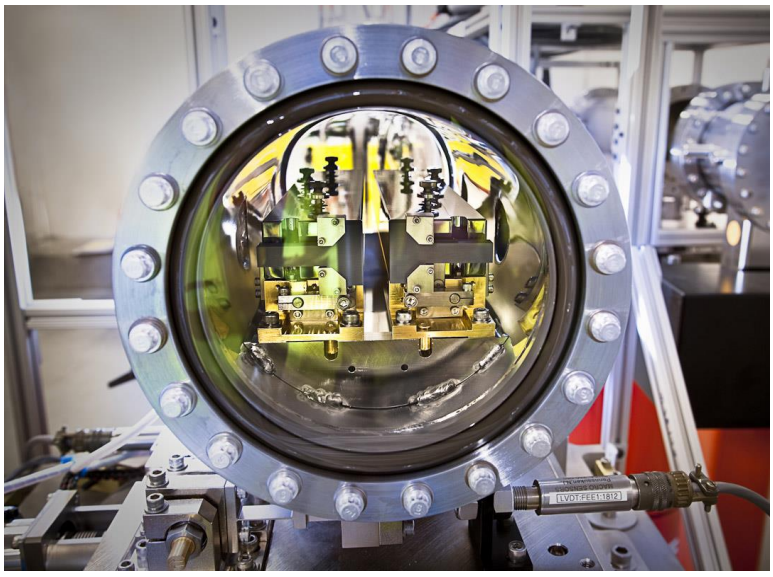
NATIONAL ACCELERATOR LABORATORY

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM



FY2013 ANNUAL REPORT

MARCH 2014

SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025

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APPROVALS

3/20/14

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Date

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Overview

The Department of Energy (DOE) and the SLAC National Accelerator Laboratory (SLAC) encourage innovation, creativity, originality and quality to maintain the Laboratory's research activities and staff at the forefront of science and technology. To further advance the Laboratory's scientific research capabilities, the Laboratory allocates a portion of its funds for the Laboratory Directed Research and Development (LDRD) program. With DOE guidance, the LDRD program enables SLAC scientists to make rapid and significant contributions to seeding new strategies for solving important national science and technology problems. The LDRD program is conducted using existing research facilities. The project proposals can be characterized as:

- Small-scale research and development activities or pilot projects;
- Bench-scale research projects;
- Information gathering, computer modeling, conceptual design and feasibility studies.

In addition to building new core competencies that support the DOE missions, the LDRD project proposals may also conduct scientific research and development that support the missions of other federal agencies and/or non-federal sponsors.

The LDRD program supports the SLAC mission in several ways. First, because LDRD funds can be allocated within a relatively short time frame, SLAC researchers can support the mission of the Department of Energy (DOE) and serve the needs of the nation by quickly responding to forefront scientific problems and capitalizing on new opportunities. Second, LDRD enables SLAC to attract and retain highly qualified scientists and to support their efforts to carry out world leading research. Finally, the LDRD program also supports new projects that involve graduate students and postdoctoral fellows, thus contributing to the education mission of SLAC.

In FY2013, SLAC continued to see some of the previously funded LDRD programs transition to follow on funding with the Office of Science, EERE and other agencies such as DARPA and NIH. This external validation shows that the projects selected were important to continuing forefront science and use-inspired applications with mission relevance and were delivering significant results. Also noteworthy was the filing of 5 invention disclosures in the past year based on current and prior LDRD projects.

SLAC has a formal process for allocating funds for the LDRD program. The process relies on individual scientific investigators and the scientific leadership of the laboratory to identify opportunities that will contribute to scientific and institutional goals. The process is also designed to maintain compliance with DOE Orders, in particular DOE Order 413.2B (dated April 19, 2006). From year-to-year, the distribution of funds among the scientific program areas changes. This flexibility optimizes SLAC's ability to respond to emerging opportunities. SLAC LDRD policy and program decisions are the responsibility of the Laboratory Director. The Director directs the LDRD Program Manager to initiate the program each year in February

and schedule the supporting activities. Successful proposals are usually announced in September with funds available at the beginning of the fiscal year. Normally some funds are held as unallocated to allow new ideas to be funded later in the year. After the call for proposals, the scientists confer with the scientific program ALDs before submitting their proposals. Later in the spring, review teams of distinguished researchers from inside and outside the lab meet with the proponents to hear the proposals and ask questions that may have come from reading the written proposals. The outcome of the review is a ranking of the proposals and comments back to the proposers on merits of the proposals. In the summer, the Associate Laboratory Directors meet over several weeks to prioritize and then forward their recommendations to the Director who makes the final decisions. The list is sent to the SLAC DOE Site Office for concurrence, typically in September.

LDRD accounting procedures and financial management are consistent with the Laboratory's accounting principles and stipulations under the contract between the SLAC and the Department of Energy, with accounting maintained through the Laboratory's Chief Financial Officer and Budget Office.

In FY2013, SLAC was authorized by DOE to establish a funding ceiling for the LDRD program of $4.0M, including General & Administrative (G&A) overhead. Scientists submitted 32 proposals, requesting about $8.4M in funding. Seventeen projects were funded totaling $3.55M, with awards ranging from $45K to $500K.

Costs for the FY2013 program were $3.4M, which equated to 1.03% of SLAC's FY2013 operating and capital equipment budget of $331M.

Annual reports for the FY13 project activities follow.

1.0 Functional Polymers for Lithium-Ion Batteries

Principal Investigator: Zhenan Bao. **Collaborators**: Yi Cui, Michael Toney.

Project Description

This project proposes to develop a new strategic direction within SLAC that will synergize the expertise from several fronts including polymer chemistry, nanostructure synthesis and electrochemical device testing, and structural analysis and characterization. We will develop the unique synthetic capability of hybrid energy storage nanomaterials for highly promising energy storage systems. The project is initiated to accomplish two goals. The first is to develop 3-D conductive polymer hydrogels for high performance lithium ion batteries. The second is to combine self-healing polymers with high-capacity active materials for stable high-capacity lithium ion batteries.

Accomplishments

A number of important advances were made on LDRD-funded projects this year. First, we have developed a facile and scalable solution process to fabricate high performance Li-ion battery negative electrodes by encapsulating Si nanoparticles in a nanostructured 3D porous conductive polymer framework. By taking advantage of the conductive polymer matrix, which provides fast electronic and ionic transfer channels as well as free space for Si volume changes, we successfully achieved high capacity and extremely stable electrochemical cycling. The electrode can be continuously deep cycled up to 5,000 times with over 90% capacity retention at current density of 6.0 A/g. Moreover, the solution synthesis and electrode fabrication process is highly scalable and compatible with existing slurry coating battery manufacturing technology. This will potentially allow for this high-performance composite electrode to be scaled up for manufacturing the next generation of high-energy Li-ion batteries, which are important for applications in electric vehicles and grid-scale energy storage systems that require both low-cost and reliable battery systems. This work has been published on Nature Communications.

Second, we apply self-healing chemistry to silicon microparticle anodes to overcome their short cycle life. High capacity materials, like silicon, usually suffer from fast capacity decay and short cycle life. This is mainly because Si expands volumetrically by up to 300% upon full lithium insertion (lithiation) and contracts significantly on lithium extraction (delithiation). These extreme volumetric changes can cause cracking and pulverization in the electrode, which lead to loss of electrical contact and excessive solid-electrolyte interphase (SEI) growth. Coating Si anodes with a room temperature repeatable self-healing polymer, we show that the low-cost pure Si microparticles (~3-8 μm), for which stable deep galvanostatic cycling was previously impossible, can now have an excellent cycle life. We attain a cycle life of 10 times longer than state-of-art anodes made from Si microparticles while retaining a high capacity (up to ~3,000 mAh/g). Cracks and damage in the coating during cycling can be spontaneously healed due to the presence of the self-healing polymers.

Publications

H. Wu, G. Yu, L. Pan, N. Liu, M. T. McDowell, Z. Bao and Y. Cui, "*Stable Li-ion Battery Anodes by In-situ Polymerization of Conducting Hydrogel to Conformally Coat Silicon Nanoparticles*" ***Nature Comm.***, 4, Article number: 1943, doi:10.1038/ncomms2941, 2013.

C. Wang, H. Wu, Z. Chen, M. T. McDowell, Y. Cui, Z. Bao S. Yang and T. J. Ma, *Self-healing Chemistry enables the Stable Operation of Silicon Microparticle Anodes for High Energy Lithium Ion Batteries*, ***Nature Chemistry.,*** 5, accepted (2013)

Workshops

None

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	Stanford Global Climate and Energy Program
Has follow-on funding been obtained?	Pending
Amount of follow-on funding ($K)?	1699
Number of Post Docs supported by LDRD project?	1
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	1
Number of patent applications filed?	1 provisional filed

2.0 Advance the Performance of Ultimate Storage Rings

Principal Investigator: Yunhai Cai

Project Description

In a prior study supported by LDRD funding we pursued the design of an ultra-low emittance storage ring that would fit in the PEP-II tunnel at SLAC. By using a 7-bend achromat lattice, an electron emittance of 12 pm-rad in each transverse plane with 200 mA stored beam current was achieved. This emittance is at the diffraction limit for 8-keV photons, yielding a brightness of $>10^{22}$ ph/s/mm^2/mrad^2/0.1% BW a high coherent fraction in the multi-keV X-ray range. While this performance is already spectacular and comparable to that from a much more technically difficult energy recovery linac source, it has long been recognized that even more enhanced performance would be realized from such "ultimate storage rings" (USRs) if electron beam parameters could support lasing from undulators in the ring or in switched bypass lines and/or other special modes of producing special photon properties, such as very short pulses, could be developed. With this proposal we plan to explore an expanded range of applications for diffraction-limited storage rings on the scale of PEP-X, including possibilities for lasing, with the goal of informing photon scientists of the potential performance capabilities for USRs so that they can develop more effectively the scientific case for such rings. This study will improve understanding in accelerator and beam physics that would be beneficial to many other related missions within the DOE, including the design of damping rings for a linear collider, positron/electron colliders, and muon colliders.

Accomplishments

We significantly advanced a design of an ultimate storage ring by extending its capacity to drive a free electron laser (FEL) at a nanometer wavelength in a long bypass. Several advancements made this possible:

1) Introduce many multi-cell superconducting RF (SCRF) cavities at a higher frequency to focus the bunch longitudinally achieving 1ps length while retaining adequate beam intensity;
2) Explore the concept of transverse gradient undulator to overcome large energy spread in electron beam that is stored in the ring;
3) Improve the understanding of collective instability driven by coherent synchrotron radiation in electron storage rings. Articulate an effective mitigation method.

Furthermore, our study showed that the repetition rate of the FEL is currently limited below 10 kHz by the high-order modes excited in SCRF. An order of magnitude improvement is expected within a decade. This investigation paved a path toward 1ps bunches in future storage rings.

Publications

Y. Cai, Y.T. Ding, R. Hettel, Z. Huang, L. Wang, L. Xiao, "*An X-ray Free Electron Laser Driven by an Ultimate Storage Ring*," ***Synchrotron Radiation News***, Vol. 26, No. 3. (2013).

L. Xiao, K. Bane, Y. Cai, X. Huang, C. Ng, *"High Frequency SRF Cavity Study for Bunch Shortening in PEPX,"* Proceeding of SRF2013, 16th International Conference on RF Superconductivity, Paris, (2013).

A. Novokhatski, *"Geometric Optics of Wake Fields of Very Short Bunches in Superconducting Cavities"*, Proceeding of SRF2013, SLAC-PUB-15738, Sept. (2013).

Y.T. Ding, P. Baxevanis, Y. Cai, Z. Huang, R.D. Ruth, *"High-gain X-ray FELs using a Transverse Gradient Undulator in an Ultimate Storage Ring,"* Proceeding of IPAC2013, Shanghai, (2013).

Workshops

Yunhai Cai, *"PEP-X as an Ultimate Storage Ring with Lasing Capacity,"* International Workshop on the Science and Design of Diffraction Limited Storage Rings SPring-8, Japan, December (2012), (invited).

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	Possibly from the upgrade of APS from ANL.
Has follow-on funding been obtained?	No
Amount of follow-on funding ($K)?	N/A
Number of Post Docs supported by LDRD project?	0
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0

3.0 Understanding & Controlling Elevated-Temperature Charge Transfer Reactions

Principal Investigator: W. C. Chueh

Project Description

The goal of this project is to answer the most basic question on the reactivity of oxides: how charge-transfer reactions couple to surface chemistry and structure under large driving forces. We will develop the following *in-situ* synchrotron-based electronic and structural analysis tools to probe electrochemically-active oxides at elevated-temperature and near ambient gas pressure: X-ray photoelectron spectroscopy, absorption spectroscopy, and surface diffraction. In particular, we will investigate the reactivity of oxygen gas molecules with model perovskite oxides, which are chemically amenable to a wide range of compositions. Therefore, they are ideally suited for understanding the coupling between physical, chemical and electronic structures at electrochemical interfaces.

Accomplishments

We commissioned a 248 nm excimer pulsed-laser deposition system for growing single-crystalline, metal-oxide thin films. We have successfully grown (La,AE)$FeO_{3-\delta}$ and(La,AE)$CoO_{3-\delta}$ thin films where AE = Ca, Sr, Ba, as well as CeO_2. These are reactive oxides for catalyzing a variety of electrochemical reactions. Processes to obtain atomically-flat substrates and well-ordered surfaces were also developed. They include high temperature annealing and selective etching. Atomically-flat, single-crystalline CeO_2 thin films were obtained with step terraces ~200 nm in width.

Using these thin-film oxides, we carried out surface X-ray diffraction (XRD) measurements with a high temperature cell. We successfully demonstrated the feasibility of the in-situ surface XRD measurement. Unlike conventional diffraction experiments, surface XRD gives crystallographic information on the outermost atomic layer, i.e., the surface exposed to the gas phase. In particular, we measured the 'crystal truncation rods' of epitaxial cerium oxide thin films, as well as yttria-stabilized zirconia single crystals under ambient pressure and at elevated temperature. To our knowledge, these are the first-ever in-situ measurement of these reactive oxides using surface XRD. The zirconia exhibited a 2 x 2 reconstruction, whereas the cerium oxide exhibited a 1 x 1 reconstruction. In both cases, the surface structure was insensitive to the oxygen pressure. Surface structure models were refined to the data to obtain the surface atomic positions.

Publications

None

Workshops

Y. Shi, *Surface Structure-Activity Relationship in Ceria-based Catalysts Studied by Surface X-ray Diffraction on Atomically Flat Thin Films*, Materials Research Society Annual Meeting, Dec. 2013, Boston, USA.

W. C. Chueh, *Seeing is Believing: Shining Light on Electrochemically-Active Materials*, University of Michigan, Department of Materials Science & Engineering, Sep. 6, 2013, MI, USA.

W. C. Chueh, *Seeing is Believing: Shining Light on Electrochemically-Active Materials*, Michigan State University, Department of Chemical Engineering & Materials Science, Sep. 5, 2013, MI, USA.

W. C. Chueh, *Nonstoichiometric Oxide Surfaces Far From Equilibrium*, University of Giessen, Department of Physical Chemistry, Jul. 19, 2013, Giessen, Germany.

W. C. Chueh, *Seeing is Believing: Shining Light on Electrochemistry*, SLAC National Accelerator Laboratory, Stanford Institute for Materials & Energy Sciences, Jun. 14, 2013, CA, USA.

W. C. Chueh, *Far-From-Equilibrium Behavior of Ionic, Polaronic and Adsorbate Species on Ceria Surface*, Seoul National University, Department of Materials Science & Engineering, Jun. 10, 2013, Seoul, South Korea.

W. C. Chueh, *Nonstoichiometric Oxide Surfaces Far From Equilibrium*, Nanjing University of Technology, Department of Chemical Engineering, Mar. 28, 2013, Nanjing, China.

W. C. Chueh, *Nonstoichiometric Oxide Surfaces Far From Equilibrium*, University of Tokyo, Department of Materials Engineering, Mar. 27, 2013, Tokyo, Japan.

W. C. Chueh, *Understanding Solid-State Electrochemistry Through In-operando X-ray Spectroscopy*, Stanford Synchrotrons Lightsource Annual User's Meeting, Oct. 2012, Stanford, CA, USA.

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE-BES
Has follow-on funding been obtained?	No
Amount of follow-on funding ($K)?	N/A
Number of Post Docs supported by LDRD project?	1
Number of students supported by LDRD project?	1
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0

4.0 Data Acquisition Improvement for the LBNE Experiment

Principal Investigator: Mark Convery

Project Description

The Long Baseline Neutrino Experiment (LBNE) will measure neutrino oscillation properties with unprecedented precision allowing the possibility of resolving the neutrino mass hierarchy ambiguity and measuring CP-violation in the lepton sector. LBNE will employ a very large Liquid Argon Time Projection Chamber (LArTPC) neutrino detector, which will have 500K anode wires for detecting ionization signals. In the original DAQ system proposed for LBNE, a low bandwidth connection (20 Mbit/second) is used between the front-end electronics and back-end DAQ. This requires an aggressive zero-suppression algorithm running in the front-end FPGAs to reduce the data volume to fit into the low bandwidth.

The goal of this LDRD is to investigate using the much higher bandwidth of the SLAC-developed DAQ toolkit, which is based on Reprogrammable Cluster Elements (RCEs), to read out these signals. Doing so would result in a much more flexible system as compared to the baseline proposal. In particular, the 100x higher bandwidth of the SLAC system would allow the full, non-zero-suppressed datastream to be read into the RCEs. In the RCEs, flexible and modifiable algorithms can be used to reduce the data volume to a level small enough to be managed by the online computing system. In addition to the neutrino beam physics, this would enable the study of non-beam physics topics, such as atmospheric and SuperNova burst neutrinos.

Accomplishments

The overall accomplishment of this LDRD was to demonstrate that the SLAC-developed, RCE-based data acquisition system is capable of handling the full non-zero-suppressed data stream from LBNE. This was done in two steps: first, demonstrating that the full-rate data could be read into the RCE's memory and, second, demonstrating that the data could be processed "on the fly" in order to reduce its volume by roughly a factor of 100.

To achieve the first step, we have built a Data Simulator Board (DSB) that can generate data at the rate and format expected in LBNE. Using the DSB to send data to a second-generation RCE, we were able to measure single-channel through-put rates in excess of 1 Gbit/second over cables similar to the ones planned to be used for LBNE. This rate is the maximum that is currently expected to be used in LBNE due to bandwidth limitations of its long copper cables. The DSB will also be useful for future development work as it allows us to input arbitrary waveforms into the RCE and check that the system performs as expected.

The second step is to run a "Feature Extraction" algorithm on the memory-resident data to reduce the data volume by about a factor of 100. Prototype code was written and run on a Zynq chip that forms the core of an RCE. One RCE is assumed to handle the data produced by 288 anode wires, which is sent over 8 high-bandwidth channels. The signal from each anode wire is digitized at 2 MHz and 12 bits, yielding an input data volume per RCE of 6.9 Gbit/second. A simple software-based zero-suppression algorithm was run on this data and the performance measured. It was found that with a processor speed of 666 MHz, the algorithm could not quite keep up with the

expected rate, falling short by about 10%. The production RCE's will have an 800 MHz processor speed, and so the expectation is that they will be able to keep up with the expected rate, with about 10% headroom. This, however, is not considered to be enough safety margin for reliable running. More headroom may be obtained either by splitting the data over more than one RCE, or using the FPGA and DSP resources of the RCE to speed up processing. The latter is preferable and will be explored in post-LDRD work. It is expected that moving parts of the algorithm into firmware will improve its speed by at least a factor of two.

We submitted a proposal to the LBNE project to use the RCE-based DAQ toolkit in the LBNE 35-ton LArTPC prototype as part of a technology "down-select" that was held in April 2013. In part due to the work of this LDRD, the RCE-based DAQ toolkit was selected over two other proposals for use in the 35-ton prototype and will be supported by LBNE Project funds. Using our higher bandwidth solution will allow the full datastream to be read into the RCEs, where it can be analyzed and reduced with flexible software and firmware algorithms. This should allow us to take data even in the presence of unanticipated noise sources or other electronics issues. This work will continue in FY14 as part of the LBNE project.

The 35-ton prototype is expected to take cosmic data starting in FY15. Once this full readout system is demonstrated there, we think it is likely to be adopted for the full-scale LBNE detector and to be supported by LBNE Project funding. This will give to LBNE a powerful and flexible DAQ and to SLAC an important role in this exciting flagship experiment.

Publications

None

Workshops

M. Convery, *Trigger/DAQ Technologies Needed for Physics at the Intensity Frontier*, Instrumentation Frontier Community Meeting, Sponsored by DOE, Office of Science, Argonne National Laboratory, January 9-11, 2013.

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	LBNE Project
Has follow-on funding been obtained?	Pending
Amount of follow-on funding ($K)?	103 (FY14)
Number of Post Docs supported by LDRD project?	0
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0

5.0 In-situ Single Particle Plasmon Catalysis

Principal Investigator: Jennifer A. Dionne

Project Description

Designing an efficient catalyst requires careful consideration of electronic, optical, thermodynamic, and kinetic aspects of reactions. These aspects have been challenging to unravel in ensemble measurements, where catalyst heterogeneity conceals many important and interesting structure-dependent catalytic properties. For example, the catayst dimensions, surface structure, and the catalyst-support interface could all have profound consequences for catalytic activities. Accordingly, there is significant reason to explore catalytic reactions on single particles, *in-situ* and in real time.

This project investigated energy-relevant catalytic processes on single nanoparticles using *in-situ* microscopy and spectroscopy. Attention was given to two systems: 1) Ag@TiO_2 core-shell nanoparticle mediated photocatalysis and 2) metal nanoparticle hydrogenation.

As part of the proposal, we developed new optical and electronic probes of photocatalytic activity that can readily monitor single-particle reactions, with the potential for single-molecule to single-electron precision. For example, on the Ag@TiO_2 systems, we developed techniques to monitor liquid-cell catalysis on individual catalysts, and correlate the catalytic activity with catalyst structure. In particular, we could optically detect electron transfer and accumulation in the metal co-catalyst by looking at the frequency shift of its plasmon resonance. Thereafter, we could map the structure of individual nanoparticles using transmission electron microscopy (TEM). Similarly, on the metal hydrogenation system, we used environmental TEM coupled with electron energy loss spectroscopy (EELS) to probe hydrogen-loading reactions on individual palladium nanoparticles. The particles were imaged with atomic-scale resolution in the TEM. Simultaneously, EEL spectroscopy was used to monitor the plasmon resonance of the Pd nanoparticle – a signal which is very sensitive to hydrogen absorption in the particles.

Our results yielded unprecedented insight into the dependence of the catalytic structure on the catalyst efficiency, and provided the foundation for optimizing both water-splitting and energy-storage catalysts.

Accomplishments

The research supported by this one-year LDRD grant was very successful. For our Ag@TiO_2 photocatalytic studies, we first developed a reproducible solution synthesis for the preparation of monodisperse Ag@TiO_2 core@shell nanoparticles (NPs) with a tunable core size. The synthesis consisted of the colloidal preparation of the Ag cores, a ligand substitution, and sol-gel hydrolysis and condensation of a titanium precursor on the surface of the metal NPs. Core sizes of 25, 35 and 50 nm were prepared with narrow size distributions, while TiO_2 shell thicknesses were reproducibly ~10 nm.

To investigate single particle photocatalysis, we constructed a flow cell for an optical microscope. First, nanoparticles were dispersed onto a transmission electron microscope silicon nitride grid.

The TEM grid was then transferred to an aluminum support and used as one of the windows of the flow cell. The opposite window of the flow cell was made from quartz, to allow for UV transparency. Single particle dark-field scattering spectra in an optical microscope were acquired on individual nanoparticles both in air and in EtOH. Upon UV irradiation in deaerated EtOH, blue-shifts were detected on individual nanoparticles – corresponding to electron transfer from the TiO2 to the Ag. Electron transfer kinetics were monitored during both 'charging' and discharging of the nanoparticle. Subsequently, the nanoparticles were imaged using high-resolution TEM. We found that the degree of asymmetry in the nanoparticles significantly impacted their catalytic response and electron charge transfer kinetics, and electron storage capacity.

For our metal hydrogenation catalysis studies, we used environmental TEM-EELS to probe hydrogen-loading reactions on individual palladium nanoparticles. While bulk palladium undergoes a well-understood mechanism during hydrogen loading – transforming from a hydrogen-poor alpha phase to a hydrogen-rich beta phase – the mechanism is much less clear at the nanoscale. We prepared single crystalline Pd nanoparticles using standard colloidal techniques and used TEM-EELS to monitor the plasmon resonance of the Pd nanoparticle – a signal which is very sensitive to hydrogen absorption in the particles. As hydrogen was introduced into the chamber, we monitored the alpha to beta phase transition. At low hydrogen pressures, the EELS signal peaked at energies of 7.5eV, corresponding to the bulk plasmon resonance of alpha-phase PdH. As the hydrogen pressure was increased to 1mbar, the plasmon resonance exhibited an abrupt shift to lower energies, corresponding to the beta-phase of PdH. These measurements have been repeated on particles with sizes ranging from 40nm down to 10nm. They represent the first single-particle isotherms of hydrogen loading in palladium nanoparticles, and provide key insight into the thermodynamics of catalysis in nano-sized specimens.

The *in-situ* studies of this proposal were very challenging, but have yielded unprecedented insight into both energy generation and energy-storage catalysis. They have begun to unravel the interplay of particle structure and function, and provided a platform for enhancing future catalytic systems.

Publications

A. Baldi, T. Narayan, S. Sheikholeslami, J. Dionne, "*Monitoring liquid-cell photocatalytic reactions on individual Ag@TiO2 nanoparticles,*" in preparation (2013)

T. Narayan, A. Baldi, A. Koh, J.Dionne "*Detecting the alpha-to-beta phase transition in individual nanosized palladium-hydride particles,*" in preparation (2013)

A. Atre, A. Garcia, H. Alaeian, J. Dionne, "*A broadband negative index metamaterial at optical frequencies* ," Advanced Optical Materials, 1, 4 (2013)

A. Garcia-Etxarri, J. Dionne, "*Surface-enhanced circular dichroism spectroscopy mediated by nonchiral nanoantennas*" Physical Review B 87, 235409 (2013)

Workshops

J. Dionne, A. Baldi, T. Narayan, A. Koh, *In-situ Single Particle Catalysis,* Workshop on Surface Plasmons, Metamaterials, and Catalysis, Sponsored by ARO, Rice University, Houston, TX, October 2013.

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE, DOD
Has follow-on funding been obtained?	Not yet
Amount of follow-on funding ($K)?	N/A
Number of Post Docs supported by LDRD project?	0
Number of students supported by LDRD project?	2
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	2 anticipated
Number of patent applications filed?	2 anticipated

6.0 New Initiative for Synchrotron Radiation-based Catalysis and Energy Research

Principal Investigator: Britt Hedman

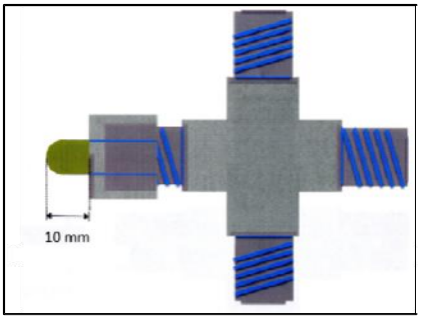
Project Description

Develop high energy-resolution x-ray emission techniques, coupled to theoretical calculations, to characterize the interactions between molecules and surfaces of catalysts under the *operando* conditions, and to enhance characterization of catalytic materials through development of high-throughput techniques, applied to x-ray absorption (XAS) and emission (XES) measurements.

Accomplishments

High Energy-resolution X-ray Emission Techniques:

The key element of the high energy-resolution x-ray emission part of the LDRD is the combination of the unique XES instrumentation on SSRL BL6-2 with construction and testing of sample cells to allow *in-situ* measurements under catalysis *operando* conditions. During FY13 a cell was researched that is based on a Be-dome design, which has the ability to withstand the required high temperatures and high pressure, and whose geometry enables both XES and XAS measurements. This cell, illustrated to the right, was engineered and put into fabrication. It will be used in experiments in FY14, with the infrastructure (gas delivery system, mass flow control, quadrupole mass spectrometer for use on-line gas product analysis) implemented in FY12.



High-throughput Technique Developments:

The high-throughput spectroscopy developments, aimed at providing enhanced approaches for rapid characterization in catalysis and energy projects, using x-ray absorption spectroscopy, are focused on synergistically coupled hardware and software implementations. Building on developments in FY12 (multiple-sample holding devices, alignment automation), a dedicated ambulatory control station was completed in FY13. The station is "plug-and-play" and can be easily moved to and integrated into any of the current XAS beam lines at SSRL. This approach provides high flexibility and efficiency in enabling high-throughput measurements on several SSRL beam lines.

Software developments in FY13 focused on a major module for automated XAS analysis, incorporating algorithms for determining the data quality while the sample is still being measured online. The software examines dynamically the quality of the data being measured, calculates statistics that is based on data noise levels, and enables the experimenter to automatically use the system intelligence to provide decisions as for when to advance to the next sample in the queue,

thereby significantly improving data quality and experimental efficiency. Together with the developments in FY12 - macros for experiment enhancements to motor motion, alignment, timing structures, and nesting, as well as a queuing system for automated multiple sample experiments - the fundamental building blocks are now in place to implement a characterization pipe-line based on XAS.

Publications

None

Workshops

Chemical and Biological Catalysis, 2012 LCLS / SSRL User's Meeting and Workshops, SLAC National Accelerator Laboratory, Stanford University, Menlo Park CA 94025, October 4, 2012

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE BES, Partners
Has follow-on funding been obtained?	No
Amount of follow-on funding ($K)?	N/A
Number of Post Docs supported by LDRD project?	0
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	1
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0

7.0 Towards In-Situ Growth and Spectroscopy of Complex Oxide Thin Films Heterostructures

Principal Investigator: Harold Y. Hwang

Project Description

This project pursues the initiation of a new strategic direction within SLAC, to bridge advanced complex oxide thin film and heterostructure growth techniques with in situ characterization capabilities. A mobile pulsed laser deposition (PLD) system will be implemented to be compatible with surface chemistry, soft x-ray, and ARPES beam-lines at SSRL.

Accomplishments

Design was finalized for a new PLD growth chamber compatible with 2 beam-lines at SSRL, as well as sample exchange chambers.

In parallel with these equipment developments, scientifically we have pursued two research directions, which have the advantage of being addressable in part using ex situ materials synthesis. In the first case, we investigate the two-dimensional highly spin-polarized electron accumulation layers commonly appearing near the surface of *n*-type polar semiconductors by angular-resolved photoemission spectroscopy. Because of the polarity and the strong spin-orbit interaction built in the bulk atomic configurations, the quantized conduction-band sub-bands show giant Rashba-type spin splitting.

The second research direction is based on our unexpected finding of interface electronic structure control by surface adsorbates (Y. W. Xie, Y. Hikita, C. Bell, H. Y. Hwang, "Control of Electronic Conduction at an Oxide Heterointerface Using Surface Polar Adsorbates," *Nature Communications* **2**, 494 (2011)). We have continued this work, finding that we can tune the interface carrier density and Hall mobility over several orders of magnitude by surface treatments. In parallel, we are spectroscopically investigating this effect using the environmental cell on BL 13-2, and which shows strong changes upon exposure to D_2O.

Publications

M. Sakano, M. S. Bahramy, A. Katayama, T. Shimojima, H. Murakawa, Y. Kaneko, W. Malaeb, S. Shin, K. Ono, H. Kumigashira, R. Arita, N. Nagaosa, H. Y. Hwang, Y. Tokura, and K. Ishizaka, *"Strongly Spin-Orbit Coupled Two-Dimensional Electron Gas Emerging near the Surface of Polar Semiconductors,"* ***Physical Review Letters*** **110**, 107204:1-5 (2013).

Y. W. Xie, C. Bell, Y. Hikita, S. Harashima, and H. Y. Hwang, "*Enhancing Electron Mobility at the $LaAlO_3/SrTiO_3$ Interface by Surface Control*," ***Advanced Materials*** DOI: 10.1002/adma.201301798 (2013).

Workshops

H. Y. Hwang, *"Emergent Magnetism at Perovskite Heterointerfaces,"* German-Japanese International Workshop on "Structure and Control of Interfaces", Berlin, Germany, January 9-11, 2013.

H. Y. Hwang, *"Unconventional Electronic and Magnetic States at the $LaAlO_3/SrTiO_3$ Interface,"* 20th International Conference on Electronic Properties of Two-Dimensional Systems, Wroclaw, Poland, July 1-5, 2013.

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	Not yet determined.
Has follow-on funding been obtained?	No
Amount of follow-on funding ($K)?	N/A
Number of Post Docs supported by LDRD project?	1
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	2
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0

8.0 X-Band Gun Evaluation

Principal Investigator: C. Limborg-Deprey

Project Description

The goal of the LDRD "X-Band Gun Evaluation" was to measure the properties of bunches generated from the X-Band rf photoinjector in the X-band Test Area (XTA) of NLCTA to verify that they agree with expectations. Simulations have indicated that the peak brightness of this source should exceed that of state-of-the-art S-Band rf photoinjectors, such as that of the LCLS, by a factor of 8 where a factor of 4 comes from the shorter bunch length and a factor of 2 comes from the reduced transverse emittance. Both are a direct consequence of operation at the higher X-Band frequency of 11.4 GHz where higher acceleration gradients are possible. Challenges were anticipated to be large dark currents, tight alignment and timing stability tolerances. The main components of the XTA linac are shown in Figure 1.

During the past year, XTA was turned into a more reliable accelerator that can deliver high brightness electron beams at 80 MeV. Short bunch lengths were measured, which agree with expectations. Relatively low emittances (0.7 mm-mrad at 20 pC) have been measured. A program to further decrease the bunch emittance and increase the bunch charge is underway.

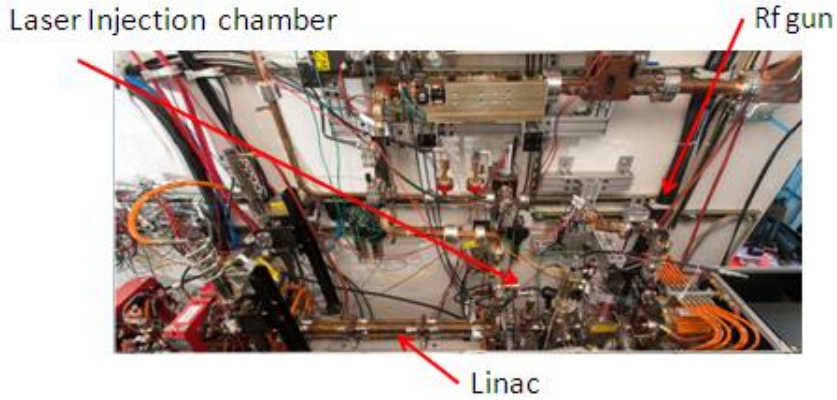


Figure 1. X-band Test Area (XTA).

Accomplishments

During Q1,we installed the transverse deflector, measured bunch lengths, reached a 65 MeV beam energy out of the linac and verified that the gun cathode can operate at 200 MV/m with tolerable dark current levels. As noted above, measurements showed that the bunch lengths are as short as expected from simulations. The gun cathode was operated between 120 MV/m and 200 MV/m with tolerable dark currents. However, to demonstrate small transverse emittances, it became clear that stabilization of both the laser and rf timing and amplitude were required.

During Q2, modifications to the laser Phase Lock Loop (PLL) were implemented and the phase jitter decreased from 500 fs rms to 150 fs rms (0.6 deg X-Band). This improvement also benefitted

the other NLCTA programs (E163 and ECHO). Transverse emittances at the 1 mm-mrad level were then measured but at low charges (~10 pC). Fine tuning of the beamline was still not possible at this point as the rf amplitude and phase were drifting at the few seconds to minutes time scale.

During Q3, the 20-year-old Station-2 LLRF system was replaced by one based on the PAC/PAD upmixers/downmixers built at SLAC for LCLS. Faya Wang imported and modified his Station-3 Matlab code to control and monitor all rf signals, and he implemented phase and amplitude feedbacks on the SLED forward rf signal. It was found that the TWT was unstable and it was replaced with a better unit. The SLED tuning feedback was also made operational. The beam phase monitor (single cell X-Band cavity) signals could then be analyzed and processed for Schottky scans and Time-Of-Flight (TOF) measurements (see examples in Figure 2a). The TOF measurements shown indicate that the cathode peak field in the gun reaches 200 MV/m. Simulations of these measurements are shown in Figure 2b for comparison. The energy out of the gun has also been also confirmed with steering magnet deflection measurements.

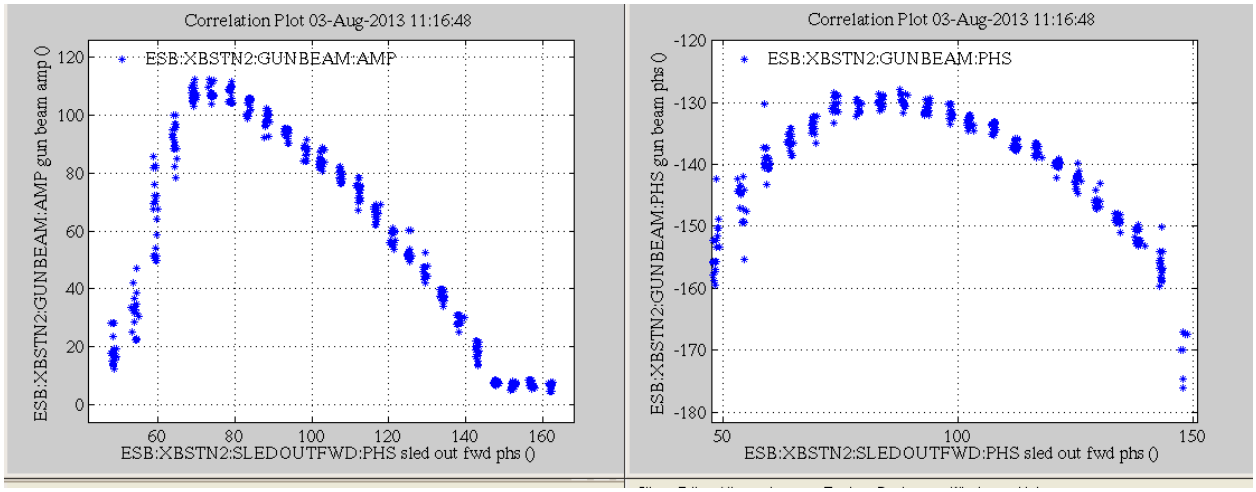


Figure 2a Schottky and TOF measurements with 108 MW SLED output power.

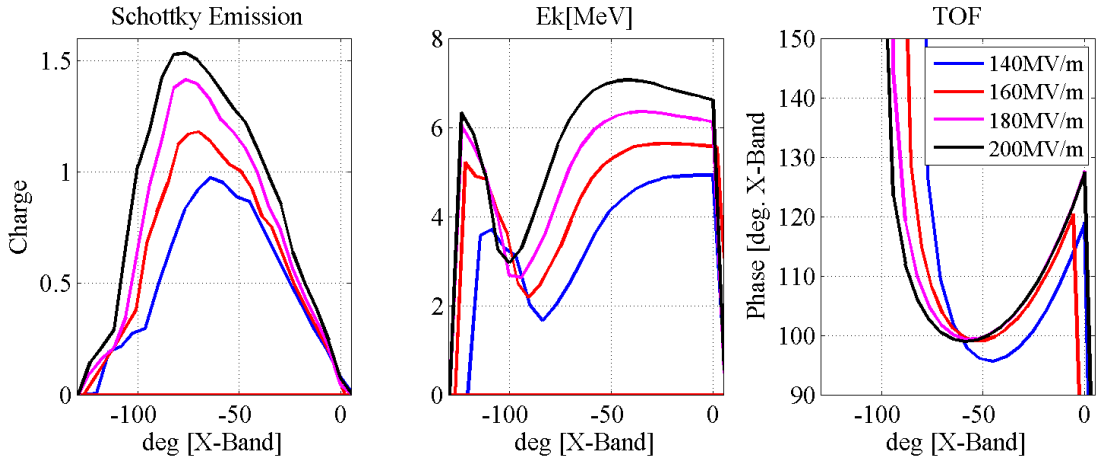


Figure 2b Simulation results for different cathode field levels.

During Q4, we installed the new T105 accelerator structure (with rounded, race-track couplers), an X-BPM (a dual cavity with monopole and dipole modes tuned to 12.85 GHz) and a passive SW X-Band structure of 20 cells (SW20) for precision beam phase measurements. The system was conditioned up to 165 MW from SLED, which produce a beam energy of 80 MeV. The energy measured with the spectrometer and that calculated from the power level out of the SLED line agreed well (it had been 10% low with the old structure, indicating that it might have detuned). With further processing, we expect to reach 100 MeV.

In September, the laser transport line was upgraded and optics on the laser table was simplified. This led to higher available UV energy on the cathode. Maximum bunch charges of 250 pC could be generated out of the gun corresponding to a QE of 2.10-5. Emittances in the 1 mm-mrad have been regularly measured for 30 pC. Recent measurements at 20 pC yielded 0.7 mm-mrad. Improvement of the laser profile uniformity and an increase in laser fluence should allow us to achieve the target emittance values. The temporal compression of the electron bunch exiting the gun was measured and proved to be in agreement with simulations (see Figure 3). Bunch lengths as short as 125 fs were measured for low charge.

Conclusion: The XTA is now an operating facility delivering high brightness beams in a reasonably reliable and stable fashion. It is the shortest photoinjector beamline delivering such a bright beam at 80 MeV. The targeted bunch lengths were demonstrated. The transverse emittances are now below the 1mm-mrad level (as low as 0.7 mm-mrad for 20 pC) and the goal in FY14 is to reach less than 0.6 mm-mrad with 100 pC bunches.

The present performance of the XTA in terms of brightness and stability is good enough to consider expanding it as an Inverse Compton Scattering Source (ICS) to produce 100 keV photon beams initially. We are presently looking for funding from DARPA and BES for such a program, and presentations at DARPA are scheduled in October. Other useful XTA applications are for a high peak power THz source and plasma acceleration, which requires ~1 kA bunch currents, and for UED development.

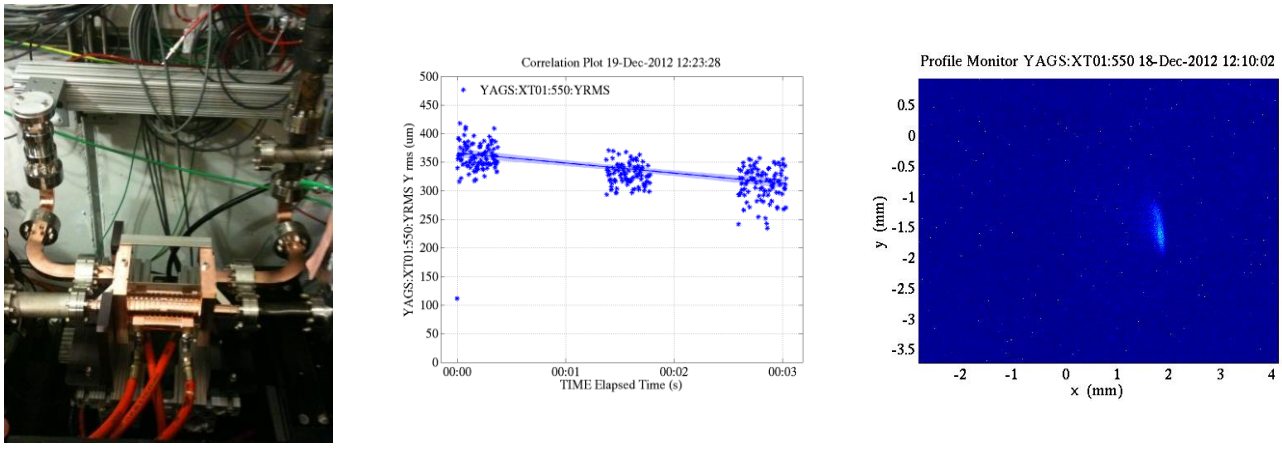


Figure 3. Left: transverse deflector installed in XTA, middle: bunch length measurements using the deflector and right: streaked bunch profile.

Publications

C. Limborg-Deprey, et. al., *"Commissioning of the X-Band Test Area at SLAC,"* LINAC 12, Tel Aviv, Israel, Sept 2012.

C. Limborg, et. al., "X-Band gun for UED" Proceedings "*WORKSHOP ON ULTRAFAST ELECTRON SOURCES FOR DIFFRACTION AND MICROSCOPY APPLICATIONS*," UCLA, Dec 2012.

C. Limborg, et al., *"Initial Performance of an X-Band gun at SLAC"* Proceedings "*PHYSICS AND APPLICATIONS OF HIGH BRIGHTNESS BEAMS*," Puerto Rico, Mar 2013.

C. Limborg, et al. *"Initial Performance of an X-Band gun at SLAC"*, contributed talk, Pasadena, Oct 1st, NA-PAC 2013 conference.

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DARPA, BES, DHS for Inverse Compton Scattering funding ; HEP for demonstration of ~ 1 kA beams
Has follow-on funding been obtained?	No
Amount of follow-on funding ($K)?	N/A
Number of Post Docs supported by LDRD project?	0
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0

9.0 X-ray Scattering from Solution-Cast Films for Organic Solar Cells

Principal Investigator: Stefan C.B. Mannsfeld (lead), Zhenan Bao, Michael D, McGehee, Alberto Salleo, Michael F. Toney.

Project Description

The objective of this project is to quantitatively relate the performance of organic solar cells to the organic materials microstructure and to explore the role of the printing process in the formation of printed organic solar cells. To meet these goals we focus on three important components: i) the development of an in-situ X-ray characterization facility for printed organic solar cells; ii) the development of materials and tools involved in the printing process; and iii) the implementation of X-ray based methods to characterize structural disorder in organic solar cell materials and relating this disorder to the performance. We want to achieve these goals by developing tools that will mimic commercial printing methods to allow systematic understanding of various factors that govern the crystallization and film growth of organic semiconductors, building a new in-situ X-ray facility at SSRL that allows the physics of the printing process to be studied in-situ, and detailed investigation of BHJ model systems to deterministically connect the BHJ materials microstructure with the efficiency with which the BHJs split excitons and conduct away the resulting free charges.

The understanding gained from this work will aid in the design and control of novel and more efficient materials for organic photovoltaics.

Accomplishments

We successfully completed most of our goals for the second year of research in this LDRD project.

We implemented a fully operable in-situ printing setup at the SSRL beamlines (PIs Mannsfeld/Bao) that allows us to take in situ X-ray diffraction data at a time resolution of a few miliseconds, thus enabling us to follow the crystallization kinetics of the printed films. We introduced micro-structuring on the shearing blade surface (part of the print head) by which we can control the nucleation density in the printed film and the crystalline quality in the film grains. With this we were able to significantly advance the printed film quality and electrical performance of a commercially available organic semiconductor to record levels of 11 cm2/Vs. This represents a major advancement in the solution-deposition of this class of materials and the results were published in the very high impact publication Nature Materials. Due to the reduced funding in FY 13, we did not complete the work on a multiple ink-capable print head. However, follow-up funding for this project was successfully obtained (BRIDGE EERE grant) and this work will be completed as part of this new project.

We successfully finished our work in the OPV polymer structure portion of the LDRD (PIs McGehee/Salleo/Toney) in which we wanted to elucidate the relationsships between device performance in bulk-heterojunction (BHJ) organic PV devices and the structural details that can be

probed in the solar cell films with X-ray scattering. In order to link the microstructure of the fullerene-rich phase to the measured BHJ device performance, an understanding of how processing affects ordering of the fullerene in the film needed to be developed. We have measured grazing incidence X-ray scattering of PCBM films that had been slowly crystallized at several thicknesses. Though all the films are crystalline with a well-defined out-of-plane molecular orientation, we find that the dominant crystal structure changes as a function of thickness, where the cross-over thickness is ~ 15 nm. This suggests that the vertical confinement in the thin film acts as a thermodynamic constraint and thus affects which crystal structure corresponds to a (local) free energy minimum. Moreover, above the cross-over thickness there appear to be at least two polymorphs, both which are different from the crystal structure of the films with small thicknesses. Since crystallization of the fullerene occurs within a blend polymer film in a working OPV cell, our observations suggest that the geometrical constraints imposed by the polymer matrix may affect the precise fullerene crystal structure that forms in the annealed blend film. The results of this part of the LDRD study was published in three journal publications including a recently accepted Nature Materials publication.

Publications

N. Cates Miller, S. Sweetnam, E.T. Hoke, R. Gysel, C.E. Miller, J.A. Bartelt, X. Xie, M.F. Toney & M.D. McGehee, *Nano Letters* 12, 1566, 2012.

Y Diao, B. C-K. Tee, G. Giri, J. Xu, D.H. Kim, H.A. Becerril, G. Xue, S.C.B. Mannsfeld, Z. Bao, *Nature Materials* 12, 665 (2013).

J. Mei, Y. Diao, A.L. Appleton, L. Fang, Z. Bao , J. *Am. Chem. Soc*. 135, 6724 (2013).

K.R. Graham, P. Erwin, D. Nordlund, K. Vandewal, R. Li, G. O., N. Ndjawa, E.T. Hoke, A. Salleo, M.E. Thompson, M.D. McGehee, A. Amassian, *Advanced Materials Early View 2013*, DOI: 10.1002/adma.201301319

K. Vandewal, S. Himmelberger, A. Salleo, *Macromolecules*, 2013, 46 (16), pp 6379–6387, DOI: 10.1021/ma400924b

K. Vandewal, S. Albrecht, E.T. Hoke, K.R. Graham, J. Widmer, J.D. Douglas, M. Schubert, W.R. Mateker, J.T. Bloking, G.F. Burkhard, A. Sellinger, J.M. J. Fréchet, A. Amassian, M.K. Riede, M.D. McGehee, D. Neher, A. Salleo, *Accepted 2013*, DOI: 10.1038/NMAT3807

Workshops

M.F. Toney, *"Use of Synchrotron X-ray Techniques in Materials Research*" 3M Corporation, TechForum seminar, April 2012, St Paul, Mn. (invited)

S.C.B. Mannsfeld , "*Revealing the Molecular Packing in Small Organic Semiconductor Films with Synchrotron X-Ray Scattering*", Materials Research Society Spring Meeting 2012, April 2012, San Francisco, Ca. (invited)

M.F. Toney, "*Role of structure and morphology in organic electronics*" University of Minnesota Center for Nanostructure Applications seminar, April 2012, Minneapolis, Mn. (invited)

S.C.B. Mannsfeld , "*Revealing the Molecular Packing in Small Organic Semiconductor Films with Synchrotron X-Ray Scattering*", Brookhaven National Lab User Meeting 2012, May 2012, Brookhaven. (invited)

G. Giri, "*Tuning Charge Transport of Organic Semiconductors Through Metastable Crystallization and Lattice Strain*", SSRL+LCLS User Meeting 2012, Oct. 2012, Menlo Park, CA (invited)

Ying Diao, *"Highly-aligned, large single-crystalline domain organic semiconductors via nucleation control*." 2012 American Institute of Chemical Engineers (AIChE) Annual Meeting.

S.C.B. Mannsfeld , "*Revealing the Molecular Packing in Small Organic Semiconductor Films with Synchrotron X-Ray Scattering*", SPIE Optics+Photonics West 2012, August 2012, San Diego, Ca.

K. Vandewal, "*Relating molecular properties to charge carrier generation, recombination and transport in organic solar cells*", I-CAMP Summer School on Renewable and Sustainable Energy, July 2012, University of Colorado

Koen Vandewal, Alberto Salleo, "*Free Charge Carrier Generation by Thermally Relaxed Charge Transfer States at Organic Donor-acceptor Interfaces*" , 2013 MRS Spring Meeting & Exhibit, April 1-5, 2013, San Francisco, California

Koen Vandewal , "*Efficient free charge carrier generation from charge-transfer states in organic solar cells*", ICMAT 2013, 7th, SPIE 2013, Optics+Photonics 25-29 August, San Diego

Koen Vandewal, "*Efficient Charge Carrier Generation from Charge-transfer States in Organic Solar Cells*", International conference on materials for advanced technologies 2013

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE EERE
Has follow-on funding been obtained?	Yes
Amount of follow-on funding ($K)?	875
Number of Post Docs supported by LDRD project?	2
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	1
Number of patent applications filed?	1

10.0 X-ray Studies of Water and Aqueous Solutions

Principal Investigator: Anders Nilsson

Project Description

Water is the key compound for our existence on this planet and it is involved in nearly all biological, geological and chemical processes. Although water is the most common molecular substance it is also the most unusual with many peculiar properties such as an increased density upon melting, increased viscosity under pressure, density maximum at 4°C, high surface tension and many more. The focus of the research is to link recent results based on x-ray spectroscopy and scattering on the structure of water with some of the major anomalies of water that are enhanced in the supercooled regime. The understanding of the molecular properties of water and aqueous systems is vital for many processes of importance for DOE related to energy systems, environmental issues, chemistry in general and biology.

Accomplishments

We have measured x-ray emission spectra of water at the SXR instrument at LCLS in October 2012 under supercooled conditions down to temperatures around 225K in order to establish the relative population of tetrahedral and strongly disordered species. The data is currently being analyzed and will be interpreted through the assistance of density functional theory spectral calculations. As a side project we also observed some non-linear phenomena using high fluence at LCLS which indicates that the emitted secondary radiation could stimulate emission. We had a 2nd beamtime at the CXI instrument at LCLS in January 2013 where we measured x-ray scattering of the water droplets at temperature down to 225 K. This was to complement the data obtained last year in order to meet some of the questions the reviewers had on our Nature submission. We have also completed our x-ray scattering study of water at ambient conditions where very precise O-O pair correlation functions could be obtained. Finally, we completed the paper on the long range order of water in HCl and NaOH aqueous solutions. Hydrated structures of H^+ and OH^- are not simple mirror images of each other. We find that protons only locally enhance local hydrogen bonds; however, hydroxide ions induce tetrahedrality in the overall hydrogen bond network of water.

Publications

C. Huang, J. A. Sellberg, T. A. McQueen, N. D. Loh, H. Laksmono, R. G. Sierra, C. Y. Hampton, D. Starodub, D. P. DePonte, J. Feldkamp, D. Nordlund, M. Beye, A. V. Martin, A. Barty, K. T. Wikfeldt, D. Schlesinger, L. G. M. Pettersson, T. M. Weiss, C. Caronna, M. Seibert, M. Messerschmidt, G. J. Williams, S. Boutet, M. J. Bogan, and A. Nilsson, *Experimental Observation of Bulk Liquid Water Structure in "No-man's Land"*, submitted

C. Chen, C. Huang, I. Waluyo, D. Nordlund, T. C. Weng, D. Sokaras, T. Weiss, U. Bergman, L.G.M Pettersson and A. Nilsson, *Solvation Structures of Protons and Hydroxide Ions in Water*, J. Chem. Phys. **138** (2013) 154506

L. Skinner, C. Huang, D. Schlesinger, L. G. M. Pettersson, A. Nilsson and C. J. Benmore, *Benchmark oxygen-oxygen pair-distribution function of ambient water from x-ray diffraction measurements with a wide Q-range,* J. Chem. Phys. **138** (2013) 074506.

Workshops

Anders Nilsson X-Ray Shine Light on the Water Mystery, Symposium on Water and Health, Caltech, Pasadena (January 2013)

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	No
Source of support for follow-on funding?	DOE
Has follow-on funding been obtained?	No
Amount of follow-on funding ($K)?	N/A
Number of Post Docs supported by LDRD project?	0
Number of students supported by LDRD project?	2
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights anticipated or filed (beyond publications)?	0
Number of invention disclosures anticipated or filed?	0
Number of patent applications anticipated or filed?	0

11.0 Screening of Alloy Catalysts for Electrochemical CO^2 Reduction

Principal Investigator: Jens Norskov, Anders Nilsson, Tom Jaramillo

Project Description

Photo-electrochemical reduction of CO_2 to fuels (artificial photosynthesis) is one of the grand challenges to science and engineering. It has all the important ingredients: a very hard problem with the possibility of leading to game-changing technology, if successful. The main problem is the complete lack of suitable catalysts – few materials work at all and all are extremely inefficient (high overpotentials). At SUNCAT we have worked to analyze theoretically the best known catalyst, Cu, to understand how it works. On this basis we have developed a model of the process, which allows us to understand trends in catalytic activity from one metal to the next. The model points to the fundamental reason why no single-component metallic catalysts have been found. The model also suggests possible strategies for changing the surface properties to achieve lower overpotentials. One possibility is to have two components in the active site at the surface, and recently we have started computationally to screen for new alloy catalysts. It is essential to couple this to synthesis, characterization, and test of new ideas. This should provide feedback to the theory and ultimately provide experimental proof of the existence of new catalysts.

Accomplishments

Design of a Vacuum Physical Vapor Deposition System

In order to provide feedback to theory with a tight development cycle, we have designed a PVD system with several requirements in mind. (1) The method should be able to co-deposit elements with *in situ* monitoring of the deposition rate. (2) The deposition method must be compatible and work immediately with a wide range of elements. (3) Precursor sources should require little monetary investment. (4) The entire deposition process must have a throughput which allows for daily electrochemical testing. Using these criteria, we chose a vacuum evaporation system rather than a sputtering system, because *in situ* deposition rate monitoring can be achieved immediately for a wide range of elements in a vacuum evaporation system by using a quartz crystal microbalance (QCM). While atomic absorption spectroscopy can be used to monitor the deposition rate during sputtering, a separate calibration curve is required for each element. Therefore, a vacuum evaporation system better throughput synthetic method.

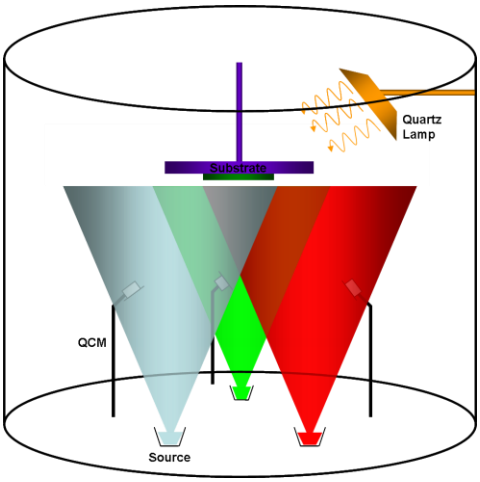


Figure 1 Schematic of three source PVD system

Together with Technical Engineering Services, we have designed a dual e-beam thermal evaporator system which allows for the uniform deposition of up to three elemental sources simultaneously onto a 4" wafer. The deposition rate of all three sources can be monitored and adjusted through a feedback loop between each QCM and the deposition controller (Figure 1). The vacuum deposition chamber is equipped with a quartz lamp to allow for *in situ* heating of the sample for improved crystallinity. The PVD system has been fully designed and is currently being assembled with a projected finish date in the Winter of 2013.

Alloy Synthesis and Characterization

In anticipation of the arrival of the new PVD system, we have developed protocols for the synthesis of binary alloy thin films at other facilities with the capability of co-deposition. The nanofabrication facility at UCSB has a dual e-beam evaporator which can co-deposit up to two elements. Each e-beam has a QCM which can monitor the deposition rate from the source, allowing for experimental control over the composition of the thin film. Out of the possible alloys which could be deposited on this instrument, our calculations show that $Au_{1-y}Pd_y$ and Au_xAg_{1-x} could have favorable limiting potentials for CO_2 reduction. Therefore, we have conducted a detailed study of these alloys by depositing a broad range of compositions.

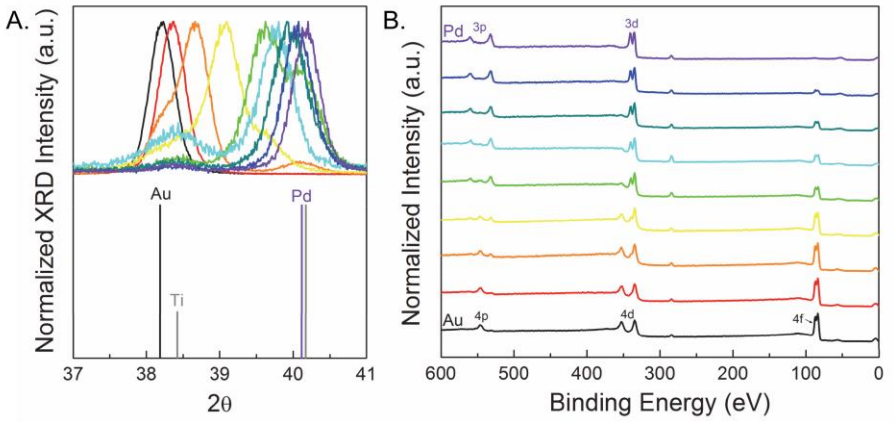


Figure 2. *(A) X-ray diffraction and (B) X-ray photoelectron spectroscopy spectra demonstrate tuning of the composition of $Au_{1-y}Pd_y$ alloys. The Pd composition increases from left to right for XRD spectra (A) and bottom to top for XPS spectra (B).*

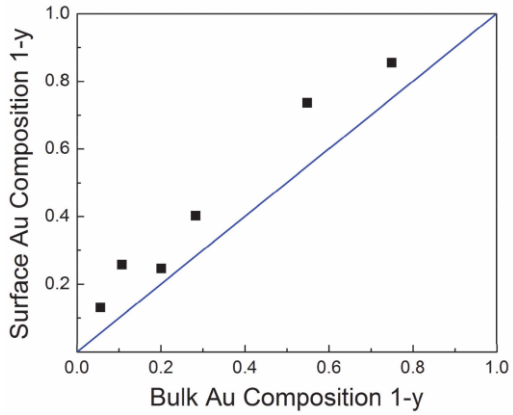


Figure 3. *A comparison of bulk and surface Au compositions of $Au_{1-y}Pd_y$ alloys shows that the surface is slightly Au-rich. The blue line represents a surface to bulk composition ratio of 1.*

Bulk and surface compositions of $Au_{1-y}Pd_y$ thin films were characterized using x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS), respectively. Both Au and Pd adopt the face-centered cubic (FCC) crystal structure but have a large lattice mismatch of 4.6%. XRD patterns in Figure 2a clearly show a shift of the $Au_{1-y}Pd_y$ FCC (111) peak towards larger diffraction angles from an increase in Pd composition. This shift in the lattice constant demonstrates that Au and Pd co-deposit as an alloy rather than pure Au and Pd, indicating that our PVD approach will work for even lattice mismatched material systems. While XRD spectra demonstrate alloying within the bulk of $Au_{1-y}Pd_y$ thin films, experimental control of the surface composition is also critical because electrochemical CO_2 reduction occurs on the surface of the alloy catalysts. XPS spectra show a similar trend in composition on the surface (Figure 2b) when compared to the bulk, indicating that the surface composition of $Au_{1-y}Pd_y$ thin films can also be tuned by PVD. A comparison of the Vegard's law bulk Pd composition and the XPS surface Pd composition shows that the $Au_{1-y}Pd_y$ thin films are slightly Au-rich on the surface (Figure 3).

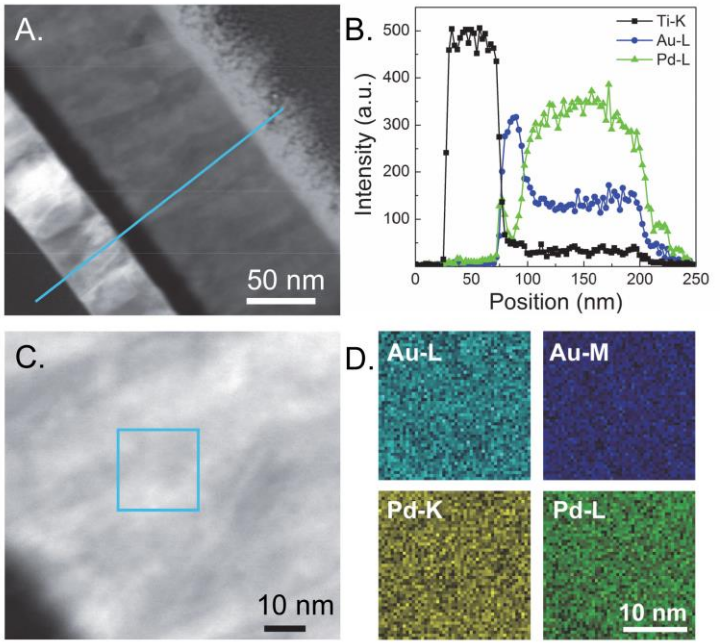


Figure 4. *(A) A dark field scanning transmission electron microscope image shows the cross section of a representative AuPd thin film. (B) An energy dispersive x-ray spectroscopy line scan shows that the composition of the AuPd layer is relatively uniform along the cross section. (C, D) Further analysis by mapping Au and Pd signals demonstrates that the composition of the alloy is uniform on a nanometer scale.*

Scanning transmission electron microscopy (STEM) was used to examine the composition of a representative AuPd thin film on the nanometer scale. A cross section of AuPd was cut with a Ga focused ion beam and subsequently transferred and bonded to a TEM grid using a micromanipulator. A dark field STEM image of the cross section can be seen in Figure 4A. The blue line represents the region where an energy dispersive x-ray spectroscopy (EDS) line scan measured the composition. The corresponding x-ray fluorescence intensities for the Ti binding layer, Au, and Pd (Figure 4B) show a sharp interface between the Ti binding layer and the AuPd

thin film. The peaks in Au and Pd intensities, at the interface with Ti, represent the region where the evaporation sources were individually calibrated to prevent cross talk with the QCMs. Further analysis using EDS mapping (Figures 4C,D) demonstrates that Au and Pd are distributed uniformly within the alloy. These results indicate that e-beam co-deposited thin films can be uniform in composition on the nanometer scale, and therefore provide an excellent platform for fundamental electrochemical studies.

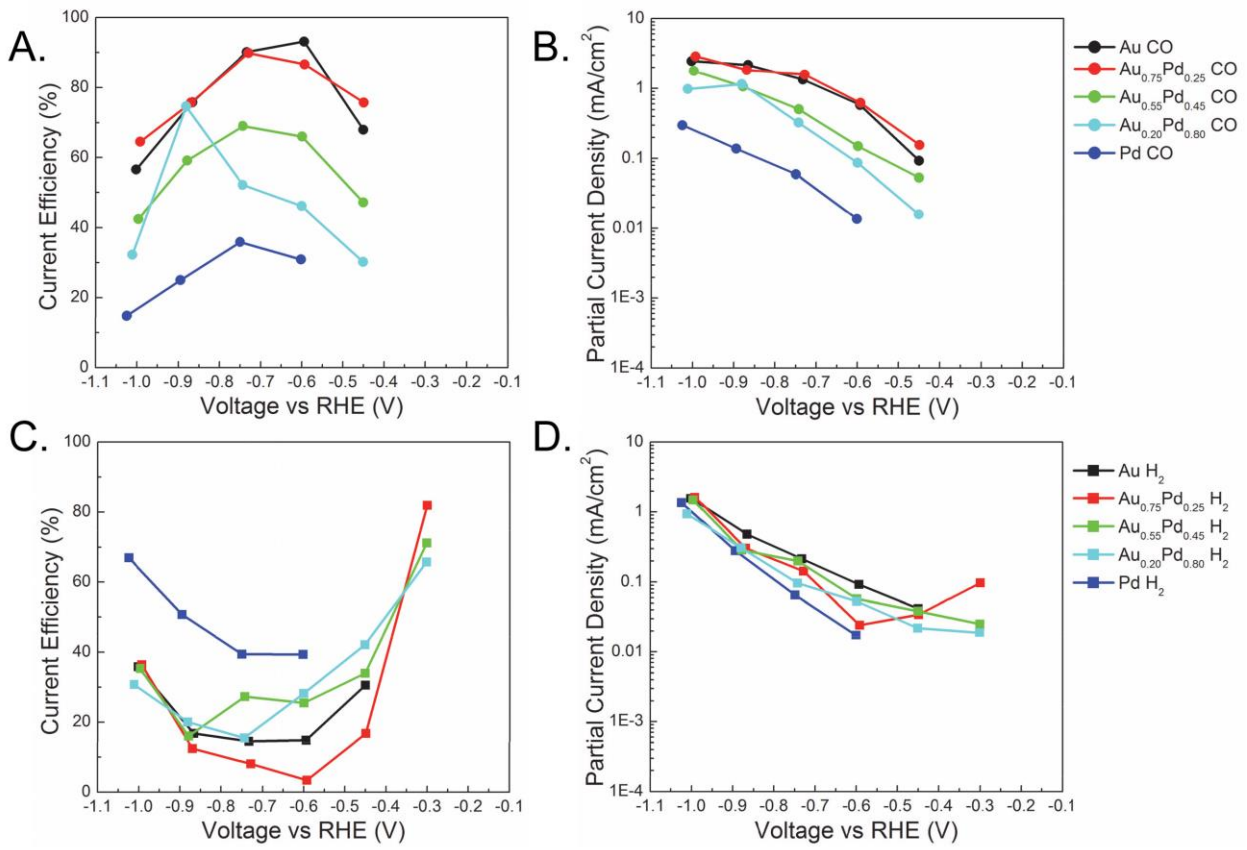


Figure 5. *(A) Current efficiences and (B) partial current densities are plotted as a function of voltage. Samples with higher Au composition are more active for CO_2 reduction to CO. (C, D) No trends were observed from similar plots for H_2.*

The CO_2 reduction activity of $Au_{1-y}Pd_y$ thin films was examined using a custom electrolysis cell. Working ($Au_{1-y}Pd_y$) and counter (Pt) electrode compartments were filled with a 0.1 M $KHCO_3$ electrolyte and bubbled continuously with CO_2. An anion exchange membrane was placed between the working and counter electrode compartments to prevent product diffusion to the counter electrode. Working electrodes were held at a fixed potential for one hour while the total current was measured. Both CO and H_2 were detected and quantified from the working electrode using a gas chromatograph (GC). Multiple $Au_{1-y}Pd_y$ compositions, including pure Au and Pd, were measured to determine the dependence of activity on the composition of the electrode. The current efficiencies and partial current densities for CO_2 reduction to CO can be compared in Figures 5A and 5B, respectively. While the $Au_{75}Pd_{25}$ alloy has a similar activity with pure Au for

CO production, an increase in Pd composition causes the activity to decrease trending towards pure Pd. No such trends are observed with the current efficiencies and partial current densities for the competing H^+ reduction reaction (Figures 5C,D). However, Pd is well known to intercalate hydrogen which could be convoluting the H_2 data.

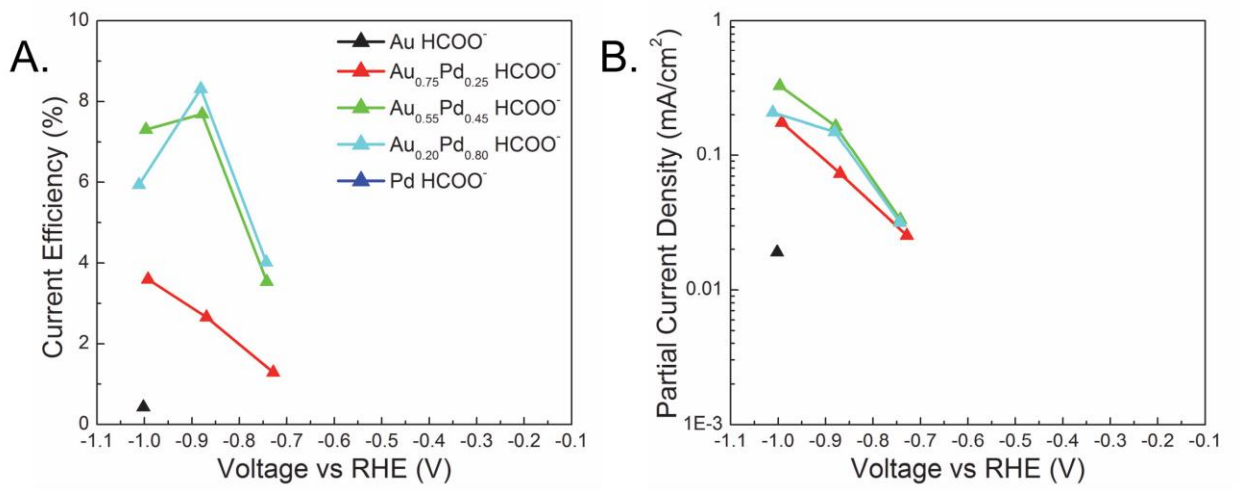


Figure 6. *(A) Current efficiences and (B) partial current densities are plotted as a function of voltage for CO_2 reduction to formate. No formate was detected for pure Pd, and all alloy samples show an increase in current efficiency and partial current density compared to pure Au.*

After the electrochemical measurement, liquid phase products were also analyzed using an aliquot of solution from the working electrode compartment. Significant amounts of formate were detected in the aliquots from solvent suppression nuclear magnetic resonance (NMR) spectroscopy (Figure 6A,B). While no formate was detected for pure Pd, all alloy compositions have a significantly higher formate current efficiency and partial current density than pure Au. One possible reason for the enhancement in formate production could be an increase in metal-hydride species from hydrogen intercalation into the Pd lattice. This increase in local hydrogen coverage could facilitate hydride transfer to an adsorbed COO^- molecule on an adjacent Au site. These measurements clearly demonstrate that alloying can have an effect on the selectivity of catalysts for electrochemical CO_2 reduction. We have established a robust PVD method to test binary alloys for CO_2 reduction and are excited to continue our studies on new material systems.

Publications

None

Workshops

None

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	GCEP
Has follow-on funding been obtained?	Yes
Amount of follow-on funding ($K)?	1700
Number of Post Docs supported by LDRD project?	2
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0

12.0 Correlated Electron Physics at Oxide Interfaces

Principal Investigator: Srinivas Raghu

Project Description

A pioneering set of experiments involving the interface between LaAlO3 and SrTiO3 (both of which are insulators), have revealed that high mobility metallic behavior, even superconductivity, occurs as the voltage across the interface is increased. These observations are certainly of fundamental importance as they point towards a new arena of designing novel phases of matter at interfaces between distinct, highly correlated electron materials. They also have tremendous scope for energy and materials applications in the next generation of devices such as field effect transistors that are based on correlated oxides instead of semiconductors. Transport measurements in these systems suggest that superconductivity occurs when there are sizeable spin-orbit interactions. Even ferromagnetism has been observed at the interface and is thought to coexist with superconductivity. Since ferromagnetism is typically a phenomenon associated with strong electron-electron interactions, it is clear that the oxide interface experiments pose a rich set of problems involving the interplay between electron correlations, spin-orbit coupling and the reduced dimensionality associated with the interface.

This project aims to establish a new direction within SLAC, wherein fundamental theoretical calculations involving a variety of analytical and computational methods will be performed to understand the basic phase diagram of these systems and to predict phenomena at interfaces between other transition metal oxides.

Accomplishments

I have developed a theory of magnetism at the interface between LaAlO3 and SrTiO3. In collaboration with physicists at Cornell (Eun-Ah Kim and Mark Fischer) we have developed a theory of magnetism from the perspective of a two dimensional electron gas with Rashba spin-orbit coupling at light densities. Our results was presented at the American Physical Society March Meeting in Boston, MA. Our paper has been published in the Physical Review.

I have written a paper with Ted Geballe on the role of screening in the transition temperature of an unconventional superconductor. We suggest that the disparity in Tc among the cuprate superconductors can be attributed to charge reservoir layers (CRLs) that are capacitively coupled to electrons in metallic layers of the cuprate materials that participate in superconductivity. By screening longer range coulomb interactions, the CRLs play a significant role in determining the optimal transition temperature of these systems. The CRLs, coupled capacitively with electrons in the copper-oxide plane form natural "oxide interfaces" that we have studied in various theoretical limits. Our studies suggest new strategies for engineering a high temperature superconductor using methods that scientists studying oxide interfaces have been developing in recent years. Our paper is published in Physical Review B and has so far been well-cited.

Recently, I have completed a paper in collaboration with Harold Hwang's group on interfacial superconductivity in a novel bilayer system. The paper has been accepted as a rapid communication in PRB.

I am in the final stages of writing a review paper titled "Frontiers of Interfacial Superconductivity" with Chris Bell and Harold Hwang.

Publications

H. Inoue, M. Kim, C. Bell, Y. Hikita, S. Raghu, and H.Y. Hwang, "*Tunable Coupling of Two-Dimensional Superconductors in Bilayer SrTiO3 Heterostructures",* arXiv:1308:2215 (2013).

S. Raghu, R. Thomale and T. H. Geballe, "*Optimal Tc of cuprates: The role of screening and reservoir layers"*. Phys. Rev. B {\bf 86}, 094506 (2012).

M. Fischer, S. Raghu, and E.-A. Kim, "*Spin-Orbit Coupling in LaAlO$_3$/SrTiO$_3$ interfaces: Magnetism and Orbital Ordering"*, arXiv:1206.1060 (2012).

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE(SIMES)
Has follow-on funding been obtained?	Yes
Amount of follow-on funding ($K)?	150
Number of Post Docs supported by LDRD project?	0
Number of students supported by LDRD project?	2
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0

13.0 Towards the SLAC Femtosecond Macromolecular Micro and Nanocrystallography Facilities

Principal Investigator: Mike Soltis

Project Description

Development of an innovative approach to the very accurate, high resolution structure determination of complex, radiation sensitive biomolecular complexes and reaction intermediates in their catalytic cycles using femtosecond LCLS x-rays and micro-to-nano crystals. Application to energy relevant problems, i.e. hydrogenase (which catalyzes the bio-production of hydrogen) and polyketide synthase (a bio-assembly line for green chemistry), drives the development of an integrated platform for streamlining and optimizing an experimental approach for the general user community, focused on sample preparation, handling and characterization, sample delivery and data analysis.

Accomplishments (2nd Year)

Activities in year 2 focused on new sample delivery methods, characterization developments, and proof-of-principle approaches to data measurement using a goniometer setup at the LCLS XPP station.

Radiation Damage-Free Structures of Myoglobin and Hydrogenase. High quality crystals of myoglobin and hydrogenase were produced in the laboratories of Soltis (SSRL) and Peters (Montana State), respectively. These samples were characterized at SSRL showing excellent X-ray diffraction to ~1.4 Å and ~1.2 Å, respectively. An SSRL-derived and developed goniometer system was installed at the LCLS XPP station, and was successfully used to measure crystallographic data at nearly a 100% hit rate using a new approach to sample delivery – grids – developed at SSRL, that contain multiple samples in fixed locations. A methodology was also developed for measuring multiple damage-free data images from very large hydrogenase crystals (1-3 mm), and this approach was successfully tested at the LCLS XPP station in June 2013. Much fewer samples were required to reach complete data sets (5-6 crystals) as compared to previous approaches using liquid jet sample delivery. Initial high-quality electron density maps for myoglobin and hydrogenase have been produced. These measurements provided break-through evidence of the capability to produce radiation-damage free data and the minimization of sample amount requirements using an XFEL beam.

Sample Characterization. Electron Microscopy (EM) was used to characterize samples that were microns to sub-microns in size. These measurements were carried out in collaboration with the Calero group at the University of Pittsburgh. This technique can be used to estimate the average particle size and particle concentration and in many cases provide evidence of crystallization. The results for several protein systems were correlated with other characterization techniques, such as dynamic light scattering. EM was also used to characterize crystals after they had exited a high-pressure liquid jet nozzle. In some cases, the crystals did not

exit the jet, indicating that they either decomposed or clogged somewhere in the jet. This study is fundamental to understanding the properties of various approaches of sample delivery to the LCLS beam for macromolecular crystallography.

Acoustic-Based Sample Delivery. Using an acoustic jet designed by Brookhaven National Laboratory macromolecular crystallography scientists in collaboration with Labcyte Inc., droplets of mother liquor containing crystals were successfully ejected directly into the LCLS XPP station beam. Operating at 1-10 Hz, the system produced a hit rate (the LCLS pulse hitting the sample) of ~50% using 40-50 micron-sized crystals in 100 μm droplets. Several data sets were recorded on several protein and enzyme systems. The data are currently being processed. This part of the LDRD development project provides an intermediary approach for sample delivery between jets and fixed target samples while minimizing sample requirements.

Microfluidic droplets for sample delivery. Compared to a continuous jet, the microfuidic droplet approach has advantages of very low sample consumption, high hit rate, insensitivity to the properties of the crystal liquor, and the straightforward extension to advanced drop manipulations (sorting, mixing, optical pumping) already demonstrated with on-chip microfluidic devices. A prototype was designed in the Photon Science Directorate at SLAC with a coaxial flow system made from an outer 360 μm capillary and an inner 150 μm capillary. The outer capillary supplies a volatile oil while the inner capillary supplies the sample of interest. The droplets are pulled periodically from the inner capillary using high-voltage pulses applied to an electrode. To reduce velocity dispersion as the drops travel in a tube much larger than their diameter, the droplets enter a – 50 μm ID capillary for transport through the dispensing jet. Initial tests will be carried out on CXI in FY14. This part of the LDRD development project provides for sample delivery methods that minimize sample requirements while maximizing efficiency.

High-speed Imaging as Online Sample Delivery Monitor. A new high-speed camera using 10x and 20x long-working distance objectives was developed in the Photon Science Directorate at SLAC. The optical setup is in principle capable of imaging at 1 million frames per second; the camera can operate at ~100 Kfps yielding useful image sizes. In addition, the new optical setup has superior resolution (1 μm/pixel at 10x, 500 nm/pixel at 20x) to the system currently installed on the CXI station at LCLS. The camera will be tested on CXI in upcoming experiments and then become a permanent part of the CXI endstation. This development enhances the ability to monitor the samples during the experiments.

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	NIH
Has follow-on funding been obtained?	No
Amount of follow-on funding ($K)?	NA
Number of Post Docs supported by LDRD project?	1
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	1
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0

14.0 Modeling Conformational Ensembles of Proteins and Complexes

Principal Investigator: Henry van den Bedem

Project Description

Macromolecules often exhibit significant conformational flexibility, especially when they interact with ligands or protein partners to form assemblies. Probing these conformational changes is essential to understanding their cellular function, yet these scientifically important molecules are often difficult to crystallize and diffract poorly. We started a computational research program to model challenging systems with experimental data from multiple sources, including protein crystallography, small angle X-ray scattering and nano-crystallography. Our approach is to extend an innovative, robotics-inspired Kino-Geometric Sampler conformational search algorithm (KGS) to fit previously determined domains or proteins to experimental data. KGS exhibits a singularly large radius of convergence and optimally reduces the number of free parameters. These unique features enable flexible 'docking' of atomic models in low-resolution data while moderating the risk of overfitting. We aim to automatically compute 3-D models, and to provide structural insights for systems that diffract poorly or cannot be crystallized. Our method will also provide insight into functionally relevant dynamics, especially for time-resolved experiments or a series of static structures

Accomplishments

A Research Assistant was hired starting Jan 1 2012 to implement a gradient descent protocol in KGS to guide conformational variability along experimental data. A post-doctoral scholar, Dr. Dimitar Pachov joined the project on Feb 1 2012. The gradient of the data is projected onto the null-space of the first-order approximation to the kinematic model, i.e. $\mathrm{d}q = NN^T\nabla\rho$, where q is the current conformation, N is a basis for the null space, and ρ is experimental data. A gradient descent is then successively applied to rigid bodies. Tests on simulated data corresponding to the closed conformation of LAO protein (PDB ID 2LAO) revealed that KGS converged to a good data fit starting from the open conformation within no more than 20-30 gradient descent cycles, spanning a radius of convergence exceeding 4.5Å . This exciting result affirms that null-space optimization maintains the performance of KGS even with a vast number of kinematic cycles, a key year 1 research objective. It reinforces the potential of KGS for efficient modeling of structural assemblies into low resolution data.

A collaboration with Dr. Julie Bernauer at INRIA/AMIB in Paris, France was initiated to extend our modeling approach to RNA and protein/RNA complexes. Supported by INRIA, Rasmus Fonseca joined the project in FY13 as a post-doctoral scholar. Dr. Fonseca visited SLAC Jan 15 – May 23, 2013 to develop methods and algorithms for KGS.

In FY13 we set the goal to extend KGS to model conformational flexibility of complexes. A challenge is to maintain inter-molecular hydrogen bonds while sampling conformational variability. We derived a mathematical model to extend the kinematic model to multiple

molecules by adding global degrees of freedom. The global degrees of freedom account for rigid body motions of the molecules, and help maintain inter-molecular hydrogen bonds. Tests on small systems show promising results, but bond lengths still show too much variation despite carefully calibrated numerical step sizes.

In FY13 we started preparing two manuscripts. The first manuscript presents the computational extension to complexes and density fitting. It describes the application of these new capabilities to the GPCR β2AR:Gs complex. The second manuscript presents extension of the kinematic model to RNA molecules. We furthermore show that the calculated chemical shifts of the sampled conformational states of RNA agree with experimental chemical shifts. Thus, the sampled states approximate the ensemble in solution.

Publications

van den Bedem, H., Bhabha, G., Yang, K., Wright, P. E. & Fraser, J. S. "*Automated identification of functional dynamic contact networks from X-ray crystallography".* Nat Meth **10**, 896-902 (2013).

Workshops

H. van den Bedem, *"Identifying functional dynamic networks from X-ray data".* Integrative Approaches for Modeling Biomolecular Complexes. Nice, France. May 2013.

H. van den Bedem, *Identifying functional dynamic networks from protein X-ray data.* International Conference for Biomolecular Dynamics: Experiment Meets Computation. King Abdullah University of Science and Technology, KSA. Feb 2013.

H. van den Bedem, *"Back to the Future: Multi-Conformer Contact Networks in Room Temperature PX Data Elucidate NMR Conformational Dynamics".* 70th Annual Pittsburgh Diffraction Conference. Stanford, CA. Oct 2012

H. van den Bedem, "*Multi-Conformer Contact Network Analysis Provides The Structural And Functional Basis For NMR Relaxation Experiments"*, Computational Methods in Structural Biology, Workshop, Hong Kong University of Science and Technology, Aug 1-3, 2012. Invited.

H. van den Bedem, "*Multi-Conformer Contact Network Analysis Provides The Structural And Functional Basis For NMR Relaxation Experiments"*, 3DSig 2012 Structural Bioinformatics and Computational Biophysics, Long Beach, CA, Jul 13-14, 2012.

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	NIH
Has follow-on funding been obtained?	No
Amount of follow-on funding ($K)?	N/A
Number of Post Docs supported by LDRD project?	1
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0

15.0 An Automated Pipeline for Cosmological Mock Sky Survey Production

Principal Investigators: Risa Wechsler, Tom Abel

Project Description

Galaxy surveys are rapidly becoming a leading probe of fundamental physics on the cosmic frontier, including dark energy, dark matter, inflation, and neutrino masses. However, cosmological inferences require precise predictions of structure formation and a detailed understanding of the relationship between galaxies and the matter distribution, for which cosmological simulations play an essential role. The work focuses on critical bottlenecks to efficient and accurate production of and access to simulated sky surveys: (1) production of multi-scale initial conditions to improve the efficiency and scaling of cosmological codes; (2) integration of post-processing codes into various modular frameworks for more rapid analysis and development, (3) developing new techniques for simulating collisionless fluids by discretizing the dark matter sheet in phase space and (4) development of database solutions for efficient access of large simulated data sets.

Accomplishments

We have developed a pipeline for resimulating galaxy clusters at high resolution, selected from large cosmological boxes, including producing halo catalogs, merger and galaxy catalogs, using new algorithms designed for this project. This has been used to produce a suite of 100 cluster mass halos, and three papers have been published on the first scientific results from these simulations. We have made substantial improvements to a computational pipeline to go from cosmological parameters through simulations all the way to a full sky survey. This pipeline is being used and further developed to create sky surveys for the Dark Energy Survey, the Dark Energy Spectroscopic Instrument, and the Large Synoptic Survey Telescope. The first few full area full depth simulation from this pipeline has now been produced, which includes a realistic galaxy population as well as the impact of weak lensing. These simulations are being actively used by the full DES collaboration. In addition, in collaboration with LSST scientists we have integrated these simulations with the LSST imaging pipeline, and are providing the simulations to the LSST Dark Energy Science collaboration. A new database server was set up to host and serve data from simulated sky surveys, and is under development.

Abel, Hahn and Kaehler developed new visualization and analysis techniques relevant for cosmological dark matter simulations. The approach allows for new numerical methods to be developed that solve the dynamics of collisionless fluids discretizing by volume. This has led to important several papers, including one outlining new simulation techniques for dark matter, and one investigating implications for gravitational lensing. In addition, these techniques have allowed a new approach to simulating warm dark matter that solves a thirty-year-old problem in the field. Kaehler and Abel also began to investigate hybrid data formats that can outperform HDF5 formats, which are the current gold standard in our area.

Publications

O. Hahn & T. Abel, "*Multi-Scale Initial conditions for cosmological simulations*", 2011, MNRAS, 415, 2101

P. Behroozi, R., Wechsler, H. Wu., "*The Rockstar Phase-Space Halo Finder*". 2013, ApJ, 762, 31

P. Behroozi, R,. Wechsler, "*Gravitationally Consistent Halo Catalogs and Merger Trees for Precision Cosmology*". 2013, ApJ, 763, 18

T. Abel, O. Hahn. R. Kaehler. "*Tracing the Dark Matter Sheet in Phase Space*". arXiv:1111.3944.

R. Kaehler, O. Hahn, T. Abel. "*A novel Approach to Visualizing Dark Matter Simulations*". arXiv:1208.3206.

O. Hahn, T. Abel, R. Kaehler. "*A New Approach to Simulating Collisionless Dark Matter Fluids*". 2013 MNRAS, 434, 1171

H. Wu. O. Hahn, R. Kaehler, Y. Mao, P. Behroozi. "*Rhapsody: I. Structural Properties and Formation History from a Statistical Sample of Re-simulated Cluster-size Halos*". 2013, ApJ, 763, 70

H. Wu, O. Hahn, R. Wechsler, P. Behroozi, Y. Mao. Rhapsody: II. "*Subhalo Properties and the Impact of Today Stripping from a Statistical Sample of Cluster-Size Halos*". 2013. apJ, 763, 70

R. Angulo, O. Hahn, T. Abel, "*The warm dark matter halo mass function below the cutoff scale*", 2013, MNRAS, 434, 337

R. Angulo, O. Hahn, T. Abel, "*How closely do baryons follow dark matter on large scales*", 2013, MNRAS, 434, 3337

H. Wu, O. Hahn, A. Evrard, R. Wechsler, K. Dolag, 2013, MNRAS, 436, 460, "*Viral scaling of galaxies in clusters:bright to faint is cool to hot*", 2013, MNRAS, 436, 460

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	SciDAC, DES
Has follow-on funding been obtained?	Yes
Amount of follow-on funding ($K)?	535
Number of Post Docs supported by LDRD project?	4
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	1
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0

16.0 An End-to-end Simulation Toolset for X-ray Photon Science Experiment and Facility Planning

Principal Investigator: Garth Williams

Project Description

Over the course of the last decade, the international community of x-ray light source users has been presented with facilities that provide ever brighter sources of x-rays. These very-high-brightness sources already provide unprecedented capabilities for performing scientific experiments, but to maximize the potential of these a detailed understanding of the experiment, from the source to the detector is required.

We seek to collect those existing tools that meet some of these needs and, combined with new ones where appropriate, unite them within a free, open and easy-to-use framework. These tools should include, at a minimum, the properties of the x-ray beam as it emerges from the source, whether it be a magnet or an insertion device; the affect of x-ray optics, including windows as well as steering and focusing optics, on this beam; the modeling of the interaction of the x-ray beam with a sample; and the expected response of a detector to the signal arising from this last interaction.

Accomplishments

The adoption of our framework is as much dependent on the community's view of the effort as it is on the technical correctness of the effort. We have engaged scientists—both from the user community by way of the SSRL/LCLS Users' Meeting and from facility scientists at various workshops and conferences—to collect input and introduce our operating principles.

Within the technical arena, we have defined a conceptual framework wherein a data object, containing the electric field corresponding to the x-ray beam, can interact with modules, each of which represents a physical interaction, thereby reproducing an x-ray experiment in a sequential series of events. The definition of the data object within the framework, the way that the data object interacts with modules, and the specification of the method of interaction between the user and the framework have been completed. The data arising from each simulation is written to a standard HDF5 file in such a way that every aspect of the simulation can be recreated in our framework or accessed from another, independent tool.

We have authored an initial version of this framework, complete with interaction to the popular Synchrotron Radiation Workshop toolkit, in the Python programming language and are in active collaboration with the simulation project at the European XFEL. This collaboration seeks to establish the most efficient method of the propagation of partially coherent radiation, an important detail in understanding cutting edge experiments in imaging and the extraction of statistical properties of matter.

Publications

G. J. Williams, A. Boehnlein, N. Graf, T. Koi, and S. Xiao, "*A proposal for a user-friendly modular framework for the simulation of x-ray experiments*", Journal of Physics: Conference Series. (under review).

Workshops

G. J. Williams, *nd-to-end simulation*, 5th Annual X-ray FEL Collaboration Meeting, SLAC National Accelerator Laboratory, Menlo Park, CA, February 4-6, 2013.

G. J. Williams, *A proposal for a user-friendly modular framework for the simulation of x-ray experiments*, 17th Pan-American Synchrotron Radiation Instrumentation Conference, NIST, Gaithersburg, MD, June 19-21, 2013.

Organized a one-half-day satellite workshop to the SSRL/LCLS Users' Meeting, October 1-4, 2013, which was attended by approximately 20 delegates.

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE BES, SciDAC
Has follow-on funding been obtained?	No
Amount of follow-on funding ($K)?	N/A
Number of Post Docs supported by LDRD project?	0
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0

17.0 Methodology Developments for Structural Studies of Post-translational Modifications of Proteins

Principal Investigator: Soichi Wakatsuki

Project Description

Post-translational modification of proteins, such as ubiquitination, glycosylation, phosphorylation and acetylation, play critical roles in many cellular events and functions, such as cell cycle control, quality control, and stem cell development. In this LDRD project, we aim to continue to develop new methodologies to discover novel functions of polyubiquitin chains and other post-translational modifications of proteins. We will further establish a research environment for protein production, purification, crystallization and biochemical and biophysical characterization. Using this infrastructure, we will enzymatically produce polyubiquitin chains of different linkages and lengths. The produced polyubiquitin chains will be used to screen protein complexes in various organisms to find new polyubiquitin signaling pathways. Novel protein complexes will be subjected to functional and structural studies using synchrotron protein crystallography and solution scattering and radiation-damage free XFEL nano-crystallography.

Accomplishments

Establishing infrastructure and collaborations:

During FY13, substantial infrastructure was established for protein expression and purification, and characterization of protein complexes involved in posttranslational modifications, in particular protein ubiquitination and ubiquitin chain recognition. An extensive survey of state-of-the-art protein crystallization robots was completed and final selection for procurement was identified. A new collaboration was formed with a group at the University of Lausanne, Switzerland, to produce protein substrates specifically and uniquely ubiquitinated for polyubiquitin chain recognition studies.

Development of a new phasing method using XFEL:

Utilization of two-color XFEL pulses for *de novo* structure determination was defined and developed, and two beamtime proposals were submitted to LCLS. Initial trials producing such XFEL beams were pursued at LCLS in collaboration with SLAC Accelerator Directorate and LCLS, SSRL, and Stanford teams. These trials successfully produced self-seeded two-color pulses with an energy separation of 45 eV at the Fe K-edge. This corresponds to 0.5 % $\Delta E/E$, about half the required energy separation, but well beyond a normal SASE band width. These beams were used to collect several hundred diffraction images from crystals of a model protein, which resulted in an interpretable electron density map. Further data analysis on the phasing power of the collected data set is in progress. Methods for achieving further energy separation

were identified. Requirements and paths forward for developing optimum two-color data collection/analysis strategies were also established.

Publications

None

Workshops

S. Wakatsuki, *XFELs in Structural Biology*, A Celebration of Open Access in Structural Biology:◎Recognizing the career and achievements of Helen M. Berman, Rutgers, The State University of New Jersey, September 26, 2013,

S. Wakatsuki, Chair of "*X-ray in the Life Sciences" session*, Gordon Research Conference, X-ray Science, Stonehill College, Boston, GRC X-ray Science, August 6, 2013

S. Wakatsuki, *Structural basis of ubiquitin chain recognition*, 35th Naito Conference, Sapporo, Japan, July 11, 2013

Questionnaire

Question	Answer
Will follow-on funding (post-LDRD project) be applied for?	Yes
Source of support for follow-on funding?	DOE BER, NIH
Has follow-on funding been obtained?	No
Amount of follow-on funding ($K)?	N/A
Number of Post Docs supported by LDRD project?	0
Number of students supported by LDRD project?	0
Number of scientific staff/technical staff hired with LDRD funding?	0
Number of copyrights filed (beyond publications)?	0
Number of invention disclosures filed?	0
Number of patent applications filed?	0