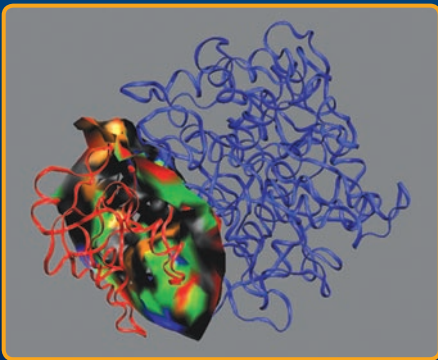




NREL National Renewable Energy Laboratory

A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

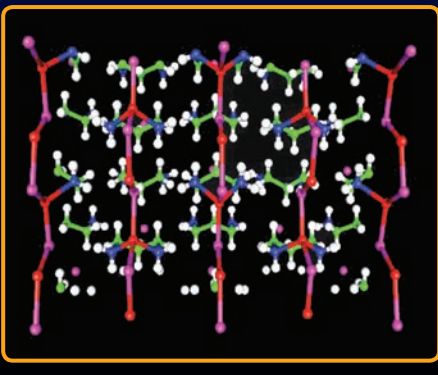
Innovation for Our Energy Future



Director's Discretionary Research and Development Program



Annual Report Fiscal Year 2006



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Director's Discretionary Research and Development Program

Annual Report Fiscal Year 2006

National Renewable Energy Laboratory

**1617 Cole Boulevard
Golden, Colorado 80401-3393**

**NREL is a U.S. Department of Energy Laboratory
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INTRODUCTION

NREL Mission

The National Renewable Energy Laboratory's (NREL) mission is to: develop renewable energy and energy efficiency technologies and practices, advance related science and engineering, and transfer knowledge and innovations to address the nation's energy and environmental goals.

Program Overview

NREL has supported scientifically innovative and analytically creative concepts through the Director's Discretionary Research and Development (DDRD) Program from 2000 to 2006. At the end of FY 2006, the DDRD Program made a transition to the Laboratory Directed Research and Development (LDRD) Program as directed by the 2006 Energy and Water Appropriations Act. This ACT enables the Secretary of Energy to authorize, at DOE-owned, contractor operated laboratories, an amount not to exceed 8% to conduct LDRD programs. The Act made NREL eligible to participate in the LDRD program. So, with the concurrence of DOE, NREL closed out its DDRD program at the end of fiscal year 2006; thus, this represents the final report on the DDRD program.

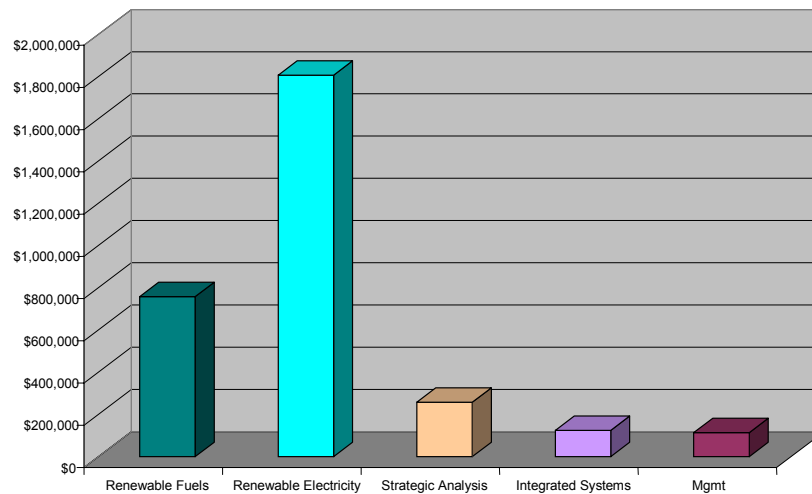


Figure 1. DDRD 2006 Technical Breakdown.

The NREL DDRD program comprises projects that strengthen NREL's four technical competencies: Integrated Systems, Renewable Electricity, Renewable Fuels, and Strategic Analysis. The majority of the 2006 funds were used for innovative projects in renewable electricity, as shown in Figure 1. Program management costs are also included.

R&D Expertise

NREL's focused R&D capabilities are positioned to advance national energy goals by developing innovations to change the way we power our homes, businesses, and cars.

NREL's R&D areas of expertise are:

Renewable electricity — solar, wind, biomass, geothermal

Renewable fuels — biomass, hydrogen

Integrated energy system engineering and testing — buildings, electric systems, and transportation infrastructures

Strategic development and analysis — economic, financial, and market analysis, planning and portfolio prioritization

DDRD Management Process

The DDRD program is managed by the Laboratory Development Office (LDO), within the Strategic Development and Analysis (SD&A) directorate. The LDO functions center on the strategic planning and development for the Laboratory. The program administrator for the DDRD process ensures Laboratory adherence to the guidance laid out in DOE Order 413.2B, and provides regular feedback to executive management on the status of the program including individual project reports when necessary. The table (above) shows that DDRD program management consumed only 2% of the overall DDRD budget, including time charged by peer reviewers for feedback on proposals reviewed during the Call for Proposals and the cost of producing the annual report.

2006 DDRD Portfolio

Portfolio Funding

In FY2006, NREL had an approved DDRD program budget of \$3,216,004. Projects spent \$2,948,725, and program management consumed \$114,561. The cost of proposal peer reviews was \$15,974. Adjustments were made for projects that ended in FY2005 but incurred costs in FY2006; the total for those adjustments is (\$15,934). The final amount spent was \$3,063,326 (Table 1).

The FY2006 Energy and Water Appropriations Act authorized the eligibility of all laboratories for LDRD funding beginning in FY2006. Conference Report, HR109-275 (which accompanies the ACT) required implementation of the accounting changes in FY2006 to apply overhead charges to these activities, consistent with cost accounting practices for direct funded program activities.

In response to the Act and Congress, the DOE CFO directed all laboratories to implement the required accounting changes. NREL responded to the requirement, adding the in-house overhead (G&A) burden to all DDRD project costs for the fiscal year. NREL's proposal for a transition from the DDRD program to an LDRD program beginning in FY2007 was approved.

Table 1. FY2006 DDRD Portfolio Funding

	<u>2006 Costs</u>
<i>Integrated Systems</i>	\$125,228
Study of Fundamental Protein/Protein Interactions Involved in Biological Energy Generation – Kim, K.	\$125,228
<i>Renewable Electricity Science and Technology</i>	\$1,807,431
Shape and Crystallography of III-V Semiconductor Nanoparticles – Ahrenkiel, P	\$57,502
Thin-Film Microelectronics for Rapid Gene Expression Analysis – Branz, H.	\$103,326
CdMgTe Thin-Films for Light Emitting Diodes – Dhere, R.; Ramanathan, K.	\$199,874
Hot-Wire Chemical Vapor Deposition of Metal Oxide Nanorods – Dillon, A.; Mahan, H.	\$137,857
Novel Electron Acceptors for Organic Photovoltaics – Ginley, D.	\$199,009
Nanostructured PbTe/PbSe Thermoelectric Materials – Hanna, M.	\$78,601
A Critical Examination of the Intermediate Band Concept for Ultra-High Efficiency Quantum Dot Solar Cells – Norman, A.	\$209,717
New Indium-Free Transparent Conductors, Group 3A & 4A Metal Oxide Based Materials – Perkins, J.; Ginley, D.	\$259,199
Photon Emission of Self-Assembled Semiconducting and Quantized Nanostructures by Scanning Tunneling Microscopy: Light from the Nanoworld – Romero, M.	\$264,457
Low Band-Gap Materials for Organic Third Generation Photovoltaics – Shaheen, S.	\$297,889
<i>Renewable Fuels Science and Technology</i>	\$757,795
Localized Carrier Dynamics in Organic Semiconductors Probed via Time-Resolved THz Photoconductivity – Ellingson, R.	\$209,850
Transition Metal Catalysis: Experiment and Theory – Nimlos, M.	\$193,014
Pentose Transport and Assay Development – Zhang, M.	\$164,884
Fundamental Properties and Application of Novel Crystalline Inorganic-Organic Hybrid Semiconductor – Zhang, Y.; Fluegel, B.	\$190,047
<i>Strategic Analysis</i>	\$258,271
Prototype Renewable Planning Model – Kroposki, B.	\$258,271
<i>DDRD Program Management</i>	\$114,561

Portfolio Highlights

In 2006, NREL attained achievements in several areas – many of which resulted in papers being presented to journals for publications and papers presented at conferences.

Advancements were made in understanding the fundamental nature of competitive protein-protein interactions involved in photobiological energy transduction process. Collaborating with computational scientists, Kwiseon Kim's team was able to improve its understanding of the mechanisms governing the protein-protein interactions involved at the metabolic branch point, and how protein engineering could tune the metabolic flux between two pathways. Her team is preparing a paper for the *Biophysical Journal*.

Principal investigators (PIs) Anne Dillon and Harv Mahan produced four papers resulting from their project, "Hot-Wire Chemical Vapor Deposition of Metal-Oxide Nanorods". They have also presented at two conferences. Their advancement in nanoparticle deposition encouraged them to submit a Record of Invention in the first quarter of 2006.

David Ginley and his team are working jointly with a team at Sandia National Laboratory on "Novel Electron Acceptors for Organic Photovoltaics". These two teams are working on improving hybrid organic photovoltaic (OPV) cells by optimizing nanostructured geometry and inorganic-organic interface. This project is new, but is already showing results on the development of improved materials for OPV. This technology is well positioned to be incorporated into the Solar America Initiative program and to become a competitive thin-film technology. The team has submitted three papers and has given talks at a SPIE conference in August.

Ginley is also working with co-PI John Perkins on "Unconventional Indium-Free Transparent Conductors." In a short time this team has demonstrated that the pulse laser deposited (PLD) based Nb:TiO₂ films are bulk conductors, that they can be sputtered, that anatase is the critical phase and that grain boundaries are important. This is the first time that the original Japanese results have been duplicated in any laboratory. This project could have an exceptional impact in the PV and electronic display industry. To date, the team has submitted three papers.

These are a few highlights of the LDRD program. More detail on these and other projects is contained in the following sections.

Project Summaries

Integrated Systems

Study of Fundamental Protein/Protein Interactions Involved in Biological Energy-Generation

Principal Investigator: Kwiseon Kim

FY06 Costs: \$125,228

➤ The goal of this study is to address the mechanisms governing competing protein/protein interactions involved in photobiological energy-transduction processes and their potential impact on *in vivo* hydrogen production rates via computational modeling. ◀

We investigated the fundamental nature of protein-protein interactions involved in photobiological energy transduction processes. These can be described as a series of reactions in which electrons are transferred between molecular and macromolecular “carriers.” Photochemical energy is harvested and stabilized during these processes. In the green alga *Chlamydomonas reinhardtii*, there are two predominant and competing pathways that determine the form in which photochemical energy is stored. The first pathway, requiring ferredoxin and FNR association, produces starch. The second pathway, requiring ferredoxin and [FeFe]-hydrogenase association, produces hydrogen (H₂). We use computational modeling to improve our basic understanding of the mechanisms governing the protein-protein interactions involved at this metabolic branch point, and how protein engineering could tune the metabolic flux between the two pathways. This collaboration between biological and computational scientists will identify suitable targets for future mutagenesis studies aimed at diverting electron flux towards the H₂ production pathway, thus increasing H₂ production.

Below is the methodology we used to reach our project goals:

Protein/Protein Docking Studies. Our initial studies focus on the ferredoxin:hydrogenase interaction, keeping in mind that direct mutagenesis of hydrogenase will be the most straightforward means to engineer electron flux without disturbing the rest of the metabolism. There are no experimental structures of *C. reinhardtii* hydrogenase, ferredoxin, or complexes. We obtained docking complexes using the 3D-Dock package. We generated and scored 10,000 candidates based on a residue pair potential, and subsequently filtered them by intercluster distance. The best candidates were visually screened, and the top two candidate complexes for active electron transfer were identified. They are related by an approximate 180° rotation of ferredoxin around intercluster axis. The obtained docked complexes are used as input for free energy calculations and Brownian dynamics simulations.

Brownian Dynamics Simulations for Association Rates, Protein Spatial Distributions, and Rigid-Body Binding Free Energies. We performed Brownian dynamics (BD) simulations of protein complexes to compare the association rates between competing hydrogenase-ferredoxin docked models. We further obtained the orientational distribution of ferredoxin around hydrogenase to verify the efficacy for electron transfer of collision complexes formed during BD. Additionally, we calculated binding free energies for rigid protein conformations reflecting the two best candidate complexes from empirical docking, labeled by their docking index numbers as “16” and “42”. BD simulations using protein conformations from model complex 16 resulted in smaller contact distances, larger association rates, and lower free energies than when using complex 42 conformations. These results support our conclusion that complex 16 represents a better model for the active electron transfer complex than 42, based on relative thermodynamic stability from free energy calculations. The above data combined with more detailed binding free energy

calculations (below) and electron transfer rate estimates from future quantum mechanical (QM) studies will enable us to estimate the H₂ production rates for proposed engineered variants.

Binding Free Energy Calculations. Studies using all-atom molecular dynamics (MD) to calculate relative binding free energies of the two competing candidate complexes above were completed. To increase the robustness of the calculated energies, electrostatic, non-bonded, and strain energy values were averaged over 30,000 dynamics snapshots, each 100 fs apart. In addition, a structure averaged over these 30,000 snapshots was used to calculate rigid-body entropic terms and solvation energies. This approach should better reflect the energies involved over the thermodynamic ensemble. The calculated $|\Delta\Delta G| = 20$ kcal/mol favoring complex 16. This reverses prior results favoring complex 42 as the stronger complex, and reflects the more robust approach of averaging over the entire sampled ensemble rather than using a single snapshot followed by energy minimization. The result also agrees with Brownian Dynamics simulation results to date.

Correlated Motions of Protein: Engineering Electron Transfer on Molecular Scale. Our team analyzed molecular dynamics trajectories of model *C. reinhardtii* ferredoxin – [FeFe] hydrogenase complex. The atomistic MD trajectories generated for binding free energy studies were analyzed for correlated motion on an atom-by-atom basis. Intraprotein and interprotein correlations may suggest important potential gating elements for electron transfer.

Electronic Structure of Metalloclusters and Force Field Parameterization. We performed quantum chemical studies of the relevant valence states of metalloclusters, and created physically derived force parameters of metalloclusters for molecular mechanical (MM) simulations of [FeFe] hydrogenase. The current parameterization enables future combined QM/MM studies of [FeFe] hydrogenases on:

- Electron coupling between clusters.
- Electronic coupling to electrode surface.
- Active site dynamics and oxygen reactivity.

We have submitted a manuscript on the atomistic MD free energy calculations to *Biophysical Journal* for review. We are also working on establishing and documenting the method for studying protein interactions computationally by molecular docking. Next steps include performing BD dynamics simulations of mutant hydrogenases and the ferredoxin, and analyzing the trajectories and the docking structures in detail. We will calculate the binding free energies of the mutant hydrogenase and the ferredoxin relative to the unchanged forms; perform molecular dynamics simulations on the mutant hydrogenases to examine their thermal stability; and study the free energy landscape of the hydrogenase-ferredoxin association reaction.

Renewable Electricity Science and Technology

Shape and Crystallography of III-V Semiconductor Nanoparticles

Principal Investigator: Phil Ahrenkiel

FY06 Costs: \$57,502

➤ The goal of this work is to demonstrate the viability of transmission electron microscopy (TEM) tomography for analysis of individual particle shape and orientation and collective crystallography of nanoparticle ensembles. ◀

The characterization of particle shapes and ordering in nanoparticle (NP) ensembles is the goal of much conventional TEM (Wang, 1998). High-resolution lattice imaging provides crystallographic information of individual nanoparticles in two-dimensional (2-D) projection. However, analysis of 3-D particle shape from 2-D projections is indirect. Interparticle arrangements are usually revealed in relatively low-magnification bright-field images and hollow-cone dark-field images, as well as small-angle (large camera length) electron-diffraction profiles. For each of these methods, however, a single datum provides only a 2-D sampling of the nanoparticle configurations; most three-dimensional (3D) information structural information arises by inference. TEM tomography provides a means to merge many individual 2-D images into a single, 3-D representation, which can be directly visualized and interpreted for microstructural analysis

Tomographic analysis by reconstruction of TEM tilt series has become an important tool for generating 3-D representations of materials in biological sciences. Computed tomography was developed in the medical-imaging field, but the concept extends quite naturally to TEM analysis, primarily requiring microscope automation, a relatively large sample tilt angle, and sufficient computational power. TEM tomography has been less widely explored in materials science, because of deleterious diffraction effects from crystalline specimens.

Bright-field tomography using conventional TEM can provide much useful information on NP structure, albeit with less than atomic resolution. We demonstrate successful analysis of NP systems using TEM bright-field tomography performed at relatively low magnification under the following conditions:

- A large objective aperture is used
- A small tilt increment and large tilt range are used
- The material under study is free-standing and not embedded in a strongly scattering matrix.

The first condition minimizes diffraction contrast. The second condition serves to average out intensity variations due to diffraction contrast. The third condition assures that contrast arising from the specimen will be positive at all orientations.

This work demonstrates the feasibility of TEM bright-field tomography for relatively low-magnification structural analysis of nanomaterials. Tomographic reconstruction by transmission electron microscopy is used to reveal three-dimensional (3-D) nanoparticle shapes and the stacking configurations of nanoparticle ensembles. Reconstructions are generated from bright-field image tilt series, with a sample tilt range up to $\pm 70^\circ$, using single or dual tilt axes. Tomography reveals both cubic and hexagonal close-packing configurations in multi-layered arrays of size-selected In nanospheres. By lattice imaging and tomography, we relate the 3-D shape of PbSe octahedral nanoparticles to the underlying crystal structure. We also confirm cubic shapes and simple-cubic packing in multilayers of PbSe nanocubes. The shapes of titanium oxide (TiO_2) nanorod bundles are shown by tomographic reconstruction to resemble flattened ellipsoids.

The stacking of In spheres is an example of success with this technique. In spheres serve as catalysts in the colloidal synthesis of nanoparticles, particularly with nanorod and nanowire geometries, by solid-liquid-solid reactions. The sphere size provides a means to affect the rod diameter. Like most spherical nanoparticles, monolayers of size-selected nanospheres, deposited by slow evaporation of solvent on a surface, such as a carbon support film, naturally tend to condense into triangular lattices, which are readily identified by their projections in conventional TEM bright-field images. When the local coverage exceeds a monolayer, adjacent monolayers assemble into 3-D arrays, but the contrast in projected images of these 3-D, ordered regions becomes a superposition of contributions from multiple layers, greatly complicating the image interpretation (Figure 2).

The full 3-D packing arrangement of the nanospheres is revealed by tomographic reconstruction. Two distinct types of packing are prevalent in three-layer stacks: cubic-close packed (ccp) and hexagonal close-packed (hcp). These two packing arrangements and their differences are extensively documented in numerous textbooks (Brandon & Kaplan, 1999). A ccp stacked array has sequence of ABCABC..., where A, B, and C represent three distinct, relative layer alignments. Bulk ccp stacking generates the face-centered cubic lattice. The hcp structure has an ABAB stacking sequence.

The determination of stacking arrangements is significant in that such self-assembly may influence optoelectronic properties. The reconstruction is manipulated to view the layers in projection oriented precisely perpendicular to the layers. Slices are then taken through the regions of highest density to more clearly reveal the relative positions of NPs within adjacent layers. With sufficient refinement of the vertical structure, the arrays can be viewed in cross-section, which would be entirely impossible from a single projection image.

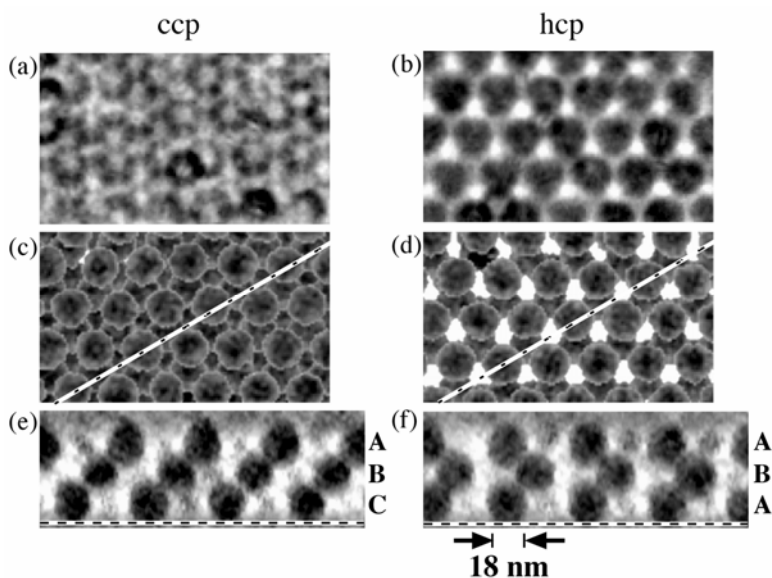


Figure 2. Cubic close-packed (ccp) and hexagonal close-packed (hcp) stacking configurations among size-selected In nanospheres: (a,b) original, 0°-tilt images; (c,d) superpositions of three tomographic slices; (e,f) cross-sectional slices taken along the diagonal lines shown in c and d. Dotted lines indicate sectioning planes. Dashed lines indicate plane of contact with support film.

The results of this work demonstrate the viability of TEM tomography for analysis of individual particle shape and orientation and collective crystallography of nanoparticle ensembles. TEM tomography has many potential applications in materials nanoscience. We have shown the direct access available to 3-D structural information. However, for crystalline nanoparticles, the resolution is limited by diffraction contrast. Although many important questions in the microscopic regime can be addressed by conventional bright-field TEM tilt-series tomography, it is anticipated that these results could be greatly surpassed using field-emission instruments, with Z-contrast imaging capability. Such equipment would be of tremendous value for addressing 3-D nanoparticle shapes and configurations.

Thin-Film Microelectronics for Rapid Gene Expression

Principal Investigator: Howard Branz

FY06 Costs: \$103,326

➤ The goal of this project is to develop cutting-edge genomics research tools through an interdisciplinary effort among NREL semiconductor physicists and microbiologists. The project team will research and develop a new type of DNA micro array based on thin-film microelectronics technology to accelerate gene expression studies at NREL and elsewhere. The research addressed two problems crucial to rapid gene expression assays accelerated by application of an electric field:

- Understanding and control of rapid electric-field enhanced DNA binding and hybridization
- Development of techniques for E-field enhanced detection of complementary DNA hybridization in samples containing mixed DNA.

We deposited and tested several candidate insulating films, and have succeeded in silanizing a glass slide coated with an insulating film of electron-beam evaporated silicon dioxide (SiO_2). A short incubation with a solution containing the precursor molecule (APTES) is sufficient, but it appears that a one-hour anneal at about 100°C is important to form a complete coating. Silanization is a notoriously difficult process, but it must be consistently mastered before cross-linker molecules can be attached and DNA can be immobilized on the surface. This silanization is confirmed through an FITC-based fluorescence assay of the surface, which we learned from our Portuguese colleagues who are working on related problems. Where silanization occurs, we see a strong fluorescence signal.

We have identified a scanning fluorescence instrument at NREL that is allowing more rapid characterization of our silanized layers. While the Colorado School of Mine (CSM) fluorescence microscope works and is better for fine resolution work, a scanner at NREL will speed up the throughput on the project.

Collaborating with the NREL team is Professor Scott Crowley, CSM Department of Chemistry and a post doc experienced in micro-Bioengineering of DNA and proteins. Crowley attends all team meetings and has been extremely helpful in the design of experimental cuvettes and improvements in chemical functionalization protocols. The CSM group brings expertise in surface physical chemistry to the collaboration.

Next steps include improving washing procedures to remove non-covalently bonded FITC molecules that sometimes give a streaky fluorescence signal when we assay even our negative silanization controls that were not exposed to APTES. Consistent washing of non-covalent molecules is critical. We will also confirm cross-linker attachment to silanized surface, immobilization of DNA probes and target hybridization. Then we will complete fabrication of the

E-field apparatus and reproduce literature results. We have designs in progress for time-resolved evanescent-field absorption, reflection and fluorescence measurements of hybridization that will elucidate the basic mechanisms.

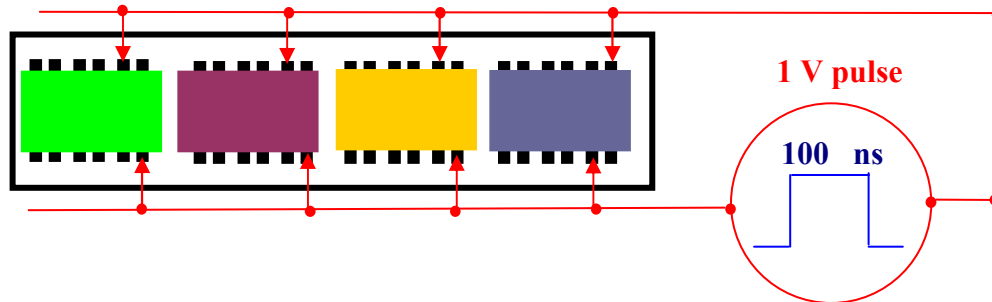


Figure 3. Schematic diagram of an electric-field addressed assay for expression of four genes.

CdMgTe Thin-Films for Light Emitting Diodes

Principal Investigators: Ramesh Dhere & Kannan Ramanathan

FY06 Costs: \$199,874

➤ The goal of this project is to prepare cadmium magnesium telluride (CdMgTe) polycrystalline thin-films, characterize them, and use them to fabricate light emitting diodes (LED). ⚡

We achieved the fabrication of polycrystalline Cd(1-x)Mg(x)Te alloy films in a wide composition range (up to $x = 0.72$) which are stable in the normal ambient. To our knowledge, this is the first demonstration of CdMgTe films in the polycrystalline form. Polycrystalline thin-films offer a number of advantages in terms of cost reduction and capability of large area depositions thus widening the scope of the application of these films. Detailed optical characterization of the alloy films was performed to establish that the optical band gap of the alloy varies from 1.5 electron volt (eV) to 2.7 eV and the transition in this range is direct. In addition, we have been able to cover the entire range due to the compositional gradient within the samples. For applications such as light emitting diodes, direct band gap semiconductors are essential. CdMgTe alloys are expected to be indirect at higher magnesium (Mg) content and determination of the region of direct gap transitions is essential for LED applications. The results show that the alloy system can be potentially useful in most of the visible spectrum.

Rectifying junctions of the type glass/ SnO₂/ CBD CdS/ CdMgTe were fabricated with alloy compositions up to $x=0.3$. The doping of the films and consequently the resistivity can be controlled by post deposition chloride heat treatments. For successful device applications, controlled doping and lower resistivities are essential. The doping effect of the treatment shows that the electronic properties of these alloys after treatment are good and are comparable to CdTe, which has yielded high efficiency solar cells.

We achieved fabrication of 8% efficient solar cells using CdMgTe alloys with band gap of 1.6 eV. We have also fabricated cells with open circuit voltage of 845 mV which is comparable to the highest values obtained for cadmium telluride (CdTe) solar cells. Quantum efficiency (QE) of these devices is high at longer wavelengths and shows that the performance is affected mainly by junction properties which can be improved with further optimization of device processing steps. High performance of these devices show that the electronic quality of these CMT alloy films is not adversely affected by the addition of Mg to CdTe system. Open circuit voltage is controlled by electronic defects in the semiconductor and high voltages achieved in these cells signify lower defect densities essential for device applications. The devices prepared from these alloys also show excellent electroluminescence (EL) for lower band gap alloys. The EL output of these samples is comparable to that of CdTe. High QE at longer wavelengths shows that the diffusion length of the minority carriers is high. Good EL response for these alloys shows that they are good candidates for LED applications. Solar cells are similar to LEDs in many respects and high QE near the band gap for these devices should translate into high performance LEDs.

NREL is better poised to compete in the solid state lighting arena where LEDs with red, green and blue emission are required for white light sources. As CdMgTe alloy system can be tailored over a wide range of band gaps, one may be able to fabricate all necessary LEDs from this alloy system. Polycrystalline thin-films can be fabricated inexpensively and are suitable for large area devices which may allow large area, e.g. whole wall size, light sources. In addition, the alloys in the lower band gap range (1.6 eV to 2.2 eV) may be ideal candidates for the development of tandem solar cells.

The remaining task in this project involves the doping of higher band gap alloy system, principally over 2 eV. This requires modification of the existing deposition system for incorporation of external dopants and experimentation with alternate post deposition treatment. Successful controlled doping will enhance the applicability of CdMgTe alloy system.

Hot-Wire Chemical Vapor Deposition of Metal Oxide Nanorods

Principal Investigators: Anne Dillon and Harv Mahan

FY06 Costs: \$137,857

➤The goal of this project is to investigate production of metal oxide nanorods and nanoparticles for use in electrochromic windows and batteries.◀

In the first quarter of 2006, in a fashion similar to the procedure used for substoichiometric tungsten oxide (WO₃) nanoparticle deposition, we have deposited molybdenum oxide (MoO₃) nanoparticle/nanorod powder having the same lateral dimensions as that for WO₃. Using this nanoparticle powder as an anode in a lithium battery conjunction, capacities of 1200 mAh/gm have been achieved, a value roughly four times higher than that obtained for a standard graphite anode. This value lasts for up to 10 cycles. The capacity then slowly degrades after ~20 cycles to ~650 milliamp hours/gm (mAh/gm), a value still twice that for a graphite anode. Work is underway to understand the stability changes and to reduce them.

We submitted a Record of Invention (ROI) in the first quarter, which documents the steps used to fabricate these highly crystalline, highly porous films.

A paper entitled "Crystalline WO₃ Nanoparticles for Highly Improved Electrochromic Applications", by S.-H Lee, R. Deshpande, P.A. Parilla, K.M. Jones, B. To, A.H. Mahan, and A.C. Dillon, has appeared in *Advanced Materials*, 18 (2006) 763.

As the year progressed, porous films containing MoO₃ nanoparticles, deposited by hot wire chemical vapor deposition (HWCVD), have been incorporated into a lithium ion (Li-ion) battery structure as the negative electrode component. We have shown that we can achieve reversible capacities (over 50 cycles) as high as 650 mAh/g, a value two times higher than that of commercial graphite negative electrodes. This improvement has been achieved by developing these small nanoparticles and by coating the nanoparticle films with a thin polymer layer, which mitigates mechanical strain issues accompanied by lithium insertion and phase changes. These results may become exceedingly important if Li⁺ battery technologies are to be realized for hybrid electric vehicle applications. These advancements could lead to the first demonstration of a solid state Li-ion battery which would be suitable for both vehicular and stationary applications. Further investigations have been performed to unravel the mechanism of this new phenomena, as our results were unanticipated. This greater understanding will lead to publication in a high impact journal.

In addition, the rate capabilities of the anode have been analyzed and shown to be superior to the state-of-the-art technologies. A patent application has been filed for this advanced battery technology.

Several publications and presentations have resulted from this research.

- *Thin Solid Films* . "Metal Oxide Nanoparticles for Improved Electrochromic and Lithium-Ion Battery Technologies" by A.C. Dillon, A.H. Mahan, R. Deshpande, P.A. Parilla, K.M. Jones, and S.-H. Lee. (under review).
- *Solid State Ionics* . "Optimization of Crystalline Tungsten-Oxide Nanoparticles for Improved Electrochromic Applications", by R. Deshpande, S.-H. Lee, P.A. Parilla, K.M. Jones, B. To, A.H. Mahan, J.D Perkins, S. Mitra, and A.C. Dillon, (under review).
- *Electrochemical Society (ECS) proceedings Volume 2, Nanotechnology*. "Hot-Wire Chemical Vapor Deposition of WO₃ and MoO₃ Nanoparticles and the Performance of Nanostructured WO₃ Electrochromic Films", by R. Deshpande, S.-H. Lee, P.A. Parilla, K.M. Jones, A.H. Mahan, B. To, S. Mitra, and A.C. Dillon (in press).

- In addition, we have been invited to submit a journal paper to *J. Mater. Chem.* “Hot-filament Chemical Vapor Deposition of High Density Molybdenum Oxide Nanoparticles”, by R. Deshpande, S.-H. Lee, P.A. Parilla, A.H. Mahan, K.M. Jones, S. Mitra, and A.C. Dillon.
- S.-H. Lee presented a talk on the present LDRD battery work at the annual Electrochemical Society Conference, Cancun, Mexico, October 30 – November 3, 2006.
- A.H. Mahan and A.C. Dillon were on the Organizing Committee and the International program Committee respectively, for the 4th International Conference on Hot Wire CVD Process, held in Takayama, Japan, October 2006. A paper was presented at the conference that summarized our complete DDRD/LDRD work.
- R. Deshpande received his Ph.D degree from the University of Tulsa. His Ph.D research centered exclusively on the work funded by this LDRD project. He has accepted a position in industry in California.
- A proposal entitled “Crystalline Tungsten Oxide Nanoparticles for Photoelectrochemical Water Splitting” is part of the NREL/University Mega-Proposal being submitted to the Office of Science in the Solar Energy Call.

This LDRD project has not only generated numerous peer-reviewed papers and high profile talks, but has also led to significant progress and the development of new concepts resulting in a patent application. Although the proposal submitted jointly with DuPont was not funded, if the NREL reviews are positive, it may still be possible to obtain partial funding. As described above, this work is also being promoted in the NREL/University mega-proposal. Finally, we have been granted additional funding to demonstrate a full battery so as to poise NREL for an upcoming battery call. We are exploring the possibility of incorporating our technologies into a solid-state battery. This would be a first-time demonstration.

Novel Electron Acceptors for Organic Photovoltaics

Principal Investigator: David Ginley

FY06 Costs: \$199,009

➤The goal of this project is to improve hybrid Organic Photovoltaic Cells (OPV) by optimizing the nanostructured geometry of the inorganic component and the critical inorganic-organic interface. The project combines the expertise of two laboratories to address this key problem in hybrid OPV: Sandia National Laboratory (SNL) – inorganics and surfactants; and NREL – polymers, oxides and devices. ◀

The laboratories are jointly involved in fabricating samples and devices and understanding the nature of the oxide/organic interface. We have purchased and activated a General Purpose Capital funded deposition system and have achieved 4% OPV bulk heterojunction cells. By integrating the GPE deposition system with our existing capability, our ability to directly address the interfacial issues is vastly improved.

A clear technical focus has evolved as a result of this joint effort, which is producing state-of-the-art results. We anticipate that a number of publications will result from this work. To date a paper entitled, “Band Offset Engineering for Enhanced Open Circuit Voltage in Polymer-Oxide Hybrid Solar Cells” has been accepted by Advanced Functional Materials and will soon be published. A manuscript on dendrimers has also been submitted to Chemical Materials and a paper on inverted devices “Inverted bulk-heterojunction organic photovoltaic device using a solution-derived ZnO underlayer” has also been accepted by Applied Physics Letters. In addition we gave talks at the Society of Photo-optical Instrumentation Engineers (SPIE) meeting August 7-15 and at the MRS meeting November 28-December 1 on the joint project.

Key personnel are accelerating our device development: Dr. Matt Reece from Yale and two graduate students – Matthew White from University of Colorado, Boulder, and Will Rance, from Colorado School of Mines.

This program is new but it is already beginning to show results on the development of improved materials for OPV. We anticipate that the increased control of the oxide and interfaces will begin to show significant improvements in efficiency. With the advent of the Solar America Initiative, this technology will be well positioned in a couple of years to be: incorporated into that program, directly transferred to companies, and become a competitive thin film technology.

Nanostructured PbTe/PbSe Thermoelectric Materials

Principal investigator: Mark Hanna

FY06 Costs: \$78,601

➤The goal of this project is to develop a process to make a high ZT nanostructured PbTe/PbSe thermoelectric material with colloidal precursors that can be scaled up to produce large-area thick thermoelectric devices. ◀

This project leveraged existing expertise at NREL in nanoparticles syntheses and materials characterization to build a foundation for new research programs in thermoelectric materials. These materials may find applications in improving the energy efficiency of vehicles through waste heat recovery, direct thermal to electrical energy conversion in solar thermal systems and as a fully solid-state heat pump in refrigeration systems.

Our team developed six chemical syntheses for preparing colloidal PbSe and PbTe nanocrystals. We thoroughly characterized the nanocrystal product by transmission electron microscopy, scanning electron microscopy, Auger electron spectroscopy, e-ray diffraction and thermally programmed desorption to identify the particle size, shape, crystallinity, composition and impurity content. These synthesis processes are simple, take place at or near room temperature and are scalable.

We developed a synthesis procedure for a single source precursor for the formation of PbSe nanocrystals or shells and investigated the synthesis of an analogous single source precursor for formation of PbTe. We attempted to produce PbTe/PbSe core-shell nanocrystal samples by coating the PbTe nanocrystals with PbSe formed from the single source precursor. This work can be used as a starting point for larger scale production of PbTe/PbSe nanoparticles and thermoelectric material for future research on thermoelectric materials.

We deposited films of PbTe nanocrystals by spray deposition which had good thermoelectric properties. It shows that good quality thin film thermoelectric material could be produced using PbTe nanocrystals.

We used the technical knowledge gained from this work to assist other divisions at NREL and outside companies with their work on thermoelectric materials. I served as technical advisor to the Freedom Car and Vehicle Technologies Program for a subcontract on advanced thin-film thermoelectric materials at Caterpillar; and assisted Caterpillar engineers in analyzing and characterizing their thermoelectric materials.

The materials synthesis and measurement capabilities that we have developed in the LDRD has put NREL in an excellent position to provide assistance to and collaborate with industry and possibly obtain new funding from DOE on advanced nanostructured thermoelectric materials. Proposed next steps would be to establish a dedicated thermoelectric materials laboratory at NREL. It would be an important step in attracting further research funding in this area.

A Critical Examination of the Intermediate Band Concept for Ultra-High Efficiency Quantum Dot Solar Cells

Principal Investigator: Andrew Norman

FY06 Costs: \$209,717

➤ The goal of this project is to critically examine, using epitaxially grown quantum dot (QD) super lattice (SL) solar cell structures and theoretical modeling, the intermediate band concept that has been proposed for ultra high efficiency, lower cost “next” or “third” generation solar cells. This work is relevant to NREL’s mission to develop renewable energy and energy efficiency technologies and practices, to advance related science and engineering, and to transfer knowledge and innovations to address the nation’s energy and environmental goals. It is also relevant to DOE’s mission to advance energy technology and promote scientific and technological innovation in support of that mission. In particular, this work directly contributes to DOE’s Scientific Strategic Goal to advance scientific knowledge and DOE’s Energy Strategic Goal to protect our security by promoting a diverse supply and delivery of reliable, affordable, and environmentally sound energy. ◀

In fiscal year 2006, we accomplished the following:

- Grew by metal organic oxide chemical vapor deposition (MOCVD) and characterized high structural and optical quality 50 period, strain-balanced InGaAs/GaAsP QD SL solar cell structures.
- Achieved 50 period strain-balanced QD SL solar cells with much improved open circuit voltages and efficiencies in comparison to non strain-balanced samples.
- Calculated the excitonic absorption spectra of lens-shaped $\text{In}_{0.6}\text{Ga}_{0.4}\text{As}/\text{GaAs}$ QDs charged with up to three electrons or holes.
- Obtained first 3D local electrode atom probe (LEAP) data from epitaxially grown III-V QD structures in collaboration with Prof. Brian Gorman (University of North Texas) and Imago Scientific Instruments.
- Based on this work, we joined the Defense Advanced Research Projects Agency (DARPA) Very High Efficiency Solar Cells (VHESC) project led by the University of Delaware.
- As a result of this project, two theory papers on carrier relaxation mechanisms and absorption transitions in QDs were published by G.A. Narvaez, G. Bester, and A. Zunger in *Physical Review B*.
- An oral presentation was given at the 2006 Materials Research Society Spring Meeting on the MOCVD growth and characterization of strain-balanced InGaAs/GaAsP QD SL solar cell structures.

We are now in a great position to supply very high quality strain-balanced QD SL samples for further study by Fourier Transform Infrared (FTIR) and time resolved optical techniques. By comparing our predictions with (InGa)As/GaAs data on interband absorption and intra-dot electron relaxation, we have demonstrated that our theoretical approach reliably predicts properties that are relevant to the operation of QD based solar cells. Thus, our approach can be applied to predict the properties of other dot/barrier combinations that are better suited as intermediate band solar cells. We are also in an excellent position to grow high quality strain-balanced QD SL solar cells to investigate their properties.

The overall impact of the project to NREL in the near-term and beyond is high because the results obtained are extremely important for critically examining the intermediate band concept for ultra-high efficiency solar cells. This third generation concept, if it is proven, may have a significant impact in the future for ultra-high efficiency solar cells based on both epitaxial and colloidal QDs or new materials possessing an intermediate band structure. We are now better positioned to experimentally and theoretically test this concept and to accomplish our goal of critically assessing its likelihood of success. If the feasibility of the concept is demonstrated by this work it will put NREL in a much better position to attract future funding.

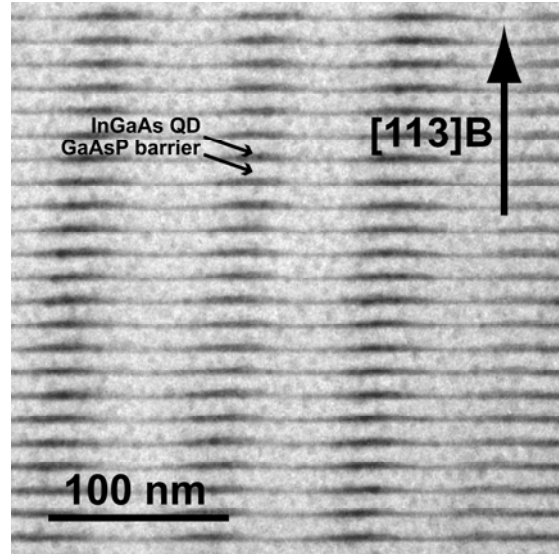


Figure 4. Cross-sectional transmission electron microscopy image of a strain-balanced InGaAs/GaAsP quantum dot superlattice grown by metal organic chemical vapor deposition for incorporation in a quantum dot solar cell.

Unconventional Indium-Free Transparent Conductors

Principal Investigator(s): John Perkins and David Ginley

FY06 Costs: \$259,199

➤ The goal of this project is to find indium-free transparent conductors to replace Indium-Tin-Oxide (ITO), a material that has increased in price 10-fold over the last two years, and which is the current industrial standard. Combinatorial high-throughput composition-spread techniques will be used to rapidly survey newly identified candidate transparent conductors (TCOs) outside the conventional TCO materials composition space. Subsequent single composition depositions will be used to focus on the identified candidate. ◀

Transparent conductors are critical to a number of key EERE technologies including PV, windows and indoor lighting. The increasing cost of indium coupled with new performance needs is creating a renaissance in the TCO area with an increasing focus on new materials.

Thus far, we have demonstrated that the pulse laser deposited (PLD) based Nb:TiO₂ films are bulk conductors. The PLD results can be duplicated by sputter deposition and the sputtered film on glass are conductive. These results demonstrate that this is a bulk transparent conducting material and not an interfacial effect, that it can be deposited by low-cost large-area approaches, and that it can be put on amorphous substrates. To date this is the first time that the original Japanese results have been duplicated in any laboratory. We have identified that it is truly bulk, that it can be sputtered, that anatase is the critical phase and that grain boundaries are important.

We have submitted our first papers to *Applied Physics Letter (APL)*, *Thin Solid Films*, and *Journal of Materials Research (JMR)*. We have a visiting graduate student from Northwestern University who is initiating investigations on the ZnSnOx system by combi techniques. She has already duplicated five year old results in this system. This kicked off the combinatorial materials development in this new system and will greatly accelerate our program in the time that she is here. This has now resulted in a manuscript in preparation in this system.

This program is showing positive results on the new in free TCO TiO₂:Nb. It has clearly demonstrated that the effect is real and that the material is viable in single crystal form. Work is focusing on improved growth on a variety of substrates and beginning to look at new systems. In the coming year, we will focus on evaluating Nb versus Ta by PLD and on exploring the deposition and transport films on amorphous substrates. We will continue to investigate the ability to dope the ZnSnO₃ system and reexamination of the Ga:ZnO system.

Photon Emission of Self-Assembled Semiconducting and Quantized Nanostructures by Scanning Tunneling Microscopy: Light from the Nanoworld

Principal Investigator: Manuel Romero

FY06 Costs: \$264,457

➤ The goals of this project are to advance our understanding of nanoscale optoelectronics in self-assembled semiconducting nanostructures, and to develop novel microscopy methods for optically detecting and imaging single molecular species (quantum dots, molecular assemblies, biomolecules, carbon nanotubes...) based on scanning tunneling microscopy (STM). ◀

This project is at the forefront of research in nanoscience and nanotechnology, with potential applications in future generations of photovoltaics. We are pioneers in the field of plasmonics – exploring the potential applications of combining plasmonics and optoelectronics in light concentration and energy conversion. Plasmons (SPs) provide a very attractive and novel approach for controlling, manipulating, and amplifying the light in the nanoscale. SPs enable us to investigate enhancement effects in the photon absorption and emission of molecular species. Plasmonic nanostructures could lead to the fabrication of more efficient light-emitting diodes and solar cells.

We observed that confinement of SPs to the metallic tunneling gap of the STM stimulates the emission of light. A quantum dot (QD) found in this optical cavity can be optically detected by the extinction of plasmons at the resonant energy. The resonances in the SP spectrum represent a fingerprint of the QD and occur at the optical bandgap owing to resonant tunneling through the dot. Figure 5 shows the SP spectrum for a series of self-assembled (CdSe)ZnS QDs.)

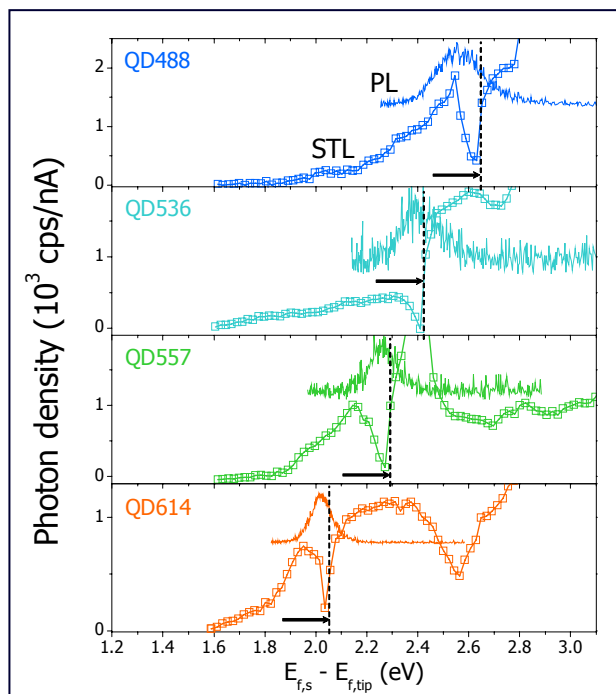


Figure 5. SP spectrum for a series of self-assembled (CdSe)ZnS QDs.)

Plasmon Resonance Imaging, which is based on the detection of such resonances in the SP spectrum, shows a great potential in nanoscale science owing to the combination of the superb resolution inherent to STM with the spectroscopy of single molecular species. To illustrate the potential of this optical microscopy, we have prepared a multidot layer combining QDs with fluorescence at 536 nm, 557 nm, and 614 nm. Figure 6 shows the plasmon resonance image of the multidot structure.

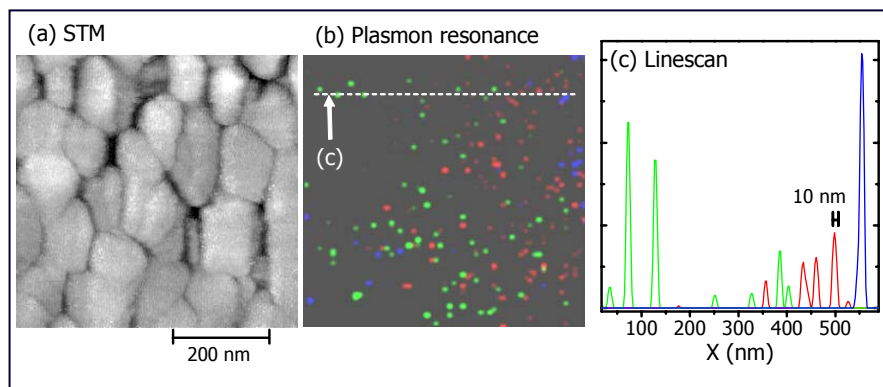


Figure 6. Plasmon resonance image of the multidot structure.

In summary, the resonant energies observed in the tunneling SP luminescence spectrum can be used to detect single molecular species. We have developed a strategy for detection and imaging based on these resonances. This detection and imaging strategy is not restricted to quantum dots. It is of great interest to an entire spectrum of nanostructures – from molecular assemblies and biomolecules to carbon nanotubes.

During the second year of this project, we are planning to: (i) control the spectrum of the SP light-source with metallic nanoparticles; (ii) investigate multilayer and cascade structures of self-assembled quantum dots; and (iii) study the optical response of quantum dots (theoretically and experimentally) in the electromagnetic field of SPs.

Low Band Gap Materials for Organic 3rd Generation Photovoltaics

Principal Investigator: Sean Shaheen

FY06 Costs: \$297,889

➤ The goal of this project is to develop a core competency in the fabrication of organic semiconductor based photovoltaic devices that are better optimized to absorb the sun's spectrum. This core competency will also include the facilities and personnel to establish NREL as a world-class laboratory in the field. To achieve this we will: develop low band gap materials that have optimized transport properties for the use in organic (plastic) photovoltaic (OPV) devices; improve the scientific understanding of the structure-property relation of these materials; improve the understanding of the physics of the operation of these devices; and develop models to guide in their advancement. ◀

This project is a cross-center effort utilizing expertise in the National Center for Photovoltaics (NCPV), Chemical and Biosciences Center, and the Scientific Computing Center to tackle all aspects of molecular design and synthesis, material characterization, and device fabrication.

Plastic solar cells offer the potential for very low cost and high through-put fabrication at reasonable power conversion efficiency. Their development is being aggressively pursued by our industrial affiliate Konarka Technologies, in order to bring this technology to full realization. Discovery of an optimal low band gap absorber would be rapidly transferred to the marketplace.

Over the last two years we have developed a new family of molecules, called *dendrimers* that exhibit more desirable fundamental properties, such as purity, molecular ordering, and electronic band structure, than existing polymeric semiconductors. Our most promising dendrimer to date possesses a lower band gap (1.8 eV) and more optimized band structure than the best polymers in the field at the moment. The results obtained so far have helped fuel the emerging OPV effort at NREL and have led directly to the initial development of a new characterization technique (time-resolved-microwave-conductivity) and device fabrication (a new electrode deposition system funded through general purpose equipment).

We were the first group to report on OPV devices made from dendrimers. They can be incorporated into several device geometries, including bulk heterojunction blends with fullerenes or nanostructured oxides (see "Novel Electron Acceptors for Organic Photovoltaics" led by David Ginley, page 18).

We have submitted and/or published three papers and given talks at four conferences.

Papers:

- *Journal of Materials Chemistry*, vol. 15, 4518 (2005). "The Synthesis and Properties of Solution Processable Phenyl Cored Thiophene Dendrimers," by W.J. Mitchell, N. Kopidakis, G. Rumbles, D.S. Ginley, and S. Shaheen (published).
- *Applied Physics Letters*, vol. 89, 103524 (2006). "Bulk heterojunction organic photovoltaic devices based on phenyl-cored thiophene dendrimers," by N. Kopidakis, W.J. Mitchell, D.S. Ginley, G. Rumbles, S. Shaheen, and W.L. Rance (published).
- *Advanced Functional Materials*. "Bulk heterojunctions based on a low band gap copolymer of thiophene and benzothiadiazole," by E. Bungaard, S.E. Shaheen, F.C. Krebs, and D. Ginley (submitted).
- *Journal of Materials Chemistry*. "The Synthesis and Properties of Soluble Spiral Thiophene Dendrimers," by W.J. Mitchell, N. Kopidakis, A.J. Ferguson, G. Rumbles, D.S. Ginley and Shaheen (submitted).

Conferences:

- American Physical Society March Meeting, Baltimore. "Pi-Conjugated Dendrimers for Organic Photovoltaics," by S.E. Shaheen, W.J. Mitchell, N. Kopidakis, J. Pris, J.J. Bozell, G. Rumbles, D.S. Ginley.
- University of Minnesota iPrime Workshop. "Nanostructured Solution-Processable Organic Photovoltaics," by S.E. Shaheen.
- Internal Conference on Complex Systems. "Molecular Self-Assembly Processes in Organic Photovoltaic Devices," by S.E. Shaheen, N. Kopidakis, J. van de Lagemaat, W.J. Mitchell, J.Y. Wang, K. Koenig, G. Rumbles, and D.S. Ginley.
- SPIE Optics and Photonics Conference. "TT-conjugated dendrimers for organic and hybrid photovoltaics," by S.E. Shaheen, N. Kopidakis, W.J. Mitchell, W.L. Rance, D.S. Ginley, and G. Rumbles.

We are attempting to pursue three avenues with the time remaining on the project:

- Improve the morphology of devices made with materials on hand.
- Develop even lower band gap materials.
- Pursue the possibility of a multi-junction OPV device using these materials.

Renewable Fuels Science and Technology

Localized Carrier Dynamics in Organic Semiconductors Probed via Time-Resolved THz Photoconductivity

Principal Investigator: Randy Ellingson

FY06 Costs: \$209,850

➤ The goal of this project is to develop time-resolved terahertz (THz) photoconductivity (TRTP) for application to organic molecular crystals as well as to other systems consisting of colloidal semiconductor quantum dot, polymeric, and/or molecular absorbers. We expected to extract detailed information about the mechanisms and dynamics of charge separation and transport in organic semiconductors. <

Developing expertise in the measurement and characterization of charge carrier dynamics in organic semiconductors and related materials supports NREL's mission to advance the science related to efficient solar energy production. On a microscopic scale, solar energy conversion begins with the absorption of a photon to generate a photoexcited state. The evolution of the photoexcited state over the first ~1 ns largely determines the potential for converting the photon's energy to electricity or to fuels. Time-resolved THz photoconductivity (TRTP) represents a unique experimental probe for monitoring the production of charge carriers on the ultra fast timescale without the need to attach wires. The TRTP technique is ideally suited for measurements of dynamics of free carrier generation and recombination in several complicated solar cell systems, such as the increasingly important "blended bulk heterojunction" device design.

We have been striving to develop TRTP for investigating organic semiconductors. We have successfully demonstrated the applicability of TRTP to systems consisting of combinations of conjugated polymers, C₆₀ metallofullerenes, and inorganic semiconductor QD. These measurements have revealed important details about the mechanisms for conversion of photons to free charge carriers in a polymer/C₆₀ "blended heterojunction" design, including how the free carrier yield varies with C₆₀ concentration. Substantial additional value continues as the TRTP technique has now been successfully applied to the characterization of local conductivity in QD arrays. The results of the project have been presented at the Materials Research Society (MRS) meeting in San Francisco. A manuscript titled: *"Photoinduced Charge Carrier Generation in a Poly(3-hexylthiophene) and Methanofullerene Bulk Heterojunction Investigated by Time-Resolved Terahertz Spectroscopy"* (by Ai, X.; Beard, M.; Knutsen, K.; Shaheen, S.; Rumbles, G.; and Ellingson, R.) has also been accepted to the Journal of Physical Chemistry for publication. Preparation of the polymer-C₆₀ manuscript represents a major accomplishment as it addresses the highly complicated response of the bulk heterojunction organic solar cell to photoexcitation within the solar spectrum. The manuscript describes a number of important processes believed to occur in such devices, including exciton generation, exciton-exciton annihilation, bound polaron (electron-hole pairs with one carrier on each of two neighboring polymer chains) generation, free carrier (polaron) generation, and trapping.

The results include a discussion of the mechanisms leading to varying performance characteristics, including the relative quantum yield of free carriers, as a function of the device composition (varying the PCBM C₆₀ weight fraction over values of 0.0, 0.2, 0.5, 0.8, and 1.0).

TRTP spectroscopy is uniquely sensitive to the conduction mechanism in low conductivity materials and is thus poised to make a significant contribution to the understanding of these important photo-conversion materials. Measuring charge carrier dynamics (e.g., generation, relaxation, and recombination) is critical to the development of novel materials and device designs for photo-production of electricity/fuels.

Application of the TRTP technique will be used to study exciton dissociation in organic semiconductors and other so-called "excitonic" solar cells. TRTP and accompanying analysis tools will be utilized to determine exciton diffusion rates, the yield of free carriers, the dynamics of interfacial recombination, and doping densities in organic semiconductors developed here at NREL.

Transition Metal Catalysis: Experiment and Theory

Principal Investigator: Mark Nimlos

FY06 Costs: \$193,014

➤ The goal of this project is to demonstrate that high level quantum mechanical calculations can be useful in guiding the development of hydrogenolysis catalysts. We propose to use a close collaboration between laboratory measurements and quantum mechanical molecular modeling to improve our understanding of catalytic processes that are important in renewable energy production and utilization. In this project we will develop hydrogenolysis catalysts that are capable of converting alcohols into alkanes. ◀

Hydrogenolysis catalysts that are capable of converting alcohols into alkanes are a novel chemical process that is thermodynamically favored but seldom observed. This reaction will be useful in upgrading the energy content of a variety of biomass derived materials. From a broader perspective, it would introduce a new simple approach to a chemical transformation that is usually quite difficult. Novel complexes have been developed at NREL that should be capable of catalyzing this hydrogenolysis reaction. The focus of this project is to demonstrate that the catalytic hydrogenolysis of alcohols is feasible, and perhaps more important, to demonstrate that high level of quantum mechanical calculations can be useful in guiding the development of these catalysts.

Our accomplishment involved:

- Demonstrating formation of key palladium and platinum hydride intermediates in the presence of strong acids.
- Demonstrating catalytic hydrogenolysis of the model substrate benzyl alcohol to toluene using a palladium catalyst.
- Obtaining trends for changes in energies of molecular orbitals with changing bite angle.
- Calculating accurate molecular geometries for palladium complexes.
- Calculating accurate relative hydricities for palladium complexes.

This represents the first example of designed metal hydride catalysts that are formed by reaction with hydrogen and are both stable in strong acid and capable of delivering the hydride ligand to a substrate to form a C-H bond. This is not only important for biomass hydrogenolysis, but can have a significant impact on fuel cell catalysis and for the utilization of hydrogen as a reductant. The success of our calculations gives us confidence to extend these to other potential catalysts.

Next, we propose to:

- Move from model substrate benzyl alcohol to glycerol
- Study catalysis in ionic liquid solvents
- Prepare more active platinum-based catalysts.
- Write a paper on calculations.

Pentose Transport and Assay Development

Principal Investigator: Min Zhang

FY06 Costs: \$164,884

➤ The goal of this project is to establish methodologies to study structure and function relationships of xylose transport proteins. We also propose to establish rapid and reliable assays for analysis of the kinetics of sugar transport. <

Xylose is the second most abundant sugar available in the world and could potentially produce one third of the ethanol from plant biomass feedstocks. Microbial utilization of xylose suffers from its low utilization rate and low product yield. Xylose transport through the cell membrane is first step in xylose utilization. Efficient utilization of xylose is the key to economical production of liquid transportation fuels from biomass feedstocks. This is critically important to EERE's strategic goals to reduce dependence on foreign oil and to create a bioindustry based on biorefineries. Efficient utilization of xylose, the second most abundant sugar in the world, could tremendously expand the biomass industry.

During this project we:

- Established xylE expression system for functional analysis. This is an essential step for the study of xylE function.
- Developed a growth assay method for screening of xylE function, which enables large scale analysis.
- Conducted site-directed mutagenesis using alanine scanning and mutant characterization. These activities allow functional characterization of the role of individual amino acids in xylE.
- Identified 11 amino acids were that are irreplaceable for xylE's active uptake sugar function. These results will be used to prepare a manuscript for submission to peer-review journals.
- Obtained a xylE mutant with significantly higher xylose transport activity and improved affinity. This unique mutant could be useful to improve biomass to ethanol process and has a potential for technology transfer to ongoing industry biorefinery projects.

Efficient xylose utilization is critical to the economical production of liquid transportation fuels from biomass feedstocks. The work potentially supports DOE goals in creating a bioindustry and reducing dependence on petroleum.

Fundamental Properties and Applications of Novel Crystalline Inorganic-Organic Hybrid Semiconductors

Principal Investigator: Yong Zhang
FY06 Costs: \$190,047

➤ The goal of this project is to obtain and understand the basic structural, electronic, and optical properties of the hybrid crystals. ◀

We are collaborating with researchers at Rutgers University and have succeeded in making films of hybrid materials with conductive polymers by spin-coating; and we are performing optical and electric measurements on these films. The success in depositing hybrid films is the first step for making these materials useful in device applications. We have been collaborating with researchers at Advanced Photon Source at Argonne National Laboratory (APS/ANL) in the study of the unusual thermal expansion of the hybrid crystals. We finished the thermal expansion measurements for all the three crystal axes for the hybrid crystal β -ZnTe(en)_{0.5} in our second trip to APS/ANL. The complete structure of the thermal expansion of the novel hybrid material was obtained – at least for one type of structure. After the experimental data are carefully analyzed, we will write a paper important to this field. The theoretical results for the phonon spectrum of the hybrid crystal β -ZnTe(en)_{0.5} were obtained in the collaboration with researchers at the University of Arkansas. The phonon spectrum is critical for us to understand the unusual Raman results we obtained a while ago, and the thermal expansion that is closely related to the temperature dependence of the phonon modes.

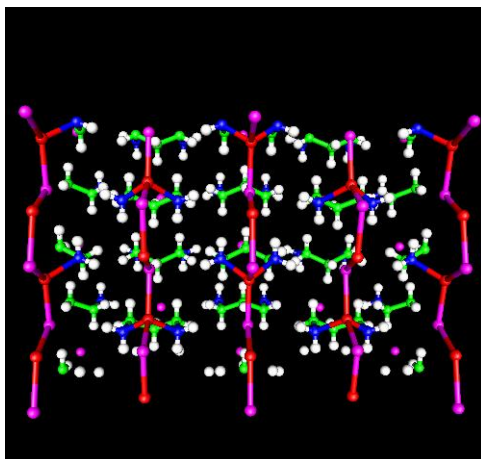


Figure 7. Beyond Nano: an array of sub-nanometer quantum wires.

In addition to collaborating with Rutgers University and the University of Arkansas, we continue to collaborate with the University of Colorado (CU), Boulder, Chemistry Department on the x-ray study of hybrid crystals. The CU collaboration provides complimentary measurements to those conducted at ANL. The collaboration with these groups has benefited all of us and significantly advanced our understanding of the new hybrid materials.

As the principal investigator, I was invited to give talks at: ANL/APS Users Scientific Seminar in August 2006; and the CU Physics Department Condensed Matter Seminar in September 2006. I presented a poster at the CU-NREL symposium, and co-PI Brian Fluegel presented a poster with me at the NREL LDRD poster review session.

Through these presentations, interest in these new hybrid materials is growing, particularly in low dimensionality, 2D and 1D, for potential thermoelectricity applications.

Our research has revealed that this new family of organic-inorganic crystals exhibit unusual properties in a larger number of aspects than we had anticipated, which offers many exciting opportunities for both fundamental studies and applications. Our effort has positioned NREL at the very frontier of this new exciting field, and improved the chance for us to receive outside funding so we can broaden the scope of our research.

Moving forward we plan to perform more theoretical and experimental studies on hybrid crystals with lower dimensionalities (2D and 1D), and will continue the effort of making n- or p-type doping and studying the conductivity for hybrid crystals.

Prototype Renewable Planning Model (RPM)

Principal Investigator: Ben Kroposki

FY06 Costs: \$258,271

➤ The goal of this project is to develop a preliminary assessment tool, the Renewable Planning Model (RPM), to integrate basic resource availability (i.e. solar irradiation, wind resource, and biomass feedstocks) with infrastructure elements (i.e. power distribution system, roads) and constraints onto a single geographic interface. ◀

In 2005, we: created a basic Web-based geographic information system (GIS) map viewer and an interface with HOMER program; received distribution system load data from Xcel Energy; and added an overlay capability to GIS mapper. In 2006, we: delved into detailing imagery – adding high resolution (1ft) imagery to select areas; started a NREL repository of high resolution imagery data; and performed PVWatts hourly simulation for a specified PV system. PVWatts is accessible as a Web-based service for external instances of the RPM tool. We also performed hourly load analysis and added access to sample power distribution feeder hourly loads through load versus time, load-simulation versus time, peak load day, and load versus hours-at-load (load duration curve). The tool now allows both large-scale (regional) and small-scale (individual buildings) basic siting analysis. The tool demonstrates “end-to-end” capability with a few selected areas and detailed data sets. This serves as a solid base upon which to build and integrate more advanced capability.

We have “system creation on map” capability – tools to draw and simulate a system on top of detailed imagery. Aggregation of individual systems into groups of systems, and further aggregation of groups into larger groups allows users to begin using the tool for broader areas and larger scale analysis. This is another baseline functionality that will serve as a base for higher level functionality. There is an internet visible application of the RPM on Linux using Apache and a local Postgres database. It is authenticated with a Digest based user/password, and NREL’s IS team has performed acceptance tests. Internet visible versions of RPM allow easy access and broad distribution possibilities. The current server will only support small concurrent user loads, but that may be sufficient for the near future.

Imagery from Denver International Airport (DIA), distribution data (lines, transformers, switch points, etc), and hourly load data obtained from Xcel has been loaded onto the system for Xcel visible Web pages. We separated a different version of the RPM configuration into separate Web URL’s and modified the code to allow easy URL creation as a way to make customized or specialized versions of RPM. For example, a “wind relevant” site that shows wind class, hides solar layers. We also have simulations using actual data in the Denver area, based on SRRL data for 2004/2005, thereby expanding the simulation data source to both “typical” and “actual” (i.e., typical metrological year and measured data). Simulations based on actual data allow a user to see more than just a composite data set, and allows relevant comparisons to actual load data for specific years. Browser support was expanded to include Microsoft’s Internet Explorer. This provides for much wider accessibility. Wind relevant data layers were expanded and a more manageable slope exclusion layer was added. Expanding wind layers enable RPM to begin a “Community Wind” assessment project with Xcel. Initial distance buffering functionality was added to RPM to expand dynamic GIS functionality.

Initial integration to HOMER as a wind simulation engine via Web service call to remote server was completed to add extensive system modeling and analysis functionality. We assembled Hydrogen relevant GIS layers into grouping for a Hydrogen Assessment (HyDRA) spin-off project, and added a variance graph for Solar resource over 30 years. This will graphically show best and worse case over long periods of time and aid in the understanding of solar for mid-level users.

The project has received reasonably high external and internal visibility. All external feedback has been extremely positive. We demonstrated the project to members of Xcel's chief corporate officers: NREL executive management including the laboratory director, and a local congressman. We are working to turn this into resources and partnerships for continued project development. RPM has been shown to Xcel's distribution planning and several members of the Amendment 37 compliance team. We also presented to the Xcel Utility Innovations group. Xcel accepted our proposal for some high-value short term functional extensions and is considering our longer term proposal for a next phase. Since the prototype has been shown to most all relevant audience within NREL, we are now doing demonstrations over the Web to possible users for additional exposure and idea gathering. The users include system integrators and utility based renewable planners. It broadens our exposure to other possible partners outside Colorado.

Xcel expressed interest in an alternate direction so we did additional strategic analysis and submitted a different proposal addressing functionality that will meet both NREL and Xcel strategic direction. This includes simulating 95% probably power levels and creating characteristic areas to allow aggregation over larger areas. We also created a project branch to show HyDRA in an interactive GIS framework. HyDRA will provide additional leverage for the current prototype system.

A distributed development environment (which includes live demonstrating, source code management, and remote PVWatts simulation model access) allows current [Xcel] and future partners to work interactively with project code base and models. The Xcel development helped to accelerate our initial schedule by at least six months.

We were able to demonstrate RPM to anyone with access to the internet through WebEx, an internet based meeting/demonstration system setup. This greatly expands our ability to show the prototype without travel expenses. Internet accessibility allows us to send links to potential users/reviewers and let them use the tool when it is convenient for them. This gives us much broader exposure and global accessibility.

Overall, the project is now pushing additional "wind based" functionality in to the tool. This will broaden the use of RPM and expand the pool of possible users. From a technical standpoint, we have integrated two additional NREL applications and have started reinforcing integration infrastructure needed to bring in additional models. We will push for expanded integration with HOMER to generalize our distributed generation functionality, and to pursue more complete wind simulation functionality.

Appendix A: Acronyms and Symbols

ANL – Argonne National Laboratory	NP – Nanoparticle
APL – Applied Physics Letter	OPV – Organic Photovoltaic
APS – Advanced Photon Source	PbSe – Lead Selenide
APTES – 3-Aminopropyltriethoxysilane	PbTe – Lead Telluride
BD – Brownian Dynamics	PCBM – (C60 is the most common carbon buckyball, and when functionalized as: [6,6]- phenyl C61-butyric acid methyl ester; it's commonly referred to as PCBM.)
CBD – Chemical Bath Deposit	PLD – Pulse Laser Deposit
CdMgTe – Cadmium Magnesium Telluride	PV – Photovoltaics
CdS – Cadmium Sulfide	QE – Quantum Efficiency
CdTe – Cadmium Telluride	QD – Quantum Dot
CSM – Colorado School of Mines	QM - Quantum Mechanical
CU – Colorado School of Mines	QM/MM - [combined] Quantum Mechanical and Molecular Mechanical
DARPA – Defense Advance Research Projects Agency	ROI – Record of Invention
DDRD – Director's Discretionary Research and Development (program)	RPM – Renewable Planning Model
DIA – Denver International Airport	SC – Solid State
DOE – Department of Energy	SD&A – Strategic Development and Analysis
ECS – Electrochemical Capacitor Society	SiO ₂ – Silicon Dioxide
EERE – Energy Efficiency and Renewable Energy	SL – Super Lattice
EL – Electroluminescence	Sn – Tin
[FeFe]-hydrogenase – Iron-Iron hydrogenase (hydrogenase containing the two Iron metal cluster)	SnO ₂ – Tin Oxide
FTIR – Fourier Transform Infrared	SP – Plasmon
FITC – fluorescein isothiocyanate	SPIE – Society of Photo-optical Instrumentation Engineers
FNR - Flavin-nicotine amide dinucleotide phosphate (NADP+) oxidoreductase	SRRL – Solar Radiation Resource Lab
Ga – Gallium	STM – Scanning Tunneling Microscopy
GPE – General Purpose Equipment	TCO – Transparent Conductors
H ₂ – Hydrogen	TEM – Transmission Electron Microscopy
JAP – Journal of Applied Physics	THz – Terahertz
JMR – Journal of Materials Research	TRTP – Time Resolved Terhertz Photoconductivity
LDO – Laboratory Development Office	TiO ₂ – Titanium Dioxide
LEAP – Local Electrode Atom Probe	TMY – Typical Meteorological Year
LEDs – Light Emitting Diodes	VHESC – Very High Efficiency Solar Cells
Li – Lithium	WFO – Work for Others
Li-ion – Lithium Ion	WO ₃ – Substoichiometric (The W is not fully oxidized.)
mAh/gm – Milliamp Hours/gm	Zn – Zinc
Mg - Magnesium	ZT – (A dimensionless figure of merit for thermoelectric materials. $ZT = S^2 \sigma T / k$ – <i>S is the Seebeck coefficient, σ is the electrical conductivity, k is thermal conductivity, and T is the temperature.</i>)
MOCVD – Metal Oxide Chemical Vapor Deposition	
MoO ₃ – Molybdenum Oxide	
MM – Molecular Mechanical	
MRS – Materials Research Society	
Nb – Niobium	
NCPV – National Center for Photovoltaics	