed, optimized, and quantified a laboratory imaging system required for accurate venous imaging. By combining a digital camera and a broadband light source associated with a monochromator, we capture hyperspectral images of the skin, from which the location of the subcutaneous vein's center lines are extracted. By combining the two-dimensional (2-D) location of the veins with the 3-D location of the surface of the arm (obtained by active optical triangulation using a projected structured light pattern), one can compute the 3-D path that will guide robotic needle insertion in the vein.
2. To improve the response of our system to variable skin structure (e.g., skin tone, fat concentration, hydration), we performed multispectral analysis on a limited number of Institutional Review Board–approved skin datasets captured with our vision system. We defined a multispectral image processing method for subcutaneous structure classification based on linear data reduction techniques (e.g., Principal Component Analysis and Linear Discriminant Analysis). Preliminary results were presented at the OSAV'08 conference, and further developments of this technique are currently subject to an ORNL invention disclosure.

3. To evaluate the influence of the topography and molecular structure of the skin surface using image processing techniques and to simulate intensity images as seen by an imaging camera, we developed a tri-dimensional Monte Carlo light propagation model. Ongoing research investigates light propagation techniques to retrieve skin molecular structure and blood vessel depth in order to reconstruct a full 3-D model of the subcutaneous vascular system.

Publications and Patent

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00460

Regeneration for Energy Efficient Fluid Power Systems

John Jansen, Lonnie Love, and Peter Lloyd

Project Description

Tremendous energy savings potentially can be achieved through focused research on energy-efficient hydraulics for industrial hydraulics and heavy equipment. These energy savings will require energy regeneration. Regeneration, commonly used in electric motor drive systems to attain high levels of efficiencies, has had limited success with fluid-based systems due to the fundamental differences in the governing physics. Fluid power regeneration offers the opportunity to significantly impact the energy efficiency of existing hydraulics systems. Two fundamental problems had to be solved to enable fluid-based regeneration. First is the lack of a switching element that's analogous to the power transistor found in power electronics. To solve this deficiency, a compact high-flow, high-speed, low-cost fluid-switching control element that can accurately modulate fluid flow with low fluid energy losses is needed. The second problem is a lack of a control methodology for using these switching elements to realize the potentially significant energy recovery.

Mission Relevance

Due to the pervasiveness of hydraulics across a broad spectrum of industries, the application of energy-efficient hydraulics has tremendous potential and is directly relevant to the DOE mission of energy efficiency. Energy efficiency is of critical importance for many mobile applications. These include excavation and construction equipment, and mobile manipulation such as explosive ordinance disposal (EOD) robots used by police department bomb squads and the military. Mobile robotic systems are sensitive to power and energy requirements, particularly those that are battery operated. Potential beneficiaries of this research include the Department of Justice, the Navy's EOD Tech Center (interservice EOD lead), and the Technology Support Working Group (a cooperative effort of the Departments of Justice, Defense, and Homeland Security attempting to put counterterrorism technology into the field).

Results and Accomplishments

The major accomplishment of this project was the development and demonstration of a novel two-stage valve that enables high-efficiency fluid control with large flow rates and low energy losses that is inexpensive to fabricate. An invention disclosure has been filed at ORNL, entitled "A Hydraulic Flow Control Device by Means of a Two-Stage Digital Poppet Valve" (05-686). This invention disclosure has been elected to be retained by UT-Battelle. Initial work was also undertaken on a fluid control methodology to achieve energy recovery by means of regeneration through these valves. While it was possible to show significant energy recovery for specific cases using the above-mentioned valve elements, a general control methodology is still an ongoing research effort.

00461

Combined Real Time Quantitative Phase and Fluorescence Biological Microscopy by Digital Holography

Christopher Mann, Philip Bingham, Jeffery Price, Yisong Wang, John Biggerstaff, and Michael Zemel

Project Description

Biological processes and structures in transparent objects that produce refractive index changes or variations of the shape are of particular interest in the field of life sciences. For most existing phase-contrast techniques, the phase-to-amplitude conversion is nonlinear and the phase information is not quantitative. Digital holography offers an excellent approach to quantitative phase imaging, providing an optical thickness resolution of a few nanometers. On the other hand, while digital holography provides morphological information about a sample with nanoscale precision, the application of fluorescence imaging reveals specificity and functional details. Currently, instrumentation for generating fluorescence and quantitative phase information simultaneously is lacking. The objective of this research is to construct and develop a new, combined, dual-mode quantitative phase-and-fluorescence instrument that will enable robust, real-time imaging**,** and also to develop and apply total internal reflection digital holographic microscopy (TIRHM) to visualize and quantify cellular interactions.

Mission Relevance

This research in biological microscopy and imaging analysis supports the DOE Office of Science in the area of biological and environmental research. The underlying technology being leveraged for this project was developed at ORNL through research supporting the Office of Energy Efficiency and Renewable Energy and the Industrial Technologies Program. The original work was performed in the area of industrial automation and is now being applied to cellular and biological imaging.

Results and Accomplishments

The holographic-fluorescence microscopic system was built recently, and we are entering the testing and optimization period. The microscopic system incorporates a newly designed fiber-optic delivery system in a conventional microscope. This novel and robust system is highly attractive to biomedical researchers who require 3-D morphological information from their samples in combination with functional information. So far our research has yielded unparalleled subnanometer resolution measurements and excellent image clarity. This bodes well for future metrological analysis and application to biological problems. Over the last year this work has resulted in a conference presentation, the submission of three invention disclosures, and the publication of a journal paper.

We have solved some of the wider issues that had precluded the day-to-day use of this technology in conventional real-time biological microcopy. Some of the problems we have solved include wave-front aberration correction, auto focusing, and accurate mounting of the sample. With the promising image quality and resolution we have so far achieved, we expect that our instrument will provide high-resolution, real-time, unambiguous imagery and that the utilization of the proposed techniques will generate new scientific knowledge in the biosciences.

Publications

Mann, C. J., et al. 2008. "Quantitative Phase Imaging by Three-Wavelength Digital Holography." *Opt. Express* **16**, 9753–9764.

Mann, C. J., et al. 2008. "Three-Wavelength Phase Imaging Digital Holography of MEMS Motion." *OSA Digital Holography and Three-Dimensional Imaging (DH) Conference*, St. Petersburg, Fla.

00469

Nanostructured Materials for Enhanced Radiometric Forces at Atmospheric Pressure

Brian D'Urso, Slobodan Rajic, Nickolay V. Lavrik, and Panos G. Datskos

Project Description

Radiometric forces are the result of thermal effects in gases in the presence of a temperature gradient. Crookes' radiometer, which is enclosed in a low-pressure chamber and operates by sunlight, is an example that utilizes these forces. For the past century, Crookes' radiometer found no practical application because of the small mean free path of air molecules at atmospheric pressure (<100 nm), which necessitates operation in a partial vacuum. Recent advances in nanofabrication enable the fabrication of nanostructured surfaces with features of the order of the mean free path in air under ambient conditions. In addition to operation in atmospheric pressure, such structures experience much larger radiometric forces in the presence of temperature gradients. We seek to develop nanostructured materials and objects with the appropriate geometry to experience drastically enhanced radiometric forces. A team with experience in nanofabrication and measurement of small forces will develop nanostructured surfaces and measure the enhanced radiometric forces. Potential applications include microelectromechanical systems (MEMS) devices, cooling, and waste heat recovery.

Mission Relevance

If successful, this research will result in a material that can convert small temperature gradients into mechanical motion. This could be relevant to the DOE energy security mission by leading to the development of devices that could extract useful work or energy from low-grade waste heat from power production or other industrial processes. The potential enabling feature of these materials for waste heat energy recovery is the large force that potentially could be produced from even a 1°C temperature difference. This project will benefit agencies in the Department of Defense, particularly the Defense Advanced Research Projects Agency. By converting temperature differences to mechanical motion, the material we develop may provide a means of propelling micro-air vehicles for use in surveillance or offensive systems.

Results and Accomplishments

We have completed most of the nanofabrication of materials for enhanced radiometric forces, and we have prepared a system for measuring the Knudsen forces on those materials in a temperature gradient. We have fabricated membranes with nanoscale thickness and porosity over approximately 1 cm^2, and we have separated these membranes from their original substrate. One critical step, opening the pores from the back side of the membrane, remains in the fabrication. The system for measuring Knudsen force on the membranes using a calibrated torsion pendulum has been prepared and is awaiting completion of the membrane fabrication process. We have also planned the remainder of the project. We expect to complete the nanofabrication of materials for enhanced radiometric forces and measure the forces on those materials in a temperature gradient with the apparatus we have developed. This will include opening the pores on the back side of the membranes to complete the fabrication of membranes with nanoscale thickness and porosity over areas of at least 1 cm^2. The material will be characterized by exposing it to temperature gradients at different pressures from atmospheric pressure to a partial vacuum while it is suspended on a torsion pendulum. An optical readout of the deflection will provide a measurement of the Knudsen force enhancement due to the material nanostructure for comparison to the current theory of thermal transpiration and a measure of the success of the project.

00484

Novel Method to Achieve High-Resolution Neutron Microscopy

Philip Bingham

Project Description

The goal of this project is to develop and demonstrate a coded source imaging system for neutron radiography that will significantly improve the resolution for neutron microscopy. The world's best resolution achievable through conventional neutron radiography is on the order of 100 μm, with significant progress being made towards achieving 10 μm resolution using expensive, experimental refractive optics and new detector technologies. The goal of this project is to demonstrate resolution in the 25 μm range and provide a clear path forward to achieve <1 μm resolution using conventional technologies. We propose a new implementation of the coded aperture for neutron radiography that uniquely encodes the source of neutrons passing through an object as opposed to an encoding of radiation emitted from an object.

Mission Relevance

It is anticipated that this project will provide a proof of concept that supports the investigation of microscale structures such as microchannel heat exchangers, fuel cell components, and biological microscopy for pharmacology and drug delivery research. The application areas for the neutron microscopy method being developed cover many DOE missions. In particular, heat exchanger and fuel cell research both fall under energy resources and environmental quality; biological microscopy imaging is a valuable tool for biofuel research, environmental quality study, and basic sciences research. One key goal of this project is to establish the technical feasibility for a neutron imaging instrument at the Spallation Neutron Source (SNS). If successful, the capabilities developed in the project will provide an instrument useful to many federal agencies.

Results and Accomplishments

Although the project began late in FY 2008, several key accomplishments were made. First, a contract was put in place with North Carolina State University (NC State) that provides support from Dr. Ayman Hawari and his students as well as access to the neutron imaging instrument at NC State. Second, working with Hassina Bilheux of SNS, we identified a potential manufacturer of the gadolinium masks that will be needed for the prototype system. Third, linear stages suited for positioning the aperture and anti-aperture masks were identified and purchased for the system. Funding and effort are continuing in FY 2009.

00488

Actuation and Control of Wearable Robotics

Lonnie Love, Peter Lloyd, and Randy Lind

Project Description

The focus of this project is the development of high-pressure (>2000 psi), microfluidic actuation (<0.063 in. diam) that will enable a new class of compact, lightweight, wearable robotic devices. Our first task focuses on the development of a high-pressure (>2000 psi), very-low-flow (0.5 mL/s) control valve. Actuator motion is controlled by this valve. Due to the very small orifices (<0.003 in. diam), flow is controlled by pulse width modulation rather than a variable orifice area. This introduces our second problem, pressure pulsations in the fluid that will introduce noticeable vibration on the actuators. Our second task is focusing on controlling the timing between adjacent flow control valves to mitigate vibration. The final task is the development of a single-joint, wearable, finger mechanism to demonstrate the compactness and fidelity of fluid-based wearable robotics.

Mission Relevance

The primary relevance of this project is the development of a new class of actuators suitable for miniaturized fluid power systems. The utility of such actuators to DOE is in the area of wearable haptic devices to aid in remote handling of hazardous materials. The relevance for the medical community relates to physical rehabilitation for stroke recovery, active orthotics, and advanced prosthetic devices. This work has already led to a new program, in collaboration with OrthoCare Innovations, in the area of prosthetic alignment devices. In terms of military relevance, this technology has utility in morphing wing technologies for advanced flight control surfaces.

Results and Accomplishments

The project consists of three tasks: development of a high pressure, low flow control valve; development of a control methodology to accommodate pressure pulsations; and development of a force–controlled, wearable finger mechanism. For the first task, we successfully developed a control valve that is suitable for wearable robotics. For the second task, mitigation of pressure pulsations, we demonstrated the fidelity of the approach through simulation. However, we discovered a revolutionary new approach to the control of fluid-based wearable robotics that simultaneously mitigates pressure pulsations while changing the behavior of fluid-powered actuators. This approach is more mechanical in nature and enables the control of the wearable device to be more like traditional haptic interfaces. There are two distinct characteristics of this approach. First, the actuation consists of a pair of antagonistic actuators driving an involute cam. The antagonistic actuators eliminates backlash in the system and the need for a rod seal (reducing friction and complexity). The involute cam provides a constant transmission ratio, which likewise reduces complexity and actuation size. Second, each actuator has a fixed orifice between the supply pressure and actuator chamber and a control valve between the actuator chamber and return pressure. The remaining activities will focus on experimental validation of the control of the wearable finger mechanism.

00494

Novel Method for Three-Dimensional, Depth-Resolved Imaging of Highly Scattering Samples

Justin S. Baba, Philip R. Boudreaux, and Seung Joon Lee

Project Description

Depth–resolved, three-dimensional (3-D) imaging of highly scattering samples (e.g., aerosols, the atmosphere, murky water, subterrain, biological tissues) is significant for varying segments of the commercial and military/law enforcement arenas. Although the literature is full of endeavoring approaches based on eliminating multiple scattered photons from the image plane via spatial, time, or coherence gating techniques, we propose a paradigm shift. It exploits underlying scattering physics to detect varying degrees of radiation scatter as a means to generate 3-D images of samples. Our technique utilizes state of polarization gating (SOPG) to localize reflected radiation from varying depths to generate stacked 2-D images. Depth imaging performance of this novel technique is expected to be 2–3 times greater than that of optical coherence tomography but less than that of ultrasound, with the added advantage of simplicity for easy miniaturization and future low-cost implementation.

Mission Relevance

This project is applicable to DOE energy, environmental, atmospheric, aerosol, and oceanic research that requires imaging through highly scattering samples (e.g., air pollutants, aerosol particles, murky waters). It is also applicable to the National Institute of Health and the Department of Defense (DOD) (medical imaging of high scattering tissues for rapid assessment of skin pathologies, wounds, and burn conditions); to law enforcement efforts (locating objects in murky waters); and to DOD and the Department of Homeland Security (imaging subterranean and other high scattering sites or objects for explosive devices).

Results and Accomplishments

We are in the process of assembling the system instrumentation; future results will be reported.

00498

Optical Resonance Disk-Based Infrared Thermal Detectors

S. Rajic and P. G. Datskos

Project Description

Detection of infrared radiation (IR) is important for a variety of activities, and microdisk resonators are proposed as very sensitive thermal detectors. The quality factor of microdisks can be greater than 106, which would provide excellent thermal IR sensitivity. A thermal microdisk detector consists of a waveguide, a microdisk resonator, and a thermal isolation region. When probe light with wavelength λ is introduced into the microdisk of radius r and refractive index n, for example, by side-coupling it with an optical waveguide, a substantial reduction of photon transmission will occur in the waveguide at the resonance wavelength. The thermal absorber converts incident IR photons to thermal power, causing a rise in temperature of the resonant microdisk. Thus a very small thermal expansion shift in the microdisk dimensions would produce a substantial perturbation in the probe transmission wavelength. This is the detection mechanism we plan to exploit in this project.

Mission Relevance

The general phenomenon of optical resonant microdisks is relevant to the DOE Office of Science. The ultimate development of this approach into an infrared imaging sensor tool is relevant to the DOE national security mission. The Department of Defense (DOD) has obvious interest in this area of sensor development in the infrared. In fact, once the basic feasibility of the approach is established, we anticipate additional collaborative work with several DOD and Department of Homeland Security programs.

Results and Accomplishments

The microfabrication and modeling and design tasks were started during FY 2008. System architectures have been explored that would be both amenable to our fabrication techniques and relatively optimized for the role of sensitive IR detectors. Several wafers have been processed with the circular glass layer and substantially undercut supporting structure. The supporting structure needs to be as small in diameter as possible to provide substantial thermal isolation. This goal is in conflict with the need to next melt the exterior part of the glass disc and reform it into a perfect toroid of glass. This glass then becomes the ultralow-loss waveguide shown to exhibit optical resonant Q-values in excess of ten million. The challenge we are facing is that the well thermally insulated glass can very quickly melt in whole and not just at the edges as desired. Small diameter variations in the supporting structure can have large thermal conductivity implications and thus very quickly produce a thermal runaway situation in the entire device. Our approach to this first fabrication challenge has been to produce a uniform energy density CO_2 laser beam and illuminate a two-dimensional array of test structures. These test devices vary in glass diameter in one direction and in supporting structure diameter (thermal isolation) in the other array direction. Thus, we should be able to determine the correct combination of device geometry and required thermal energy during FY 2009.

MATERIALS SCIENCE AND TECHNOLOGY DIVISION

00433

Organic Magnets: Phenomenological and First-Principles Approaches to Layered Bimetallic Oxalates

Randy S. Fishman and Fernando A. Reboredo

Project Description

Organic magnets (also called molecule-based magnets) are a broad class of bulk materials that have come under increasing scrutiny during the past 15 years. While organic magnets exhibit some of the same variety of behavior found in more conventional magnets, they also pose unique challenges and opportunities due to the sensitive dependence of their properties on the choice of organic cation. Although experimental work on organic magnets has been quite active, fundamental understanding of these materials has lagged far behind. In this project we have applied modern phenomenological and first-principles approaches to one particularly intriguing system of organic magnets: layered bimetallic oxalates.

Mission Relevance

The advanced state of organic synthesis and the wide range of potential applications make organic magnets quite attractive to both fundamental and applied scientists. Most organic magnets are functional materials that display a remarkable interplay between magnetic, electrical, and optical properties. As a result, they can play important roles in many areas of interest to DOE. Organic magnets like the bimetallic oxalates have potential applications as sensors and coatings.

Results and Accomplishments

Based on symmetry and energetic considerations, we developed a phenomenological model of the Fe(II)Fe(III) bimetallic oxalates that contains both exchange and spin-orbit interactions. This model is used to explain all of the important behavior of this class of materials, including the stability of magnetic order in well-separated layers and the magnetic compensation (the cancellation of the magnetization on the two sublattices) in compounds with certain cations between the layers. We have predicted that the negative magnetization can be optically flipped by near-infrared light. Breaking the C_3 symmetry about each of the Fe(II) ions, either through a cation-induced distortion or uni-axial strain in the plane of the bimetallic layer, is predicted to increase the magnetic compensation temperature. The spontaneous breaking of C_3 symmetry by an Fe(II) displacement is responsible for an inverse Jahn-Teller transition from a distorted phase at intermediate temperatures to a nondistorted phase at low temperatures. This phenomenological analysis has been confirmed with both first-principles calculations and numerical simulations.

Publications

Fishman, R. S., and F. A. Reboredo. 2008. "Coercive Field of a Polycrystalline Ferrimagnet with Uni-Axial Anisotropy." *Journal of Magnetism and Magnetic Materials* **320**, 1700.

Fishman, R. S., and F. A. Reboredo. 2008. "Giant Negative Magnetization in a Layered Organic Magnet." *Physical Review Letters* **99**, 217203.

Fishman, R. S., and F. A. Reboredo. 2008. "Magnetic Anisotropy in the Fe(II)Fe(III) Bimetallic Oxalates." *Physical Review B* **77**, 144421.

Fishman, R. S., S. Okamoto, and F. A. Reboredo. 2008. "Inverse Jahn-Teller Transition in Bimetallic Oxalates." *Physical Review Letters* **101**, 116402.

Reis, P. and R. S. Fishman, 2009. "Spin-Waves in Antiferromagnetically-Coupled Bimetallic Oxalates." *Journal of Physics*: *Condensed Matter*, accepted for publication.

Reis, P., R. S. Fishman, F. A. Reboredo, and J. Moreno. 2008. "Magnetic Compensation in the Bimetallic Oxalates." *Physical Review B* **77**, 174433.

00438

Can the Quantum Confinement Effect Be Exploited for Spin Injection in Organic Spintronics?

Jian Shen, Chengjun Sun, and Xiaoguang Zhang

Project Description

For spintronics applications, organic semiconductors are particularly attractive because the spin scattering rate is orders of magnitude smaller than that of ordinary inorganic semiconductors. The major technical challenge in organic spintronics devices is to achieve efficient spin injection. We seek to achieve a possible 100% spin polarization of quantum well states in magnetic nanodots to boost the efficiency of spin injection. For this proof-of-principle study, we will fabricate a prototype spin valve device that uses cobalt nanodots and a manganite thin film as two ferromagnetic electrodes and an organic molecule layer as the spacer layer. Scanning tunneling microscopy will be used to measure local tunneling magnetoresistance and determine spin injection efficiency as a function of the size of cobalt nanodots, bias voltage, and temperature. Our goal is to optimize the efficiency of spin injection and the magnitude of magnetoresistance, which can have a substantial impact on future technology.

Mission Relevance

While this project focuses on providing a fundamental understanding of how to control spin injection in organic spintronics, we fully anticipate that it will grow into a much broader program with an impact on diverse technologies. The novel application of organic spintronics in electroluminescence and photovoltaics could spearhead a new direction in the effort of "Science-to-Energy" using organic spintronics devices, which is high on the agenda of both DOE and ORNL. Hence, this work would also provide a basis for use-inspired basic materials research related to energy (such as the areas of photovoltaics and solid-state lighting). Much of the spintronics research in the United States is funded through the Defense Advanced Research Projects Agency, National Aeronautics and Space Administration, Air Force, and Army. It is likely that this work will further advance the realization of flexible spintronics and flexible electronics in general and lead to future programs that will comprehensively investigate the effects of spin injection and transport on (1) spin-polarized excitons dissociation (photovoltaics), (2) spin-polarized charge trapping and releasing (nonvolatile memory), (3) spin-polarized electron-hole recombination (EL), (4) new materials as electrodes for efficient spin injection and transport, and (5) correlation of spin transfer with interfacial contact.

Results and Accomplishments

We fabricated organic spin valves in the architecture of $LaSrMnO_3$/MEHPPV/Co nanodot with aluminum as the cover layer. The tunneling magnetoresistance measurements indicated that the spin injection from cobalt nanodots to organic semiconductor MEHPPV was achieved, reflecting that the fabricated devices are suitable for studying the spin injection from a single cobalt nanodot using scanning tunneling microscope. On the theory side, we showed that when quantum well (QW) resonances are important, they have an opposite effect on spin-dependent tunneling for a magnetic QW state than on a nonmagnetic QW state. We demonstrated that in the case of a statistical distribution of nanodots, it is more appropriate to apply the sequential tunneling model based on a continuous density of states than the resonant tunneling model with a set of discrete energy levels. We achieved a significant enhancement of magnetoresistance using buffer layer–assisted growth to form cobalt nanodots. A paper is being written for *Physical Review Letters*.

00439

In Situ Nanopatterning of Single-Crystal Multiferroics by Strain for Terabit-Scale Data Storage

Ho Nyung Lee and Matthew F. Chisholm

Project Description

During the last 50 years, tremendous, steady progress has been made in hard disk technologies. The current technique for increasing the storage density over the terabit scale will meet a limitation within a few years, however, due to the intrinsic behaviors of materials, including the thick magnetic domains. Although continued improvement in conventional semiconductor designs to decrease the length scales has addressed these issues to some extent, there is increasing motivation to consider alternatives to patterning materials at the nanoscale. In this project, we propose an innovative approach to pattern nanostructures by using so-called vacuum etching. We will focus mainly on the investigation of the feasibility and underlying mechanism of vacuum etching. The outcome of this work is expected to be especially useful for patterning single-domain nanomaterials and thus for applying such nano-multiferroics to ultrahigh-density information storage and nonvolatile memory.

Mission Relevance

Single-crystal nanostructures can offer rich scientific opportunities. For instance, our single-crystal nano-multiferroics proposed here are of great interest for realizing high electromagnetic coupling by epitaxial strain and nanostructuring. Moreover, the materials to be investigated are highly relevant to DOE missions because of their potential usefulness in various applications, including information storage, sensors, and actuators. Therefore, this project is an ORNL opportunity for world leadership in understanding yet unveiled physical properties of single-crystal nanoferroics. The quest for multifunctional multiferroics will contribute to a broad range of basic research programs. Our innovative approach to patterning nanocrystals will potentially benefit industry and federal agencies such as the Defense Advanced Research Projects Agency, since the multiferroics are very promising for many technical applications, such as sensors, energy and information storage, and piezoelectric devices.

Results and Accomplishments

We have (1) successfully prepared atomically flat, single-stepped crystalline films on strontium titanate and sapphire substrates as required for patterning; (2) grown epitaxial lead zirconate titanate (PZT) and bismuth ferrite ($BiFeO_3$) nanostructures thereon; (3) produced irregular-shaped, nanometer-sized islands confirming that the concept of vacuum etching works; (4) established a technique to pattern metallic electrodes by lattice mismatching; and (5) visualized the subangstrom-scale ferroelectric displacement, confirming that the electronic boundary condition at the interface of ferroelectric capacitors can completely destroy the ferroelectricity due to the depolarization field formed to screen the ferroelectric polarization.

Publication

Yang, S. M., J. Y. Jo, D. J. Kim, H. Sung, T. W. Noh, H. N. Lee, J. G. Yoon, and T. K. Song. 2008. "Domain Wall Motion in Epitaxial $Pb(Zr,Ti)O_3$ Capacitors Investigated by Modified Piezoresponse Force Microscopy." *Applied Physics Letters* **92**, 252901.

00444

Photon-Assisted Thermoelectric Devices

Hsin Wang, David Mandrus, and David Singh

Project Description

The objective of this study is to determine experimentally the effect of photocurrent on thermopower and thermoelectric performance for two wide bandgap semiconductors and selected thermoelectric materials. A theoretical study also will be conducted to understand the fundamental interaction of photons and electrons in these thermoelectric materials. It will predict and specify the class of materials where photons will have the greatest enhancements of thermoelectric properties. The main purpose is to develop a good understanding of the photon effect in thermoelectrics and use the knowledge to develop a new thermoelectric research effort at ORNL.

Mission Relevance

The recent solar energy initiative of the DOE Office of Science, Basic Energy Research recognized the potential benefit from a thermoelectric generator. A specific solar thermal energy conversion area was mentioned in the initiative. If the combined thermoelectric and solar cell can be utilized, the two important functions will benefit each other. On the one hand, thermoelectric devices can convert unused heat into power. On the other hand, extra light can enhance the performance of the thermoelectric devices. The effort of this project will help to improve energy conversion efficiency. In the programs of the DOE Office of Energy Efficiency and Renewable Energy (EERE), alternative energy sources are the main focus. Thermoelectric materials are of particular interest because they can convert heat directly into electricity with no moving parts. Recent EERE programs include waste heat recovery from automobiles and waste heat power generation from energy-intensive industries, such as glass plants.

Results and Accomplishments

Theory. Transport calculations as a function of temperature and doping were performed for ZnO. These were based on first principles, density functional calculations of the electronic structure using a very fine Brillouin zone sampling, as is needed for transport. We find a strong asymmetry between electron and hole transport with a nearly order of magnitude difference in the high-temperature Seebeck coefficients for electrons and holes at carrier concentrations of 0.01 to 0.05 per formula unit. In addition, we find a small anisotropy with slightly higher thermopower along the hexagonal axis relative to the basal planes for p-type carriers. This does not yet identify ZnO as promising for a photo-thermoelectric energy converter, but it does suggest a new spectroscopy that may be important. In particular, measurement of the charge collection in a thermoelectric device as a function of photon energy may yield detailed information about carrier traps in p-type ZnO. This may be helpful in understanding the difficulties in obtaining high-mobility p-type ZnO.

Experimental Results. In FY 2008 we conducted more detailed measurements on electrical resistivity of the specimens under light exposure. The most important test performed was the Seebeck coefficient measurement under ultraviolet (uv) light. Zinc oxide single crystals (needles) prepared at ORNL and polycrystalline disks from ABB (Ludvika, Sweden) were used in this study. The ABB samples we obtained were pure ZnO. The samples were machined into prismatic bars and disks. The disks were exposed under uv light during electrical resistivity measurements using an in-line probe station. The same probe station was also used to measure Seebeck coefficient of the samples. We found a 15–22% increase in electrical conductivity under uv exposure over 5–30 s. In the meantime, the Seebeck coefficient of the materials did not show any measurable change and remained at about 1.15 mV/K at 48ºC (ULVAC system). A similar effect was observed when we used the in-line four-point probe. This result indicated that the photon-excited electrons contributed mainly to the electronic conduction and had little effect on the thermopower. The enhanced power factor will improve thermoelectric performance of the material. The main problem we encountered was the lack of a high-intensity uv source. The observed effect will be more convincing if we could focus the uv energy to the specimen.

00445

Photocatalytic Conversion of CO_2: An Alternative to Storage-Based Sequestration

C. K. Narula, M. Moses-DeBusk, and A. C. Buchanan

Project Description

The state-of-the-art technology for CO_2 emissions remediation involves chemical capturing techniques using aqueous amines. However, this approach is capital intensive because it requires collection of CO_2 emissions at the source, transportation, and delivery to geological formations. An alternative to CO_2 storage is to convert CO_2 to hydrocarbons that can be used as fuel for transportation and as chemical building blocks instead of using oil-derived precursors. The goal of this project is to explore new classes of photocatalysts for CO_2 conversion to useful chemicals that can potentially function in visible light and exhibit high turnover frequencies. A perfect example of this approach is in nature, where plants convert CO_2 and water to carbohydrates via photosynthesis (employing solar energy) and then use carbohydrates as a source of energy (respiration) and break them down to CO_2. This process is CO_2 neutral. A CO_2 chemical cycle is highly desirable provided the source of energy for reduction is renewable, such as solar energy.

Mission Relevance

This project is directly related to the DOE Fossil Energy (DOE-FE) program for CO_2 sequestration, which is focused on advancing the technology of CO_2 collection at the source and storage in geological formation as a viable option for reducing the CO_2 footprint in the atmosphere. The goal of our project is to obtain preliminary results on photocatalysts that demonstrate improved efficiency for CO_2 conversion, which will form the basis for a proposal in response to an anticipated call for proposals from the DOE-FE program for CO_2 sequestration. The DOE-FE program considers photocatalytic reduction of CO_2 as one of the methods for CO_2 sequestration, and there are currently no funded projects on this topic in the DOE-FE portfolio. It is important to note that the DOE Office of Science and the Defense Advanced Research Projects Agency have issued calls on solar energy utilization, and we will explore funding possibilities with these agencies as well.

Results and Accomplishments

We initiated this work by synthesizing SiO_2-TiO_2 catalysts with identical mesoporous substructures and Si:Ti ratio but different coordination of titanium (4 and 6). The catalyst with 4-coordinate titanium was synthesized employing a template-assisted sol-gel method, and the catalyst with 6-coordinate titanium was synthesized by impregnation of titanium isopropoxide on mesoporous silica synthesized by a template-assisted process. The catalysts were characterized by standard techniques and evaluated for CO_2 photochemical reduction employing an ultraviolet (uv) source. The analysis of reaction mixture clearly showed the presence of methanol.

Our primary focus was on the design of a new catalyst that can absorb visible light and generate electrons energetic enough to reduce CO_2. With this in view, we synthesized Ru/GaN:ZnO by impregnating GaN:ZnO prepared from the ammonolysis of Ga_2O_3-ZnO_2, which was synthesized from the hydrolysis of a mixture of $Ga(OR)_3$ and $Zn(OR)_3$. Our synthesis approach leads to a homogenous, high-surface-area, catalyst system. This catalyst was fully characterized by chemical analysis, X-ray difrection, and scanning transmission electron microscopy. The catalyst absorbs visible light and has been shown to dissociate water. We carried out the photochemical CO_2 reduction on the catalyst in the presence of water employing uv and found it to be selective to produce CO. Thus, this catalyst system can selectively produce CO from CO_2 and H_2 from H_2O or essentially a syngas composition that can be converted to a variety of organics via Fisher-Tropsch synthesis.

Publication

DeBusk, M. M. and C. K. Narula. 2009. "Chemical Routes to Photocatalysis: Nanosizing Ru/GaN:ZnO." *American Chemical Society National Meeting,* Mar. 22–26, Salt Lake City, accepted.

00447

In Situ Studies for Ductility Improvement of Bulk Metallic Glasses

C. H. Hsueh, P. F. Becher, and C. T. Liu

Project Description

Although bulk metallic glasses (BMGs) constitute a new class of metallic materials with extremely high strength, they often deform by the formation of localized shear bands and display little plasticity before catastrophic fracture at room temperature. This inability to permanently deform limits the use of BMGs in engineering applications. To improve the ductility of BMGs, particle reinforcement has been attempted. However, both ductility enhancement and embrittlement have been reported for BMG composites subjected to compression tests. Also, it appears that reinforcing particles have little effect in improving the ductility in tension. To resolve this controversial issue, it is imperative to understand how shear bands interact with reinforcing particles. Also, shear fracture of BMGs has been found to depend not only on the shear stress but also on the stress normal to the shear plane, and the Mohr-Coulomb criterion, an empirical equation accounting for the effects of normal stresses on shear fracture, has been adopted to characterize shear fracture of BMGs. However, systematic verification of the Mohr-Coulomb criterion for BMGs is nonexistent because of the difficulty of controlling the normal to shear stress ratio on the shear plane in existing tests. Hence, we proposed to use a cleverly designed test fixture that allowed one to control (1) the location of shear fracture and (2) the normal to shear stress ratio on the shear plane. This would provide for in situ observation of the interaction between shear bands and reinforcing particles during shear fracture of BMGs. It would lead to a mechanistic understanding of ductility enhancement and provide a basis for modeling and prediction of particle reinforcement in BMGs. The fixture would also provide a means to verify the applicability of the Mohr-Coulomb criterion for BMGs. Furthermore, while BMGs are known to be subject to strong residual stresses because of the high cooling rate during the solidification process, studies of effects of residual stresses on mechanical properties of BMGs are lacking. Because the residual stress has a certain distribution profile in BMGs, controlling the location of shear fracture enables the systematic study of effects of residual stresses on shear fracture.

Mission Relevance

Success of this project will lead to a predictable way of improving the ductility of BMGs using particle reinforcement. A variety of uses for BMGs has been identified, including sport and luxury goods, and electronic, medical, and defense applications. The potential beneficiaries include the Office of Naval Research, the Army Research Laboratory, Air Force, and the Defense Advanced Research Projects Agency. Also, completion of this work will establish proof of principle that our test fixture has the capabilities of controlling (1) the location of shear fracture and (2) the normal to shear stress ratio on the shear plane, which cannot be achieved by existing tests performed on BMGs. These capabilities can extend our work to (1) systematically characterize how the residual stresses can be utilized to improve the ductility of BMGs and (2) verify the applicability of the Mohr-Coulomb criterion for BMGs which, in turn, will generate funding opportunities from basic programs (e.g., DOE Office of Science, Basic Energy Sciences and the National Science Foundation).

Results and Accomplishments

During FY 2008 we made significant progress in four areas.

1. We were successful in fabricating controlled-shear test fixtures with inclined angles of 30º, 45º, and 60º. These different inclined angles allow us to apply different ratios of the normal to shear stress on the shear fracture plane, and we were able to verify the applicability of the Mohr-Coulomb criterion for shear fracture of zirconium-based BMGs.
2. Compared to the conventional uniaxial compression test, we found that the controlled-shear test not only exhibited the typical vein-like structure on the fracture surface of BMGs because of the sudden fracture of the specimen but also showed a region of pure shear fracture on the fracture surface. This finding is significant because it offers a means to study the size effect. Specifically, when the specimen is sufficiently small, the vein-like structure may disappear from the shear fracture surface.
3. Two invention disclosures have been submitted: "Invention 2079–Controlled Shear/Tension Fixture" and "Invention 2081–Controlled Shear/Compression Fixture."
4. A paper entitled "Controlled Normal/Shear Loading and Shear Fracture in Bulk Metallic Glasses" has been drafted and will be submitted for publication.

Publication

Hsueh, C. H., H. Bei, C. T. Liu, P. F. Becher, and E. P. George. 2008. "Shear Fracture of Bulk Metallic Glasses with Controlled Applied Normal Stresses." *Scrip. Mater*. **59**(1), 111–114.

00454

An Innovative Low/High-Temperature, Repetitive Pressure-Pulse Apparatus for Cavitation Damage Research

John Jy-An Wang, Narendra Dahotre, Seokho H. Kim, Peter Blau, and Steve Pawel

Project Description

Cavitation damage has manifested itself as a major obstacle in many advanced technology developments either at room or at high temperatures (e.g., in spallation sources, modern high-speed turbomachinery, rocket engines, gas and steam turbines, diesel engines in heavy vehicle propulsion, spacecraft and high-speed marine vehicles, commercial power generating systems, propellers, pumps, bearing components). We propose to demonstrate the feasibility of a novel, laser-assisted, repetitive pressure-pulsed apparatus able to generate controllable cavitation events. In support of this demonstration, we will develop models to determine the cavitation parameters, such as pressure magnitude, and estimate the cavitation damage. This undertaking will support efforts to elucidate some of the fundamental hydraulic-mechanical processes associated with cavitation and its effects on target materials. With the main focus on the controllable cavitation parameters, such as pressure magnitude and temporal characteristics, as well as on damage characterization, the research carried out will have a wide-ranging impact on several important industrial sectors and their supply chains.

Mission Relevance

The success of this project will greatly increase our understanding of the underlying mechanisms of cavitation damage and our ability to develop strategies that would prevent or mitigate this form of damage. This work will impact programs within DOE and the Department of Defense (DOD) that focus on advanced engine development, advanced materials development, and their effective lifetime estimates under cavitation damage arena (e.g., mercury target cavitation event of the DOE Spallation Neutron Source project, potential plasma cavitation in the International Thermonuclear Experimental Reactor fusion reactor environment, naval fleet and aircraft integrity surveillance, National Aeronautics and Space Administration space propulsion program, DOD gas turbine engine development, DOE Office of Nuclear Energy nuclear power reactor system, and DOE Heavy Vehicle Propulsion Materials program).

Results and Accomplishments

In 2008 we developed a closed-loop system, including the cavitation chamber and the associated cooling system, in addition to the open-loop design developed in 2007. An in situ pressure pulse measurement device also was developed and is attached to the cavitation chamber for in situ measurement/calibration of the pressure wave intensity. The visualization windows at the sides of the cavitation chamber provide real-time monitoring of the cavitation events. To generate and simulate genuine cavitation damage events, a series of optimization protocols were developed for control the laser pulse energy input, the deposit energy profile in the water media, the boundary condition of the cavitation chamber geometry, and the coolant flow rate and path through the target sample. This first prototype of the closed-loop pressure pulse system was tested successfully with a 1064 nm YAG high-power laser device (with average energy level of 50 J/pulse) on stainless steel samples. The pressure wave–induced cavitation damages were investigated further and validated through postmortem scanning electron microsopy examinations. The project will continue in FY 2009.

00458

Deterministic Growth of Oxide Nanostructures by Pulsed-Laser Deposition

Hans M. Christen and Gyula Eres

Project Description

Complex oxide materials provide unique properties that have not been exploited in actual applications due to the lack of methods suitable to process them into nanoscale devices. An alternative is needed to construct nanoscale oxide structures “bottom-up” (i.e., to apply patterning techniques to masks and catalysts and then grow the desired nanostructures at the predetermined locations, eliminating the need of post-processing). Pulsed-laser deposition (PLD) has been highly successful in the synthesis of a broad variety of oxide materials of highest quality in thin-film and superlattice forms. In this project we address the challenge of directly synthesizing metal-oxide nanorods and nanorod assemblies by exploiting the highly nonequilibrium processes in PLD to generate the prerequisite growth selectivity.

Mission Relevance

This research relates to a number of DOE goals and missions, with energy-related applications motivating many of them. In particular, solar energy conversion (photovoltaic and solar fuel) will benefit strongly from the anticipated results. Using epitaxial nanorods allows otherwise mutually exclusive requirements (long photon absorption path, short electron extraction length) to be combined. Other energy-related applications, such as increased flux pinning in superconducting tapes, and their potential use as catalyst supports, are also of great relevance to the DOE Office of Science, Basic Energy Sciences and to the DOE Office of Energy Efficiency and Renewable Energy. In addition, the use of nanomaterials for sensor and detector applications will be of interest to the Defense Advanced Research Projects Agency, the Office of Naval Research, and the Department of Homeland Security, again enabled by the opportunity to combine requirements that are mutually exclusive in bulk materials.

Results and Accomplishments

The research of this project consisted of two parts: (1) the synthesis of oxide nanorods using metal particles as catalysts or nucleation sites and (2) the synthesis of “heterojunction nanorods,” i.e., nanorods that are (along their length) composed of dissimilar materials. Gold particles were synthesized by annealing a thin layer obtained by PLD or electron-beam evaporation. Magnesium oxide and yttria-stabilized zirconia nanorods were then grown by PLD. Contrary to published reports for zinc oxide, nanorod growth was observed exclusively in those areas of the substrate that were coated with the metal, thus demonstrating the desired selectivity of the process. For the magnesium oxide nanorods, scanning electron microscopy (SEM) was used to determine the morphology as a function of the deposition parameters, yielding a reproducible recipe for the formation of rods with lengths of several hundred nanometers and diameters below 50 nm. These rods were then subsequently used as “substrate” for the deposition of strontium titanate—a more complex oxide that could not easily be formed directly using a similar catalytic process. A recipe involving deposition of an additional catalytic layer followed by the deposition of strontium titanate yielded more complex nanostructures, including some “cube-on-rod” and branched nanorod formations. This finding, which delayed the development of a truly deterministic growth process, was not anticipated before this work and shows a promising new direction for future research.

00463

Atomic-Level STEM Imaging of Bias-Induced Phase Transformations: Applications to Information Technology

Albina Y. Borisevich and Sergei V. Kalinin

Project Description

We propose to develop an experimental framework to address the role of individual defects on the dynamics of first-order phase transitions in ferroelectrics on the atomic level. The combination of scanning transmission electron microscopy (STEM) with scanning tunneling microscopy (STM) or atomic force microscopy (AFM) experiments, implemented on recently acquired Nanofactory (S)TEM-STM and (S)TEM-AFM systems, will allow us to combine the atomic resolution and electronic sensitivity of STEM with the local electrical/mechanical excitation capabilities of STM/AFM. The unique feature of this setup is that electrical bias or force can be applied *locally* to a chosen point of the sample, providing the means to compare dynamics of switching (e.g., at and away from a dislocation or a structural defect). The local observations of polarization dynamics will allow elucidation of the mechanisms for domain wall motion, domain nucleation, polarization-induced changes of interface properties, and contact effects.

Mission Relevance

Electrically based phase, structural, and chemical transformations extend well beyond information technology to areas such as fuel cells, solid-state electrolytes, solid-state lighting, and photovoltaics, subjects of critical importance to DOE. This project will demonstrate the capability to probe the local aspects of these transformations in situ. To complement applications, in situ microscopy in general has recently emerged as a high priority for the DOE Office of Science, Basic Energy Sciences. The research combining STEM and STM/AFM capabilities will fall directly under the auspices of current and future programs in this direction and will be a potential benefit.

Results and Accomplishments

During the past year, the primary effort focused on the installation and operation of the STEM-SPM holders as well as development of model systems. The single-tilt holder was successfully delivered and installed. The preliminary results on in situ characterization of electronic transport in SnO_2 nanowires as a function of applied strain (i.e., piezogalvanic effects) were obtained. Work is in progress on similar studies in VO_2 nanowires, which possess a bias-induced metal-insulator phase transition. We have performed extensive characterization (STEM, electron energy loss spectroscopy [EELS]) of $BaTiO_3$ and PZT samples for STEM-SPM studies and demonstrated (1) atomic resolution structure imaging, (2) EELS imaging across the interface, and (3) imaging dislocation structure. These results were used in an invited presentation and also in two manuscripts being prepared for publication (tentatively in *Physical Review Letters* and *Applied Physics Lett*ers). In parallel, we developed and tested sample preparation routines for thin-film samples with a free-standing edge and 10° miscut, required for experiments with the double-tilt STM holder, which was delivered October 25, 2008 (delayed from the originally projected February 2008 date).

00465

Low-Cost, Multicrystalline Silicon for Photovoltaics

Joachim H. Schneibel, Ilia Ivanov, Michael P. Brady, Terry Tiegs, John Vitek, and J. A. Horton

Project Description

The goal of this project was to establish proof of principle for the use of low-cost metallurgical-grade (MG) silicon for multicrystal photovoltaic cells by utilizing novel in situ gettering approaches to manage the impurities that degrade cell efficiency. Current costs for solar-grade silicon are \$65–120/kg, and the DOE 2015 cost goal is \$20/kg. If successful, this approach will enable the cost-effective manufacturing of solar-grade silicon from MG silicon, which currently costs less than \$10/kg. Two approaches were evaluated: (1) direct single-step consolidation of MG silicon powder with a small fraction of widely spaced dispersoids added to act as sites for segregation and precipitation of the impurities and (2) alloying additions of elemental and compound gettering agents to cast silicon followed by heat treatment to control impurity phase precipitation.

Mission Relevance

The high cost of solar cells is a major reason for their small market share (less than 1%) in energy production. The goal of this project, to dramatically lower the cost of photovoltaic-quality silicon, is relevant for many DOE programs and missions, such as the Office of Energy Efficiency and Renewable Energy, reduced reliance on oil imports, and environmental quality. This project also potentially benefits the Energy Star program (a joint program between the Environmental Protection Agency and DOE) on projects such as green buildings.

Results and Accomplishments

The key challenge to implementation of the powder dispersoid approach for in situ impurity gettering was the covalent nature of silicon, which results in very low self-diffusion rates. Therefore, pressure-assisted densification methods, hot pressing and hot isostatic pressing (HIPing), were chosen for evaluation. MG and high-purity-grade silicon powders, with a range of acid leaching pretreatments and Al_2O_3, CaO, and MgO dispersoid gettering additions, were processed by hot pressing and HIPing. Evidence was obtained for impurity phase precipitation at dispersoids; however, the silicon matrix grain size remained quite fine (<10 μm) and significant porosity was present. It was concluded that the goal of achieving a coarse grain size (>>100 μm) in a fully dense silicon matrix required melt processing. Because it is difficult to obtained uniform distributions of oxide dispersions such as Al_2O_3, CaO, and MgO during melting and solidification, direct alloying of gettering additions during arc-casting of silicon was subsequently pursued.

The effects of 2 wt % additions of yttrium, gallium, and La_2S_3 to 98.5% purity MG silicon was explored. These additions represent a wide range of Si-X phase equilibria conditions with potential to in situ segregate impurities to coarse, isolated grain boundary precipitates. Fully dense microstructures with >100 μm grain size were achieved. Impurity elements and gettering additions were observed to segregate to silicon matrix grain boundaries. Characterization of these microstructures was pursued by scanning and transmission electron microscopy, impedance spectroscopy, and confocal micro-Raman techniques.

Surface impedance was found to be sensitive to both silicon impurity level and thermal annealing. Over a 3.5-fold difference in surface impedance was observed between cast MG silicon and cast high-purity-grade (99.999%) silicon. Annealing of the MG silicon for 24 h at 1175°C reduced the real part of the impedance by a factor of two, in the direction away from that of the high-purity silicon, consistent with back diffusion of impurity elements from the grain boundary precipitates to the grain interiors. In contrast, although the addition of yttrium to MG silicon also reduced the real part of the impedance of MG silicon by a factor of two (similar to the effect of the 1175°C anneal of MG silicon), 1175°C annealing of yttrium alloyed MG silicon resulted in a threefold surface impedance shift toward the high-purity silicon direction, which suggests a degree of gettering of impurities by yttrium to the grain boundary regions. Raman spectroscopy results also correlated well with the drop in spatially resolved vis photoluminescence from the grain interiors to the grain boundaries associated with the migration of impurities towards the boundary.

The annealed MG Si + 2 wt % Y (effectively 96.5 wt % purity) exhibited 1.5 times the real surface impedance of 98.5% MG silicon, but still only <40% of the value of the 99.999% silicon. These results suggest that in situ impurity gettering of MG silicon is possible; however, the degree of the gettering achieved in the present work was likely not sufficient to significantly impact photovoltaic behavior. One potential future route forward would be evaluation of smaller levels of gettering additions such as yttrium (<0.1 wt % range instead of 2 wt %), in order to minimize detrimental effects of the gettering additions themselves, to an intermediate grade (<99.9%) silicon, which requires a lesser extent of impurity gettering than does 98.5% MG silicon. Further optimization of the thermal annealing envelope may also result in an improved degree of impurity gettering.

00468

Developing an Innovative Field Expedient Testing Protocol for Concrete Materials

John Jy-An Wang, Ken C. Liu, and Dan Naus

Project Description

Failure of concrete structures is accompanied by cracking of concrete. Understanding and modeling of how and when concrete fails not only are critical for designing concrete structures but also are important for developing new cement-based materials. As high-strength, high-performance concrete gains importance, so does the study of its fracture behavior. The behavior of high-strength concrete is closer to that described by linear theories of fracture and the concrete is more brittle than lower strength versions. There is no consensus on a standard method for a direct measurement of concrete fracture toughness, K_{IC}, with confidence, and the key challenge is related to the large specimen size requirement of existing fracture toughness approaches. We propose to investigate the feasibility of using the novel Spiral Notch Torsion Test (SNTT) approach for fracture toughness testing of materials to obtain valid fracture mechanics data for concrete. The challenge of the specimen size requirement can be addressed through the proposed technical approach, which will potentially lead to improved codes of practice for the design of reinforced concrete structures.

Mission Relevance

This project can improve understanding of concrete fracture behavior and, in turn, aid the development of advanced high-performance concrete so that its enhanced properties can be utilized more effectively while at the same time improving safety. Specifically, the project can benefit the DOE Office of Nuclear Energy power reactor safety programs related to the design of concrete barriers and concrete containers for waste management. The project can also benefit the DOE hydrogen initiative for building a large hydrogen storage facility. (A hydrogen pressure vessel concept using concrete and steel pressure vessel composite design has been proposed to DOE.) The project can also benefit infrastructure integrity (Department of Transportation) and advanced concrete research (Federal Aviation Administration, Federal Highway Administration, Department of Defense, Army Corps of Engineers, and National Science Foundation).

Results and Accomplishments

The SNTT system operates by applying pure torsion to uniform cylindrical specimens with a notch line that spirals around the specimen at a 45° pitch. Application of the SNTT method to metallic, ceramic, and graphite materials has been demonstrated. Due to the quasi-brittle nature of concrete materials, the end-grip fittings of the SNTT testing protocol were modified to efficiently transmit the torque to the concrete composite sample without damaging the sample at the grip-ends. The 40.6 mm diam by 177.8 mm long SNTT test samples were made from a Portland cement–based mortar. The estimated K_{IC} of the tested mortar samples with compressive strength of 34.45 MPa was found to be 0.19 MPa $m^{1/2}$. The SNTT system represents a practical and effective approach for testing fracture toughness of concrete materials. SNTT overcomes many of the limitations inherent in traditional techniques and introduces new possibilities for improved fracture toughness testing of cementitious material: (1) it conforms to the classical theory of fracture mechanics; (2) it allows miniaturization of test specimen to appropriate sizes, which makes the test method economically attractive and test equipment portable for on-site testing; and (3) for concrete material only a shallow notch is needed, thus further reducing the specimen size required for generating a valid K_{IC} test.

Publications

Wang, John Jy-An, Ken C. Liu, and Dan Naus. 2008. “Developing An Innovative Field Expedient Fracture Toughness Testing Protocol For Concrete Materials.” Technical Report ORNL/TM-2008/155, Oak Ridge National Laboratory.

00473

Root Causes of Circumferential Cracking of Waterwall Tubes in Supercritical Boilers

C. H. Hsueh and I. G. Wright

Project Description

The leakage and rupture of boiler tubes in power plants is a serious problem that often leads to unscheduled and costly outages. The predominant failure location of current concern is in the furnace waterwall section; circumferential cracking on the fireside of waterwall tubes has been identified as the main failure mode. Although there is basic agreement that cracking results from a combination of thermal fatigue and corrosion, a complete explanation of the basic phenomena needed to establish the root causes of this problem is still lacking. The purpose of this project is to determine the root causes of the circumferential cracking experienced on the fireside of waterwall tubes of supercritical boilers. The success of the project will lead to a predictable way to delay or avoid circumferential cracking and improve the reliability of boiler tubes.

Mission Relevance

According to statistics from the Electric Power Research Institute, boiler tube failure incidents in the United States represent more than an 80% share of the thermal power outage incidents. These failures result mainly from circumferential cracks on the fireside of waterwall tubes. Completion of this project will lead to a mechanistic understanding of the root causes of these circumferential cracks and will benefit the Advanced Research Materials Program of the DOE Office of Fossil Energy. Completion of the project also will lead to improved reliability for electricity generation, benefitting the Electric Power Research Institute.

Results and Accomplishments

During FY 2008 we made significant progress in two areas.

1. We were successful in developing an analytical model to analyze the tensile stress responsible for initiating circumferential cracking on the fireside of waterwall tubes. Based on the results, we have suggested ways for reducing tensile stresses in waterwall tubes.
2. A paper entitled "Origins of Tensile Stress-Induced Circumferential Cracking of Waterwall Tubes in Boilers" has been submitted to *Materials at High Temperatures* for publication.

00474

Development of a Device for Low-Cost, In-Reactor Loading of Materials

Lance. L. Snead, Thak Sang Byun, Roger G. Miller, and Joel L. McDuffee

Project Description

Domestic and international programs have a great interest in developing an inexpensive, conceptually simple vehicle for irradiation-creep measurements in the High-Flux Isotope Reactor (HFIR). In its simplest case, within a HFIR rabbit a pressurized bellows would transmit force to a sample to induce creep strain during irradiation. The technical and programmatic benefit of such a design is that upon creep, the bellows internal pressure, hence applied load, undergoes negligible change and, in principle, the vehicle could be examined and re-irradiated. The current state of the art is for an irradiation campaign of several years and several million dollars. Successful demonstration of this technology would allow for a much more rapid and inexpensive means of obtaining critically needed data. Moreover, as the cost for in-reactor sample loading has to date been prohibitive, this design would allow new opportunities to carry out the basic science of irradiation effects. The main goals of this project are to construct a creep load-train with a pressurized bellows and to demonstrate that the principle works.

Mission Relevance

Through discussion of the preliminary concept, interest in this research has been indicated by ongoing DOE programs (U.S. Fusion, International Fusion Collaborations, Generation IV, and Naval Reactors) as well as by outside interests (British Energy [BE] and Pebble Bed Modular Reactor [PBMR] in South Africa). U.S. Fusion and Naval Reactors programs have indicated interest in using our device for future irradiations in HFIR. This implies construction, irradiation, postirradiation examination, and evaluation of data would be carried out at ORNL. Moreover, an expression of interest for carrying out graphite irradiation, if successfully demonstrated, has been transmitted by both BE and PBMR (though likely in a collaborative BE/PBMR program).

Results and Accomplishments

The first prototype load frame using pressurized bellows was designed and constructed. The materials for parts, pure molybdenum and Inconel 718, were selected for high-temperature applications. An Inconel 718 open-ended bellows was selected and purchased, and Inconel 718 end-caps were machined and welded to the bellows in an electron beam welding machine. An SS-3 type steel tensile specimen and the end-capped bellows were assembled in the molybdenum frame, and the bellows was pressurized by helium gas through a pinhole in an end-cap to about 15 MPa. After pressurization, the pinhole was closed by laser welding to contain the gas pressure in the bellows. One of the end-caps was designed to protrude out the end of the molybdenum frame so that the bellows can be loaded in a testing machine to measure load-displacement response. This capability is important because the actual load applied during irradiation can be measured experimentally after irradiation at the same temperature.

The load-displacement response of the pressurized bellows in the load frame was measured in a mechanical testing machine at different temperatures. A set of testing jigs was manufactured to hold the creep frame in the vacuum furnace. The creep frame was capable of a load of about 400 N at room temperature and about 500 N at 300°C, which can apply, respectively, about 350 and 450 MPa tensile stresses to the tensile specimen. Since actual irradiation creep tests are performed at higher temperatures, a higher stress can be introduced by the same pressure due to gas expansion. In most cases, irradiation creep will occur at less than 100 MPa (110 N) for an SS-3 metallic specimen and 10 MPa (or 500 N) for a rod-type graphite specimen with 8 mm diam (500 N). This result demonstrates that the bellows-loaded creep frame can easily induce irradiation creep. For a typical ferritic steel specimen, the stress level is enough to induce even, instant plastic deformation at higher temperatures.

The main hurdle we faced in construction of the load frame was leak after welding. The elastic deformation by internal pressurization produced failure at the weld and thus constrained the edges of the bellows when the welding chamber was depressurized. The internal pressure, 15 MPa, is believed to be nearly maximum pressure at which the weldment can sustain up to 300°C. Also, the buckling of the end-confined bellows at high temperature resulted from the high internal pressure. Both of these problems should be resolved by reducing the internal pressure to ~5 MPa or lower. In FY 2009, the load-displacement curves will be produced over a full range of temperatures up to 850°C using a load frame with a lower internal pressure. As a final task, the design will be optimized, and thermal and safety performance will be calculated for the optimized design.

00476

Development of Inorganic Membranes for Water Reclamation from Wet Gas Streams—An Opportunity to Simplify Water Management Operations

M. Moses-DeBusk, B. Bischoff, and K. D. Adcock

Project Description

We will evaluate the efficacy of porous inorganic membranes to separate liquid water from a wet gas stream at higher efficiency than possible by thermodynamic condensation. We plan to investigate three separate membranes with different pores sizes, fabricated in our laboratory, to determine which will yield the greatest enhancement on water reclamation. The most efficient membrane for water recovery will be tested using simulated diesel exhaust stream. Water recovery efficiency and purity from the simulated diesel exhaust will be the starting point for future funding.

Mission Relevance

The results of this project will impact national security missions related to energy resources by reducing fuel consumption required by the U.S. military for transport of potable water for soldiers’ daily basic needs. Efficient use of fuel and personnel by the Army is impeded by the need to transport large amounts of bottled water, ~5 gal per soldier per day. The results of this project will promote the development of a high–efficiency, on-vehicle water reclamation system, reducing resources required for bottled water transport. The project results are of great interest to the Army and the Department of Defense.

Results and Accomplishments

Our goal of accomplishing all of the project objectives is on track for completion in FY 2009. The project was initiated by fabricating the ~6 nm porous alumina membrane on a 400-series stainless steel support tube. The unique membrane holder required to maximize heat removal from the two-layer membrane was designed and constructed to have a minimal permeate collection space (~6 mL) and a large recirculating water jacket space. The membrane was tested for capillary condensation employing the newly constructed holder and testing platform. Under air flow containing ~10% H_2O vapor without artificial pressure differences, a reduction in relative humidity was observed, but no liquid water was collected. Lack of liquid water collection under these conditions was expected. Once the pores filled with water, there was no differential pressure across the membrane to push the liquid water out of the pores and make room for continued capillary condensation. When only a small pressure difference was applied across the membrane, liquid water collection was observed. The platform testing setup is being adjusted to obtain reproducible water collection results under optimal conditions. These results will be compared to results obtained when using a membrane containing smaller pores.

00482

Novel Infrared-Processed Titanium Composites for High-Temperature Galling Resistance

Peter J. Blau, Evan K. Ohriner, and Donald L. Erdmann III

Project Description

The objective of this research is to develop a novel infrared (IR) surface treatment that synthesizes layers of hard, particle-reinforced composite materials on the surface of high-performance titanium alloys. These engineered surfaces are designed to greatly improve the alloys' resistance to mechanical contact damage known as *galling* at elevated temperatures. By applying the IR process, lightweight, corrosion-resistant titanium alloys could be used for load-bearing surfaces in advanced, fuel-efficient engines as well as aerospace and nuclear power generation systems. ORNL's unique, high-intensity IR lamp system will be used to synthesize multiphase composite surface layers in situ. A high-temperature galling test method will be developed to quantify the performance advantages of the engineered surfaces. Once the new high-temperature galling test procedure is established, it will be used to compare the galling resistance of the titanium composites to that of conventional steels, coatings, and surface treatments. This effort is intended provide at least two benefits: (1) the new IR surface treatment will enable wider use of lightweight titanium alloys in vehicles and energy conversion systems, and (2) ORNL will acquire a unique capability to assist U.S. industry in developing improved high-temperature, galling-resistant materials and surface treatments.

Mission Relevance

Recent developments in the processing of titanium promise to reduce material cost and extend their application to component parts for energy-efficient, low-emissions automobiles, trucks, and power generation systems. By enhancing the resistance of titanium alloys to surface damage at elevated temperatures, these lightweight aerospace alloys can now be utilized more widely in the power generation, industrial, defense, and transportation sectors. Therefore, this project has multisector benefits while also serving the mission of energy efficiency and renewable energy. For example, the development of galling-resistant titanium surfaces is expected to benefit the aerospace and the defense sectors (e.g., National Aeronautics and Space Administration, Air Force, Army, Navy) by its applicability to components for jet engine compressor section vanes, aircraft control surface linkages, anti-jamming lightweight rifles, and wear-resistant arresting cable sheaves on aircraft carriers.

Results and Accomplishments

This project began in mid-year FY 2008 and is scheduled for completion in FY 2009. During FY 2008 progress was made in the following areas: (1) a high-temperature galling test configuration was designed; (2) fixtures were custom-machined from high-performance nickel-based alloys and fitted to an existing torsion testing machine; (3) a furnace chamber was designed and ordered; (4) several metallic alloys, to be benchmarked against the titanium composites, were procured and machined into galling test specimens; and (5) a preliminary set of IR heating experiments was conducted on a titanium alloy, and composite layers were created successfully.

Designed to utilize simple, easy-to-fabricate, specimen shapes, the galling test configuration consists of three cylindrical pins oscillating in a circular arc against a flat tile. With this configuration, it will be possible to measure the time-dependent torque response, and thus galling initiation and subsequent damage propagation, as a function of material combination, temperature, and contact pressure.

Preliminary IR processing experiments to form composites on titanium alloy substrates used two types of hard, ceramic reinforcing particles mixed with titanium powders in various proportions. Initial results were promising. Compared to the underlying titanium substrate, the hardness of the composite layers was higher by a factor of at least 1.5 to 2. The degree to which these marked hardness improvements translate into improvements in galling resistance will be investigated in FY 2009 when the high-temperature test system is completed. Results will be benchmarked against stainless steel and cobalt-based superalloys that are gall tested under similar conditions.

Publication

Ohriner, E. K., and P. J. Blau. 2009. "Novel Infrared-Processed Titanium Composite Coatings for High Temperature Galling Resistance." *Symposium on Surface Structures at Multiple Length Scales, 2009 TMS Annual Meeting and Exhibition,* Feb. 15–19, San Francisco.

00483

Tip-Enhanced Optical Assembly of Plasmonic Nanostructures

Zhenyu Zhang, Katyayani Seal, and Gyula Eres

Project Description

Metallic nanostructures offer immense opportunities for conceptual discoveries in fundamental research and may also enable a myriad of novel technological applications. Materials with ordered arrangements of metallic nanostructures promise exotic phenomena, such as optical cloaking and lensing, and are of vital importance in diverse areas such as optical circuiting, chemical and biological sensing, and nanoelectronics. Recent advances in nanofabrication have witnessed the development of a variety of innovative methods for controlled engineering of metallic nanostructures, but each has its own limitations. In this project we are developing a new approach for deterministic growth of metallic nanostructures, the initial purpose being plasmonic device applications. The method, tentatively termed optical-tip lithography (OTL), is rooted in the ability to achieve plasmon-mediated growth of metal, and the proof of the principle is to be demonstrated on ferroelectric surfaces by utilizing an atomic force microscope tip and an elegant optical illumination scheme. Our approach provides new control mechanisms to fine tune the growth process, providing access to new functionalities for plasmonic nanostructures. The active role of the ferroelectric will further demonstrate the novel use of “smart” substrates in controlling the synthesis of plasmonic nanostructures as well as their device performance. Our novel OTL method has tremendous scope for advancing technology related to plasmonic applications, from chemical sensing to high-speed data transfer. This work will combine several existing research directions, providing a strong impetus for further research in the area of nanoplasmonics, a consequence that will help ORNL to better position itself in this important area of research.

Mission Relevance

This project is directly relevant to DOE’s research portfolio in basic science. It is particularly relevant to DOE initiatives in nanoscience and materials science. The capacity to be developed may prove an essential component of the Center for Nanophase Materials Sciences at ORNL. The project may also benefit the Defense Advanced Research Projects Agency and the National Institutes of Health.

Results and Accomplishments

The project was initiated only a few months ago. We started the experimental work by exploring the potential effect of the atomic force microscope (AFM) tip on the nucleation and growth of silver on functionalized ferroelectric substrates with the combined system under illumination of light. These early studies identified a problem in the setup: the AFM tip cast a shadow that prevented light illumination of the potential “hot spot” defined undernearth the tip. The instrumental setup is currently being improved. In support of the experimental work, we are performing theoretical model studies of the effect of multiferroelectric domains provided by the substrate on both the optical and (electrical) transport properties of the metal overlayers and other types of low-dimensional materials, including a single layer of epitaxially grown graphene. Here we pay particular attention to fundamental processes involved in energy conversion from one form to another (such as electrical to thermal at the atomic and nanoscale). Findings from such model studies are specifically important for guiding the optimization of the OTL experiments in the current project, but they also have a broader significance for related processes such as electromigration and thermoelectricity.

00493

Novel, Hafnium-Doped Al_2O_3 Permeation Barriers for Oxygen and Hydrogen Barrier Applications

Theodore Besmann, James Haynes, Karren More, and Bruce Pint

Project Description

The objective of this project is to form thin films of highly adherent, hafnium-doped α-Al_2O_3 on conventional iron-based alloys via microstructural control of thermally grown alumina. Due to their chemical stability, dense layers of stable, adherent α-Al_2O_3 have potential to be very effective oxygen permeation barriers in oxidizing environments and a candidate hydrogen permeation barrier. However, the adherence and stability of alumina films to conventional structural alloys are problematic. The most effective approach to forming adherent alumina films is to aluminize a conventional alloy and then oxidize the surface to form thermally grown alumina. Recent work at ORNL has shown that hafnium doping of the oxide grain boundaries is extremely effective in improving α-Al_2O_3 adhesion to coatings on superalloys. In this project, diffusion aluminide coatings will be fabricated on hafnium-doped, iron-based and nickel-based substrates by chemical vapor deposition (CVD), followed by controlled oxidation of the surface of the coatings to form α-Al_2O_3 permeation barriers. The microstructure, phases, hafnium content, and adherence of the resultant Al_2O_3 films will be characterized. The goals of the work are to demonstrate that (1) hafnium additions to the alloys can significantly improve the quality of the α-Al_2O_3 layer by changing the microstructure and improving adhesion, and (2) pre-oxidation conditions are critical in the formation of a durable α-Al_2O_3 layer by characterizing the thin oxide layer via analytical transmission electron microsopy.

Mission Relevance

Improved oxygen and hydrogen permeation barriers are critical to the success of a number of energy-related technologies of vital interest to DOE, including gas turbine engines, fuel cells (e.g., heat exchanger, ducting), nuclear power plants, and potential fusion applications. Improved oxidation barriers would provide the capacity to further increase firing temperatures in gas turbine engines, thus improving efficiency. Alumina permeation barriers in fuel cell applications eliminate the problems associated with chromium poisoning of fuel cells. Hydrogen barriers in nuclear applications significantly improve hydrogen containment. For hydrogen permeation, in the nuclear energy area, the results of this work and the demonstration of ORNL expertise and capabilities could be brought to the attention of the DOE program related to tritium-producing burnable absorber rods. This concept also could be applied to containment for hydride fuels to increase their operating temperature.

Results and Accomplishments

Task 1 began in August and included casting, rolling, and machining of hafnium-containing and hafnium-free versions of each alloy (316 stainless steel and Hastelloy X). This task was completed successfully, and coupons were machined for coating.

Task 2 began in September and includes CVD aluminizing of the alloys to form Fe-Al coatings on the surfaces. Significant effort was invested in preparing the CVD reactor to successfully aluminize iron-based alloys, which are much more sensitive to CVD conditions than the nickel-based alloys normally aluminized in the ORNL CVD reactor. Five batches of candidate aluminide coatings were fabricated on various 316 and Hastelloy X substrates to evaluate various CVD conditions. These coatings are being characterized by scanning electron microscopy and X-ray diffraction. Results show that our deposition conditions consistently formed Fe-Al coatings on alloys with and without hafnium. Electron microprobe data was collected on selected coatings and is being analyzed. Task 2 is continuing.

Initial oxidation work (Task 3) is under way to identify the best conditions for the controlled oxidation of the alloys to form thin Al_2O_3 layers.

00499

Fabrication of Single-Crystal Thin Films: The Missing Link in Understanding High-Temperature Superconductivity in the Iron Pnictides

Jian Shen, Pengcheng Dai, Zheng Gai, Lifeng Yin, and Wenguang Zhu

Project Description

The recent discovery of superconductivity in the iron pnictides, LnOMPn (Ln = La, Pr, Ce, Sm; M = Fe, Co, Ni, Ru; and Pn = P, As), has generated such excitement that most condensed matter physicists consider it the biggest observation since the discovery of high-temperature superconductivity in cupurates. Despite the initial success, further advances rely critically on the synthesis of single-crystal samples. Here we propose to use laser molecular beam epitaxy to grow single-crystal, iron-pnictide, thin films on GaAs(001) substrate. Our goal is to optimize the growth condition of the thin films, manipulate the surface, and compare with bulk polycrystal transport and magnetic measurements. As proof of principle, we will initially study the CeOFeAs parent compound and fluorine-doped superconductors. The tools and procedures that we develop in this project will be applicable to a range of other iron-based pnictides that have exciting possibilities for understanding high-temperature superconductivity.

Mission Relevance

As a part of the energy strategy for the future, there is a clear need for understanding superconductivity, as revolutionary new power transmission and control solutions based on superconductors will provide instantaneous power regulation without energy loss and, therefore, solve the challenge facing the current electricity grid to provide abundant, reliable power to the increasingly large populations. The discovery of the iron pnictides gives a boost to research along this direction. This project will help to understand the mechanism of high-temperature superconductivity and develop future solutions to efficient use and transmission of electricity. Although the technology associated with traditional low-temperature superconductivity materials is relatively mature, the scientific foundations for the newly discovered high-temperature superconducting materials are in a more rudimentary state, and the engineering parameters required for definition of possible realms of exploration are largely unknown. Within the limitations imposed by these unknown factors, a five-year program has been opened by the Department of Defense Superconductivity Research and Development Program.

Results and Accomplishments

This project started in the last month of FY 2008. We have successfully grown epitaxial thin films of CeOFeAs and observed a previously unknown robust ferromagnetic phase in the ultrathin regime. To ensure perfect epitaxial growth, we selected GaAs(001) as the substrate because the lattice mismatch is negligibly small (~0.03%) and the surface polarities are similar. The latter helps to decrease the interfacial energy and is thus beneficial for epitaxial growth. The epitaxial relationship between the film and the substrate is $[100]_{CeFeAsO}$ // $[110]_{GaAs}$ and $[001]_{CeFeAsO}$ // $[001]_{GaAs}$. Within a narrow growth temperature window around 560^{o}C, we can achieve high-quality epitaxial thin films as confirmed by reflection high energy electron diffraction, which is used for monitoring the growth. Direct dc magnetization measurements from the CeFeAsO thin films demonstrate a clear ferromagnetic behavior. The magnetic susceptibility of a 23 monolayer thin film is almost three orders of magnitude larger than that of the bulk parent compound. This means that the thin film is not in an antiferromagnetic spin density wave state. In fact, the film is in a typical ferromagnetic state as indicated by both the magnetic hysteresis loop and the saturated field cooling curve at 22 K. The ferromagnetic T_c is close to room temperature. The easy axis is lying in plane, and no out-of-plane component can be detected.

NEUTRON SCATTERING SCIENCE DIVISION

00452

Fundamental Studies of CO_2-Coal Interactions Using Novel Neutron Scattering Techniques at Conditions Relevant to Subsurface Sequestration

Y. B. Melnichenko, G. D. Wignall, D. R. Cole, A. Radlinski, and M. Mastalerz

Project Description

Carbon dioxide (CO_2) is the greenhouse gas that makes the largest contribution to global warming, and roughly one-third of the CO_2 emissions in the United States are generated by fuel-burning power plants. Capture and storage of CO_2 in underground geologic structures may significantly reduce CO_2 emissions to the atmosphere. Sequestration of CO_2 in unmineable deep coal seams is particularly attractive, as many coal-burning power plants are located near sites potentially suitable for geological storage. In this project we will apply small-angle neutron scattering (SANS) as well as ultrasmall-angle neutron scattering (USANS) techniques to study CO_2-coal interactions and structure modification of several reference samples of coals at temperatures and pressures similar to those found in deep coal seams likely to be used for industrial-scale underground storage of CO_2. ORNL has extensive experience and expertise in applying SANS to investigate the phase behavior of fluids in engineered porous materials. These capabilities will be extended to studies of confined fluids in natural porous structures and enhanced by using the new state-of-the-art SANS instrumentation now available at the High-Flux Isotope Reactor.

Mission Relevance

This research is relevant to core research activities in geosciences research (Chemical Sciences, Geosciences, and Biosciences Division) and neutron and X-ray scattering (Materials Sciences and Engineering Division) within the DOE Office of Science, Basic Energy Sciences. It supports the President's clean coal initiative "to advance technologies that can help meet the nation's growing demand for electricity while simultaneously providing a secure and low-cost energy source and protecting the environment." The practical implications of this work may also be of great value to select projects within the DOE Office of Fossil Energy's carbon sequestration research portfolio. This study will help to elucidate the reasons for the variable CO_2 injectivity at different storage sites observed during field tests. The ability to predict the effectiveness of CO_2 sequestration is important for economically viable sequestration practices, which may contribute to a reduction in greenhouse emissions and thus improve environmental quality in the United States and elsewhere.

Results and Accomplishments

During FY 2008 SANS/USANS experiments were conducted at the National Institute of Standards and Technology, ORNL, and the Institute Laue-Langevin (France). Coals samples were selected from various basins and depths to represent the range of underground CO_2 conditions (from subcritical to supercritical) that may be realized in the deep subsurface environment. The experiments demonstrated that the porous matrix of all coals remained essentially unchanged after exposure to CO_2 at pressures up to 200 bar. Each coal responded differently to CO_2 exposure, and this response appeared to vary in pores of various sizes within the same coal. For the Seelyville coal at reservoir conditions (16°C, 50 bar), CO_2 condensed from a gas into liquid, and the average fluid density in the pores was a factor of three to four higher than the density of bulk CO_2 (ρ_{CO2}) under similar thermodynamic conditions. At in situ conditions for the Baralaba coal (35°C, 100 bar), the average fluid density of CO_2 in all pores was lower than that of the bulk fluid. Neutron scattering from the Bulli 4 coal did not show any significant variation with pressure, a phenomenon assigned to the extremely small amount of coal porosity in the pore size range above 35 Å. The results demonstrate the unique capability of the neutron scattering techniques to monitor the evolution of microstructure and adsorption capacity of coal exposed to CO_2 environment at subsurface-like temperature and pressure conditions. The observed phase behaviors of the injected CO_2 under confinement, particularly the densification from a gaseous phase to a liquid state, have significant ramifications for operations and reservoir capacity when assessing the suitability of unmineable coal seams for use as CO_2 sequestration reservoirs.

NUCLEAR SCIENCE AND TECHNOLOGY DIVISION

00412

A Novel Radioluminescent Glass Designed for Safe User Applications

C. W. Alexander, R. W. Smithwick, L. A. Lewis, and L. A. Boatner

Project Description

The goal of this project is to develop an approach for producing radioluminescent materials by incorporating a radioactive activator into a glass phosphor. The incorporation of an activator will be achieved by in situ irradiation of ^{6}Li (lithium) to produce ^{3}H (tritium) upon exposure to a neutron flux. Incorporation of tritium will facilitate a 4π luminescence activation region within the glass phosphor. This should greatly increase the luminescent output and create a radiologically safe material that may be applied to both bulk and nanoscale materials. The final product will be (1) self-powered by the incorporated tritium, (2) luminescent, (3) unique in its emission wavelength, (4) environmentally rugged and safe to personnel and equipment, and (6) amenable to fabrication in a variety of configurations.

Mission Relevance

The new materials developed in this effort will provide a unique approach to evaluating potential applications in support of radiologically safe products, such as radioluminescent (i.e., self-powered) lightweight marking and signaling media, egress-marking additives, paint, and other applications. Interest in such radioluminescent materials is extremely high within the Departments of Defense, Justice, and Homeland Security, and other agencies for the purpose of monitoring individuals, high-value assets, radioactive material, and military personnel.

Results and Accomplishments

Three irradiation experiments were conducted at the High-Flux Isotope Reactor (HFIR), and all failed to produce luminescence. Although the lack of luminescence is not fully understood, some insights were gained: (1) radiation-induced darkening can be minimized by irradiating samples far from the HFIR core, and (2) internal hydrodynamic pressures due to the near-instantaneous production of ^{3}H and helium may cause significant rupturing of the glass and loss of ^{3}H (the activator).

00418

Carbonate Thermochemical Cycle for the Production of Hydrogen

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Project Description

This project explores the feasibility of a novel thermochemical cycle that uses the formation of stable uranium compounds to produce bulk quantities of hydrogen. Uranium is one of only a few metals capable of more than one valence state under easily attainable conditions. Changes in the uranium oxidation state can drive the decomposition of water into hydrogen and oxygen. Sodium carbonate is added to facilitate and control the transitions in uranium oxidation states. This thermochemical cycle has several advantages over competing processes because the chemical mechanisms proposed have (1) no more than two hydrogen-producing steps to minimize equipment requirements, (2) no inventory of volatile hazardous chemicals, and (3) operating temperatures compatible with common materials of construction. This proposed work will (1) corroborate the postulated mechanisms, (2) analyze the process efficiency, and (3) establish the technical and environmental viability of the process.

Mission Relevance

This project directly supports national initiatives to develop the hydrogen economy. Replacing fossil fuels will require massive quantities of hydrogen to supply fuel for cars and other industrial purposes. The DOE Hydrogen Program will benefit the most from the success of this project. It is generally accepted that thermochemical cycles are the most efficient methods to produce hydrogen at large scale. Because this uranium carbonate cycle releases no CO_2 and the thermochemical process can use heat provided by green sources such as nuclear reactors and the sun, it represents an environmentally acceptable bulk-hydrogen source. Therefore, DOE nuclear research programs will benefit from the development of this process. The Department of Defense also will benefit because of its critical need for hydrogen to feed fuel cells and serve as an alternative fuel for battlefield vehicles.

Results and Accomplishments

Several experiments were performed during FY 2008 to verify the production of hydrogen using uranium oxides as the starting material. In addition, thermodynamic calculations were completed based on possible reaction equations for various uranium oxides to assess which oxides can produce the most hydrogen. The team of researchers involved in this work is continuing to search for additional resources to further the development of this technology and conduct the recommended efficiency analysis. The accomplishments of this project include the successful laboratory-scale development of the carbonate thermochemical hydrogen generation cycle, preliminary thermodynamic assessment of the cycle, development of a conceptual industrial process flowsheet, and progress toward establishing future funding sources.

00448

Molecular Engineering of Core-Shell Interfaces Toward Controllable Production of Brighter, Optically Tunable Quantum Dots

Michael Z. Hu, Reza Dabestani, and Lei Shao

Project Description

Quantum dots (QDs), which are semiconductor nanocrystals, have been investigated extensively due to size-dependent quantum confinement effects and such applications as biomedical labeling, molecular imaging, solar cells, lasers, light-emitting diodes, and coding materials for soldiers. Core-shell QDs are preferred because a semiconductor core coated with a larger bandgap shell offers the composite better stability and optical properties. The objective of this project is to (1) demonstrate a novel "molecular engineering" approach to create innovative core-shell QD nanostructures that could provide higher quantum yield (thus, higher stability and brightness) and (2) enable a precise control of the optical coupling and decoupling properties. The proposed approach could allow precise tailoring of the core-shell surface with conjugated molecules in the form of self-assembled monolayers (SAM). The SAM-modified surfaces can be designed to grow or link a wide range of inorganic QDs or shell materials with better shell uniformity and well-controlled nanostructures. In addition, SAM layer thickness and functionality can be adjusted by design to enable optical coupling/decoupling between core and core-shell. Proof of principle of the proposed approach could lead to a route to massively produce high-quality and reproducible QDs, a long sought-after goal in this field.

Mission Relevance

This fundamental work on core-shell QD structures could impact many applications, including solid-state lighting, solar cells, biomedical imaging, biological labeling, anticounterfeiting, military, homeland security and counterespionage, light-emitting diodes, and nonlinear optics. Demonstration of the proof of principle of higher brightness and dual-wavelength emissions from a single core-SAM-shell QD, would benefit DOE and other federal agencies, including the National Institutes of Health, Department of Defense, National Aeronautics and Space Administration, and Department of Homeland Security, as well as industry. For example, the more stable QDs will clearly benefit DOE initiatives in solar cells. Our research will strengthen ORNL's position as a leader in nanomaterials and nanotechnology and as an innovator in the application of nanotechnologies to energy, biomedical, biology, and security.

Results and Accomplishments

We developed chemical synthesis methods and characterized material and optical properties of discrete or molecularly linked core and core-shell QDs with unique structures. Our study showed that CdSe core QDs are not very stable in optical emission after molecular linkage via SAMs. Therefore, our development of capability in the synthesis of optically stable CdSe–ZnS core–shell QDs is a fundamental but essential step to demonstrate a molecular tuning effect on fluorescence resonance energy transfer (FRET) between QDs or between the core and shell of QD materials. To conduct FRET studies using CdSe-ZnS as an applicable QD unit, 3–5 monolayers of ZnS are needed. In collaboration with Steacie Institute, we have developed a new mixed-solvents synthesis approach that shows a possibility of producing QDs with thicker shell layers of ZnS. The observation of CdSe–ZnS core–shell QDs by high-resolution aberration-corrected electron microscopy revealed that these core-shell QDs exhibit nonepitaxial structures with the appearance of amorphous surface constituents, a phenomenon never before reported and of unclear cause.

We have created novel, molecularly linked and interspaced QD structures (QD-molecule-QD) that are critical to the proof of principle on tuning QD fluorescent properties by varying molecular spacing between QDs or between core-QD and shell. The images we obtained by scanning transmission electron microscopy may be the first observed QD structures with organic molecules coupling the core and the shell. We achieved the ability to control the interspacing by varying the length of molecular SAM linkers and tailoring the cluster size of molecularly linked QDs. We also confirmed the optical tunability by the fluorescent emission spectra (i.e., a demonstration of 5 times higher emission peak height for molecularly engineered core-shell QD clusters, relative to discrete core-shell QDs).

00450

Development of Hybrid Computational Phantom

Hatice Akkurt and Keith F. Eckerman

Project Description

The first heterogeneous computational phantom models of human anatomy were developed at ORNL more than three decades ago. In these phantoms, the organs were described by simple mathematical equations to facilitate radiation transport calculations. They became the standard for the assessment of organ doses from internal or external exposure to radiation in the fields of medical, occupational, and environmental radiation protection. Recently, medical image data have been used to construct voxel phantoms (i.e., phantoms constructed using a fine mesh based on imaging data). In these phantoms, the organs are represented in great detail and realism; however, computational challenges (e.g., increased computational times and memory requirements), as well as major difficulties in modeling realistic exposure configurations, are noted in their application. To address these issues, this project introduced the concept of a hybrid phantom—a voxel representation in areas where detail is required (e.g., the head and torso) coupled with mathematical descriptions where a high degree of detail is not required and flexible modeling of the configuration is desired (e.g., the arms and legs). This project investigated the feasibility of this approach for radiation dose assessment.

Mission Relevance

The project is relevant to DOE national security missions. Specifically, the DOE occupational worker dose assessment program could benefit from the project for the assessment of organ doses in realistic exposure configurations. In addition to the occupational exposure program, national security programs could benefit from the evaluation of doses in the case of a nuclear or radiological terrorist event. The project has potential benefit for several agencies, including the Environmental Protection Agency, Centers for Disease Control, Nuclear Regulatory Commission (NRC), and Department of Homeland Security. For these agencies, the ability to estimate the radiation doses for realistic configurations in a practical manner is important, not only for occupational exposure but also for the public in the event of an occurrence such as a nuclear accident or terrorist incident. The National Institutes of Health is another agency that could potentially benefit from this work, since the possibility of reconstructing the whole body from partial computed tomography (CT) scans using the hybrid approach is especially important for the investigation of secondary cancers. Finally, the National Aeronautics and Space Administration will potentially benefit from this work for estimating organ doses in realistic scenarios and configurations for astronauts for future manned missions to the Moon and Mars.

Results and Accomplishments

In the second and final year of the project, all the tasks proposed in the original proposal were completed successfully. The hybrid phantom model was developed from the International Commission on Radiation Protection's (ICRP's) fully voxelized reference male phantom model. This model was revised so that the voxel-represented arms and legs were replaced with a mathematical description. During the modification, the shapes of the arms and legs were kept as realistic as possible, and special attention was given to conserve their volumes. By using the hybrid approach, the number of voxels was reduced from 7 million to 2.3 million (~70% reduction in the number of voxels). Subsequently, the computational time and memory load also were reduced by ~70%. A series of benchmark analyses were carried out to ensure that organ dose values for the original voxel and the hybrid phantom were in agreement. The computations were performed using MCNPX (Monte Carlo N-Particle eXtended), and the computed organ doses using the hybrid phantom were confirmed to be in agreement with the original phantom model within the statistical uncertainties.

Once the hybrid phantom model was developed, moving abilities for arms and legs were added. Although there is no graphical user interface (GUI) yet, a program was developed to automatically generate the input file for the desired postures. Several case studies were performed to demonstrate the importance of realistic posture for radiation dose assessments. The results and findings of the study were presented in technical papers and presentations at three conferences.

For follow-on funding, NRC is interested in funding the work on GUI development for the hybrid phantom model to assess the dose to radiation workers using realistic postures. Furthermore, NRC is interested in funding the work toward the development of a hybrid female phantom model based on ICRP's reference female model. Additionally, researchers from MD Anderson are interested in using the hybrid phantom model to assess the dose to patients during a CT scan as well as to assess the dose to the medical staff. For both these cases, dose assessment using a realistic posture is important.

Publications

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00489

Surface Interactions of Radioactive Particles and Radioactivity Effects on Transport and Deposition

Costas Tsouris, Joanna McFarlane, Rodney Hunt, Panos Datskos, Ida Lee, and Sotira Yiacoumi

Project Description

It has been reported that radioactive particles behave differently than nonradioactive particles in terms of transport, aggregation, deposition, and sedimentation. The hypothesis for the different behavior is that radioactive particles undergo a self-charging mechanism during radioactive decay. This hypothesis, as well as a theory proposed in the open literature for aerosol radioactive particles, will be tested via direct interparticle force measurements using atomic force microscopy (AFM). Measurements will be obtained in an atmospheric environment with controlled humidity and in aqueous solutions. This is the first attempt to determine in situ the effect of radioactivity on surface forces. The measurements will elucidate radioactivity effects on particle interactions and help formulate mathematical expressions for the prediction of agglomeration, transport, deposition, and resuspension of radioactive particles. This project will help predict the behavior of radioactive aerosol plumes, particle suspensions in aqueous solutions, and radioactive particles in the subsurface.

Mission Relevance

The project is relevant to nuclear reactor accidents, deliberate explosions of radioactive dispersal devices, radioactive particle behavior in waste tanks at DOE sites, and fate of radioactive particles in the environment. We expect to obtain proof-of-principle data revealing the effects of radioactivity on the surface charge of radioactive particles and, subsequently, on the behavior of radioactive particles in terms of aggregation, transport, deposition, and sedimentation. Besides DOE, the project will benefit the Department of Defense (DOD), the Department of Homeland Security (DHS), and the Environmental Protection Agency (EPA). DOD and DHS are interested to know how radioactive particles will spread in the event of an explosion of a radiological dispersal device (RDD). A number of explosions have been designed with “cold” particles to simulate explosions of RDD devices and the transport of plumes formed by such explosions. The question is whether radioactive particle plumes will behave differently than “cold” particle plumes. EPA is interested in protecting the environment from the release of radioactivity.

Results and Accomplishments

This is a progress report for the first period of the project that covers approximately 30% of the whole project. The work was based on two main tasks: (1) developing an experimental setup with an AFM to directly measure surface forces between particles and (2) obtaining force-distance profile measurements and analyzing the data. For the first task (i.e., AFM setup), after consultation with a representative of VEECO, a U.S.-based company specializing in AFM technology, we purchased a new Caliber AFM system. This system was set up on November 4–5, 2008, by a VEECO representative, who will also provide training to investigators on this project. The second task will involve measurements with ammonium molybdophosphate particles (AMP) that will be loaded with cesium via sorption. For this task, we have worked to attach AMP particles on tipless AFM cantilevers. In the remainder of the project, mixtures of ^{137}Cs and ^{133}Cs at varying ratios and the same concentration will be used to control the activity of the particles and investigate the effects of radioactivity on particle interactions. Cesium-loaded AMP particles will be used for force-distance profile measurements in both atmospheric conditions with controlled humidity and aqueous solutions. The results will be analyzed in terms of the various mechanisms contributing to the interparticle force.

00490

The Feasibility of a Reactor Powering the Earth’s Geomagnetic Field

Daniel F. Hollenbach

Project Description

The objective of this project is to examine the characteristics of a postulated naturally occurring uranium-fueled nuclear reactor located at the center of the earth. No comprehensive theory to date has adequately explained all the observed phenomena emanating from deep inside the earth. The heat that must be generated to keep the iron/nickel core liquid greatly exceeds the calculated amount in all current theories. Isotopic ratios of $^{3}He/^{4}He$ and other noble gases from deep wells vary by several orders of magnitude over what is seen on the earth's surface. These phenomena can be explained if there is a low-power, uranium-fueled reactor deep inside the earth. For this study a mass of uranium, based on the fraction of uranium found in an enstatite chondrite meteor, is assumed to have accumulated into a homogeneous lump. Computer simulations of the reactor are then performed at various average powers and starting times. Bounding assumptions for the reactor can then be derived based on these simulations.

Mission Relevance

The geomagnetic field is crucial to life on Earth. Without it the solar wind would strip away the atmosphere and increase the radiation level on the surface. The geomagnetic field directly affects all aspects of life on Earth, including navigation, weather, environment, and migration. The strength and direction of the geomagnetic field are constantly fluctuating and shifting. A basic understanding of the theory behind the geomagnetic field is crucial to understanding its behavior. This project relates to basic science and is intended to examine a possible, as yet unexplored, source of energy for the geomagnetic field. Several federal agencies are funding research on the theory behind the Earth's magnetic field, including the DOE Office of Science, the National Science Foundation Division of Earth Sciences, and the National Aeronautics and Space Administration program on Earth and Planetary Sciences. Funding from all these agencies will be sought in the future. A proposal to the National Science Foundation is being prepared with two co-principal investigators from the University of Tennessee to continue this work.

Results and Accomplishments

The working theory is that as Earth formed 4.5 billion years ago, uranium accumulated in Earth's core due to gravity, creating a reactor that helps keep the iron outer core liquid; 4.5 billion years ago uranium was ~23 wt % ^{235}U. Using this as a starting point and assuming a uranium mass based on the uranium fraction in an enstatite chondrite meteor, we ran a series of cases to determine the range of average fission power levels that would allow the reactor to operate to the present. Additionally, $^{3}He/^{4}He$ ratios were calculated for each power level and starting time. This study shows that a naturally occurring reactor could still be operating today if the power level is between 1 and 3 TW (1 TW = 10^{12} W). Cycling the power at a given average level has minimal effects on both the reactor lifetime and $^{3}He/^{4}He$ ratios; these are driven primarily by the average power. It also shows that instantaneous $^{3}He/^{4}He$ ratios up to 30 times atmospheric levels (Ra,$^{3}He/^{4}He$ atmospheric ratio) are easily obtainable and that levels up to 50 Ra are possible with high power spikes. This work is directly applicable to work being done at the KamLAND antineutrino detector at Lawrence Berkeley National Laboratory. An accurate measure of the background antineutrino flux is imperative to antineutrino oscillations studies. A paper containing these findings, entitled "Bounding Parameters of a Theoretical Deep-Earth Uranium Fission Reactor" has been prepared for submission.

PHYSICS DIVISION

00455

Computing the Electric Dipole Moment of the Neutron and the Schiff Moment of the Nucleus

D. J. Dean and M. Ramsey-Musolf

Project Description

This project begins a theoretical program ”beyond the standard model physics” which will closely tie to new experimental efforts at the Fundamental Neutron Physics Beamline (FNPB) at the Spallation Neutron Source (SNS). The project allows initial progress on two problems relevant to the experimental effort being developed at SNS: a new neutron electric dipole moment measurement and Parity Violating Neutron Scattering measurements.

Mission Relevance

The operation of FNPB at SNS represents a new forefront in nuclear physics research funded by the DOE Office of Science, Nuclear Physics program. The high-intensity source of monochromatic neutrons provided by this facility will allow experimental nuclear physicists to measure fundamental properties of the neutron and its interactions with unprecedented precision. These experiments will test basic features of the standard model of the electroweak and strong interactions and search for evidence of physics going beyond the standard model. This world-leading effort represents an important and fundamental area of experimental nuclear physics research at ORNL.

A number of theoretical computations are needed to help interpret the FNBP experiments. In the case of the neutron electric dipole moment (EDM) search, the implications of this experiment for different scenarios for charge-parity (CP) violation require a comparison of the results with complementary searches being carried out for the EDMs of the electron and neutral atoms. A comprehensive phenomenological analysis of these EDM searches in models for new CP violation remains to be completed. Similarly, new computations of the Schiff moments of neutral atoms are needed. A similar comprehensive analysis of neutron decay parameters and their implications for “new physics” remains to be performed. Finally, the theoretical framework for interpreting the hadronic parity violating experiments has recently been reformulated using the methods of effective field theory (EFT). In particular, the sensitivity of the different hadronic parity violating experiments to the “low energy constants” in EFT must be delineated for the broad array of measurements that will be performed at FNPB and elsewhere. In short, there exists an opportunity for significant theoretical advances by performing these computations and analyses.

Results and Accomplishments

We developed a plan to study a new formulation of the Schiff moment operator in both nuclei with an equal number of neutrons and protons and in asymmetric nuclei in the coupled-cluster method at the singles and doubles excitation level (CCSD). Our approach to the Schiff moment calculation requires us also to utilize the particle-removed operators within CCSD. This is called particle-removed CCSD (PR-CCSD). We developed the formalism and also coded the PR-CCSD operations. Our next step is to carry out the full implementation of the Schiff operator within this formalism.

We also made progress in studying the permanent EDM. A permanent EDM of a physical system requires time-reversal (T) and parity (P) violation. Experimental programs are currently pushing the limits on EDMs in atoms, nuclei, and the neutron to regimes of fundamental theoretical interest. Here we calculate the magnitude of the P-, T-violating EDM of ^{3}He and the expected sensitivity of such a measurement to the underlying P-, T-violating interactions. Assuming that the coupling constants are of comparable magnitude for π, ρ, and ω exchanges, we find that the pion-exchange contribution dominates. Our results suggest that a measurement of the ^{3}He EDM is complementary to the planned neutron and deuteron experiments and could provide a powerful constraint for the theoretical models of the pion-nucleon P-, T-violating interaction.

Publications

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00475

Online Software Suite for Visualization, Analysis, Management, and Processing of Nuclear Masses

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Project Description

We have built the first and only online suite of computer codes that enables researchers to quickly and efficiently manage, visualize, access, manipulate, share, compare, and analyze data on nuclear masses. Our system accommodates mass measurements, theoretical models of nuclear masses, and large tables of evaluated nuclear masses. This is a client-server system where users download an application to their computer and use it to access and manipulate data stored on our server. The goals of the project are to (1) launch the proof-of-principle suite of codes before a May 2008 international workshop where participants plan a new international evaluation effort in nuclear masses; (2) use the suite to obtain an agreement to have ORNL provide the primary software support (dissemination, file management, and analysis) for the new evaluation effort; and (3) use this agreement to seek support to expand our existing research effort in the ORNL Nuclear Data Project to include software work for nuclear mass evaluations.

Mission Relevance

In recent years, there has been a tremendous growth in mass measurement capabilities, facilities, and new results. This work serves a wide range of research activities in both basic and applied science, including theoretical models of subatomic nuclei; studies of nuclear reactions; calculations of the energy release in thermonuclear explosions; studies of the inner workings of the Sun and stars; studies of element creation in exploding stars; calculations of energy generation in nuclear reactors; feasibility studies of nuclear waste transmutation; long-term stewardship of our nuclear weapons stockpile; and utilization of radionuclides in the $10 billion per year nuclear medicine procedure industry (e.g., positron emission tomography). Unfortunately, the current means of disseminating nuclear mass information is inadequate, relying on sporadic postings of large text tables on web sites. Researchers do not routinely share their latest information, the mass tables are too long to publish in scientific journals, and each group builds tools to visualize the data—resulting in a tremendous duplication of effort. Our system will provide a means for researchers in all of these fields to freely share, update, visualize, analyze, and comment on the latest sets of data on the masses of subatomic nuclei. With the completion of our proof-of-principal suite, we are now devising strategies to reach out to these very different user communities for future support.

Results and Accomplishments

We successfully launched the proof-of-principle suite of codes at the new website, nuclearmasses.org. The website contains many resources on nuclear masses, as well as an entry point into our software system. Our system enables users to visualize and analyze nuclear mass models, compare mass models to evaluated masses, upload their own mass values, store their work, and share their work with colleagues. The visualization tools are especially robust, enabling extensive customization of views of these datasets that often contain masses on up to 5000 or more nuclei, and quick comparisons of different datasets—for example, experimental masses and theoretical predictions. The uploading tools are also robust and easy to use, with an interface similar to the "Windows Wizard" used to install a printer on a personal computer: users navigate through a series of windows, each of which requires simple input, to move their data into our system.

A presentation and demonstration of the system was made at the "Mass Olympics," an international workshop in May 2008 held at the European Center for Theoretical Studies in Nuclear Physics and Related Areas in Trento, Italy. Response among the participants was very positive, with over 30 suggestions for features to add to our system to make it more beneficial for their research. A recommendation from the meeting was that participants will upload their latest mass models and experimental results into the nuclearmasses.org system for easy sharing. Additionally, the head of a European effort for a proposed new mass evaluation activity has agreed to work closely with the nuclearmasses.org development team in the future, including their effort to compile and disseminate a 5-year backlog of new mass measurements. The Europeans will focus on compilations and evaluations, and the nuclearmasses.org team will focus on the dissemination. This is precisely the outcome we had hoped for in this meeting.

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