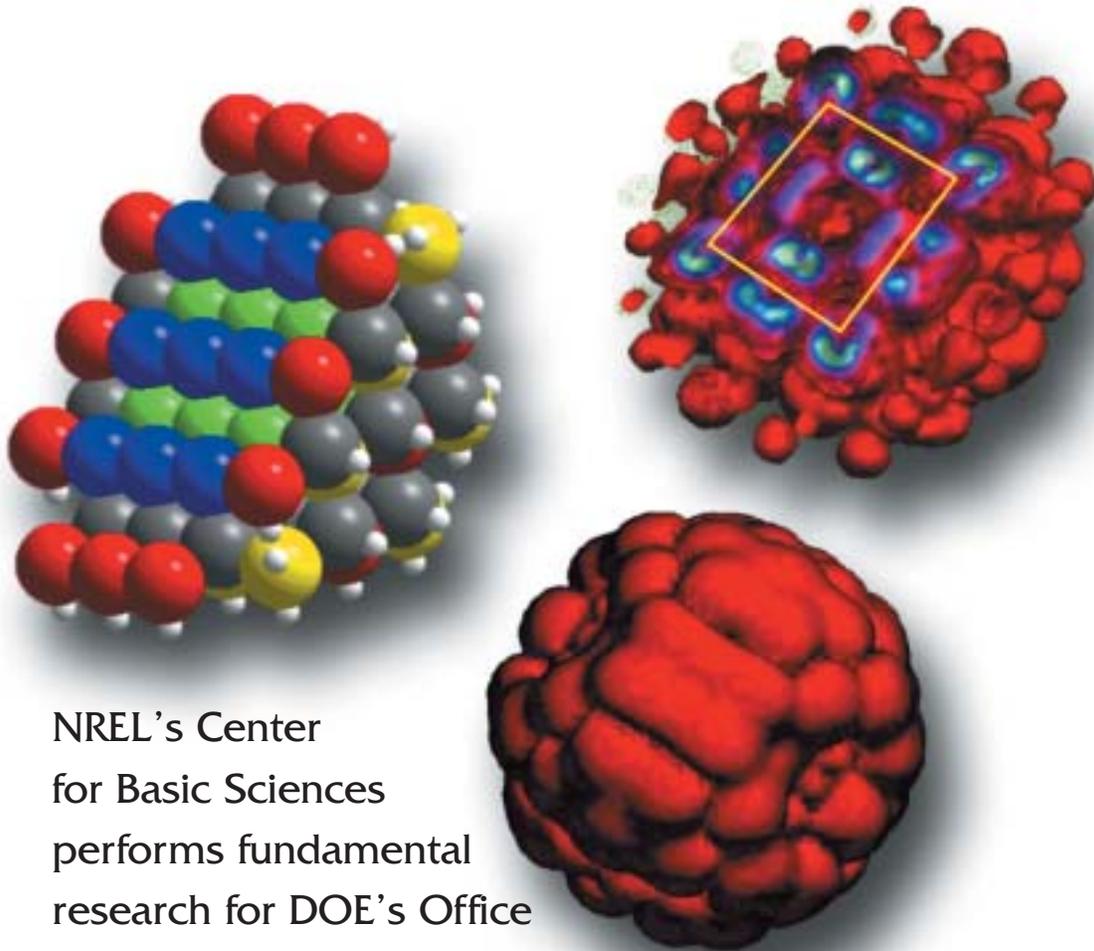


Basic Energy Sciences at NREL



NREL's Center for Basic Sciences performs fundamental research for DOE's Office of Science. Our mission is to provide fundamental knowledge in the basic sciences and engineering that will underpin new and improved renewable energy technologies. In support of this mission, NREL executes research in three areas – materials sciences, chemical sciences, and energy biosciences. NREL also integrates fundamental research with applied R&D in several projects.

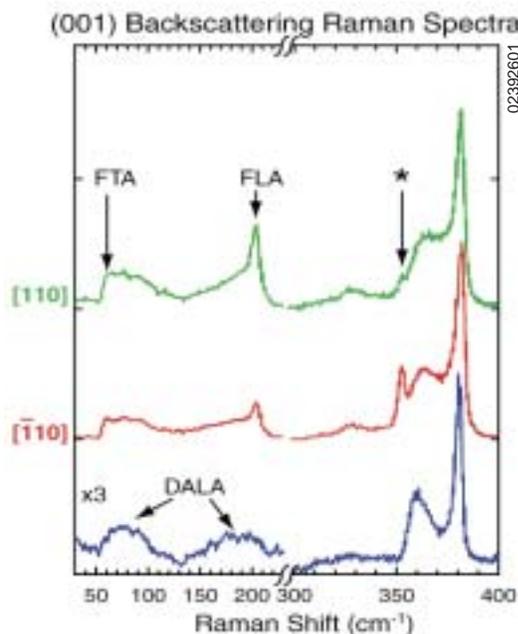
Materials Sciences

NREL's R&D activities in materials sciences include novel ordered semiconductors, composition modulation, defect-tolerant oxides, solid-state theory, doping bottlenecks in semiconductors, and carbon nanotubes for CO₂ removal.

Novel ordered semiconductors. Some III-V and II-VI semiconductor materials exhibit spontaneous ordering under certain growth conditions. Spontaneous ordering can modify band gaps, result in valence-band splitting, increase effective electron mass, affect phonon spectra, change some indirect band-gap materials to direct band-gap materials, and have other effects important to optical, structural, and electronic properties of photovoltaic and semiconductor materials.

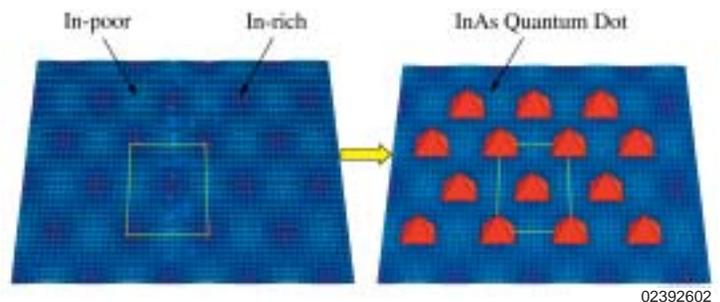
In this project, NREL researchers are:

- Using metal-organic chemical vapor deposition and molecular beam epitaxy to grow novel ordered semiconductor alloys of III-V and II-VI compounds
- Characterizing the electrical, optical, and structural properties of these compounds using in-situ probes and optical spectroscopy
- Developing a theoretical methodology to explain and predict ordering in a variety of III-V and II-VI semiconductor alloy systems. Theorists are also extending their methodology to explain ordering in borides, nitrides, and antimonides. This theoretical work should lead to experimental studies of new, order-induced phenomena.



Effect of CuPt ordering on the Raman spectrum of a GaInP₂ alloy. The blue spectrum is for a random alloy. The red and green spectra (which show three new peaks) are for an ordered alloy taken in two polarizations.

Composition modulation. When a thin binary layer of certain III-V semiconductor alloys are grown epitaxially on a substrate, under the right conditions the composition modulates in the plane of the layer. By properly orienting the substrate, the modulation can be produced in different configurations – in lateral strips, in centered rectangular arrays, and other regular patterns. Composition modulation has several potentially important applications in photovoltaics, solid-state lasers, and other technologies. In photovoltaics, for example, composition modulation can be used to vary the band gap of a material to the desired level, while lattice-matching the material to a desired substrate – important considerations for high-efficiency photovoltaic devices. Also, rectangular-centered modulation holds the potential for growing regular, consistent-sized quantum dots for use in solid-state lasers with uniform frequencies and low threshold currents.



One concept for AlInAs composition modulation is to create a centered-rectangular, two-dimensional lattice with In-rich and In-poor areas, and then to use the In-rich areas on which to grow uniform InAs quantum dots of controlled size.

This is a cooperative project in which:

- Researchers from Sandia National Laboratories are using molecular beam epitaxy to grow strained layer systems, which exhibit lateral composition modulation
- Researchers at NREL are growing materials with both lateral and rectangular modulation, and are using a variety of optical spectroscopic techniques to study the structural, electronic, and optical properties that are characteristic of compositionally modulated alloys.

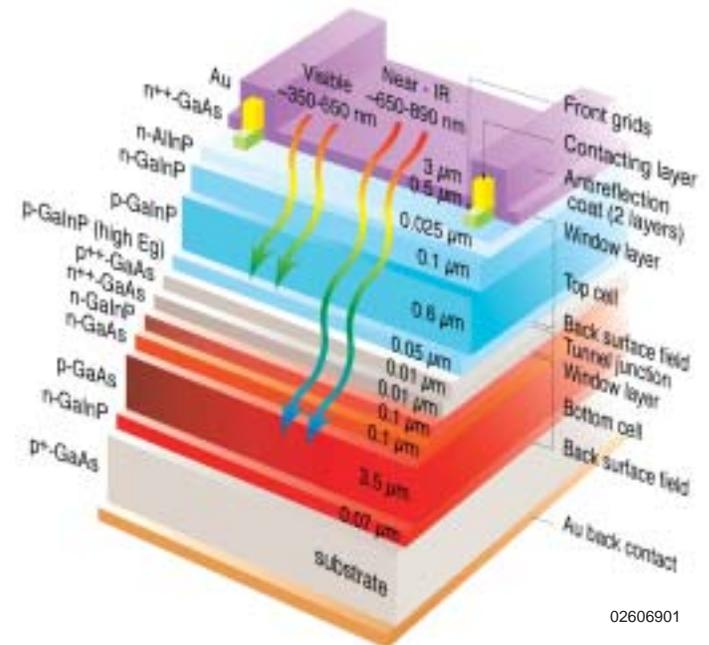
Defect-tolerant oxides. Because of their structural and electronic tolerance for large doping or defect levels, these oxides are becoming increasingly important in displays, batteries, photovoltaics, and a number of other electro-optical technologies. This program is trying to understand the relationships between structure and the electro-optical properties in these oxide materials. Initial work has focused on V₂O₅ and LiCoO₂, which are important cathode materials for Li batteries. Researchers used pulsed laser deposition to grow films of

Integration of Basic and Applied Research

NREL is making a concerted effort to integrate the basic energy research funded by the Office of Science with applied research supported by EERE. Recognizing that basic research activities provide the scientific underpinning for advancing present and future renewable energy technologies, NREL has several projects under way that have been co-funded and co-planned to meet this objective.

Dye-sensitized photoelectrochemical solar cell. This promising new cell is built of simple and inexpensive ingredients: titanium dioxide nanocrystalline films and ruthenium-based dyes absorbed on nanoparticles. Fundamental research funded by the Office of Science is directed at understanding the basic photogenerated carrier dynamics of heterogeneous electron transfer and transport in these cells and other fundamental mechanisms. EERE funds are used for applied research to optimize the device parameters that determine performance and efficiency of these cells.

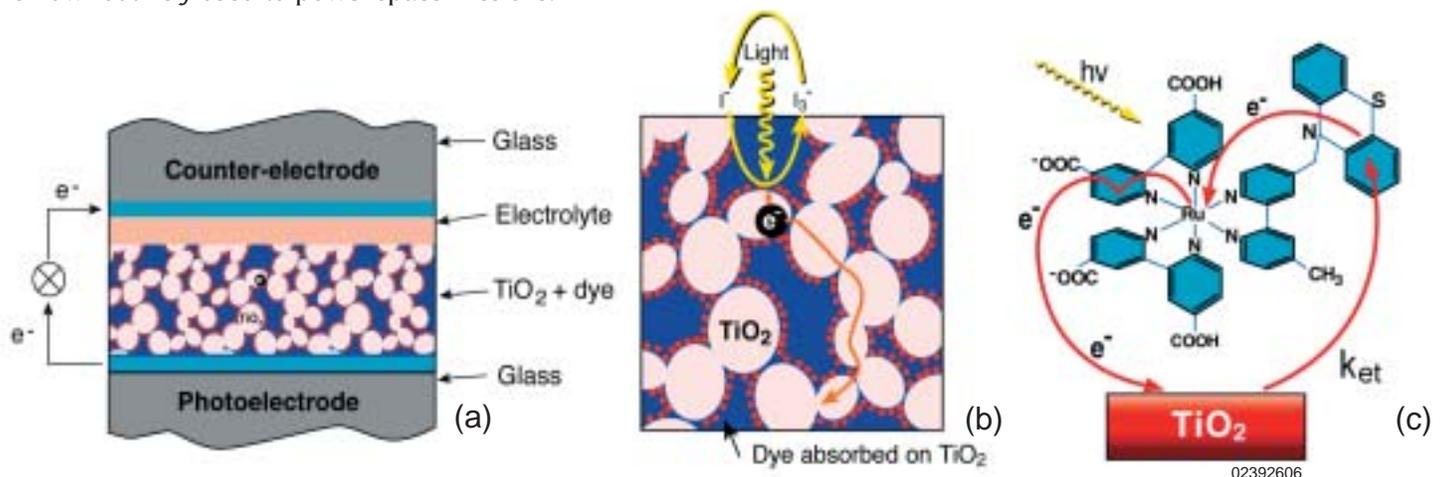
High-efficiency tandem solar cell. Development of the 30%-efficient tandem cell was among NREL's first major scientific breakthroughs. The top cell (GaInP_2) captures the high-energy part of sunlight and passes the rest to the bottom cell (GaAs) for absorption. The two materials have matching lattices, which allows them to be grown in a single reactor system. The achievement was based on gaining a fundamental understanding of the optoelectronic properties of the materials and applying this understanding to the optimization of device parameters — an integration of basic and applied research that enabled scientists to control growth conditions so they could precisely tune the characteristics of the cell materials. This technology has been transferred to industry and is now routinely used to power space missions.



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Device structure of 30.2%-efficient $\text{GaInP}_2/\text{GaAs}$ two-junction PV cell. Success with this cell is leading toward three- and four-junction cells.

DOE Center of Excellence for Synthesis and Processing of Advanced Materials. Because of its core capabilities in both applied and basic photovoltaics research, NREL coordinates the Center of Excellence. Participants include numerous labs and universities who perform collaborative research in high-efficiency photovoltaics. Recent progress in silicon-based thin films includes improved growth and characterization techniques. Regarding next-generation thin-film materials, the focused effort to develop GaInAs:N as a 1-eV material of very high-efficiency photovoltaics is proving worthwhile. Much interest has been generated within the scientific community around the effect of nitrogen incorporation on the band gap of the host material.

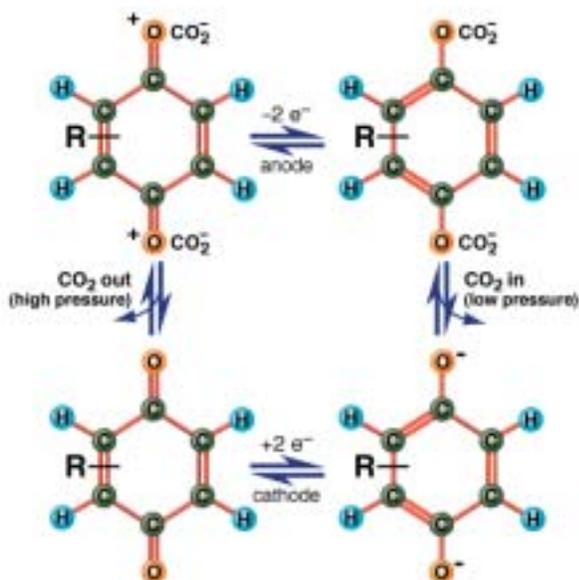


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NREL scientists helped pioneer the concept of the photoelectrochemical solar cell (a), which uses a photoelectrode comprised of nanocrystals of TiO_2 coated with a ruthenium-based dye (b). The TiO_2 absorbs UV solar radiation and converts it to electric current. Ruthenium dye (c) greatly extends the range of the spectrum absorbed and converted by the cell.

Currently, researchers are also investigating the fundamental question of whether the orientation of the excited state dipole affects the probability and polarity of the electron transfer process. In studying this question, researchers are intending to design a new class of stable, sensitizing dyes and to develop design criteria for hole-injecting dyes.

C₁ electrocatalysis. It is possible to remove CO₂ directly from the atmosphere, use catalytic electrochemical reduction to convert the CO₂ to fuels (such as methanol), and then to catalytically oxidize the fuels back to CO₂ with the production of electrical energy (using fuel cells). Doing this with electricity derived from renewable energy sources (such as solar cells or wind turbines) offers an attractive renewable route to fuels that would not produce a net increase in atmospheric CO₂ concentrations. Critical to this is the development of electrocatalysts that would enable the processes to proceed efficiently.



One scheme to separate and recover CO₂ from the atmosphere is to use a redox active carrier (in this case, a quinone) that binds CO₂ at low pressure in the reduced form and releases it at high pressure in the oxidized form. The released CO₂ can then be reduced to methanol.

With this project, NREL researchers are collaborating with researchers from several universities to:

- Develop highly efficient methods for separating and recovering CO₂ directly from the atmosphere
- Discover new C₁ electrocatalysts – using both traditional and rapid-throughput approaches – and optimize them for energy storage and utilization
- Develop a fundamental understanding of the kinetics and thermodynamics of key catalytic steps involved in the interconversion of C₁ products, e.g., C-O bond cleavage, C-H bond formation, and M-C bond formation.

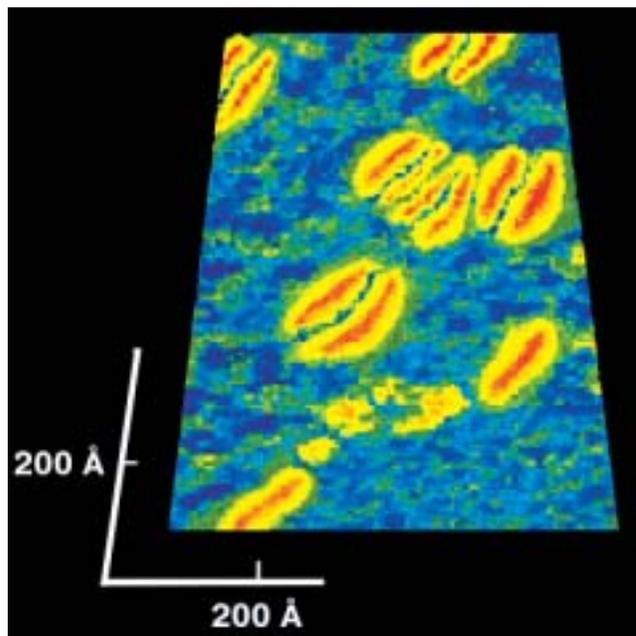
Energy Biosciences

Two Office of Science projects are contributing to the base of fundamental scientific knowledge related to photobiological conversion of sunlight into fuels and chemicals.

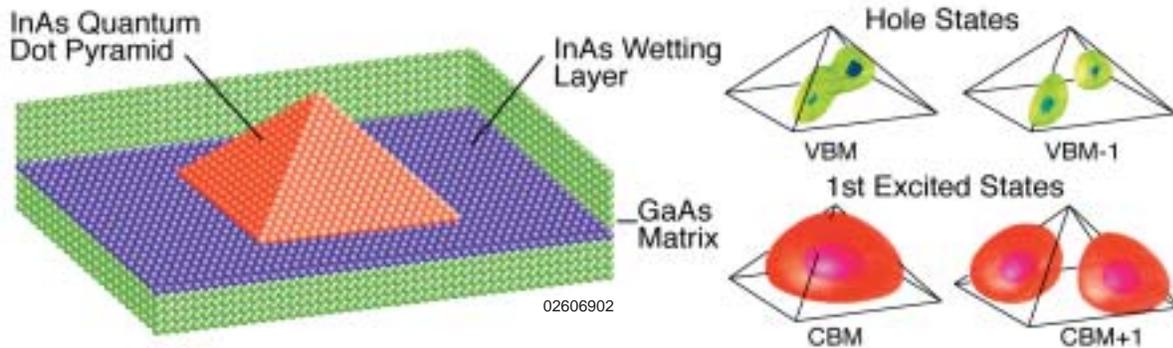
Water-splitting apparatus of photosystem II.

Photosystem II is one of two light reactions of algal and green plant photosynthesis. NREL researchers have succeeded in measuring the picosecond (trillionth of a second) time-domain, charge-separation reactions in this photosystem that provide energy to drive plant metabolism. They have also imaged that part of the membrane/protein structure that performs these basic processes, and examined fundamental aspects of the system that releases molecular O₂ from water.

Regulation of hydrogen metabolism. This research involves the regulation of H₂ and CO₂ metabolism in algae. Scientists from NREL and UC Berkeley have produced significant amounts of H₂ from water using common algae in research supported by the EERE Hydrogen Program. Their method is based on growing the algae under normal photosynthetic conditions (O₂ is evolved) and then withholding sulfur (stops net O₂ production and promotes H₂ evolution). The Office of Science is supporting work aimed at understanding this process at the molecular level by examining the mechanism of hydrogenase (the H₂-releasing enzyme) induction and partitioning of electrons from water to the enzyme to maximize hydrogen production.



This scanning tunneling micrograph shows the luminal surface of granal membrane fragments isolated from spinach, which are enriched in photosystem II water-splitting activity. The false yellow-colored protrusions are dimeric, protein core complexes that contain the photosynthetic water-splitting apparatus. The protein structure rises 5 nanometers above the membrane plane (blue areas).



The solid-state theory group performed pseudopotential calculations of the electronic structure of a pyramidal InAs quantum dot embedded in GaAs. The group is exploring the properties of InAs dots, in particular the effects on the electronic structure of altering the size and shape of the dots.

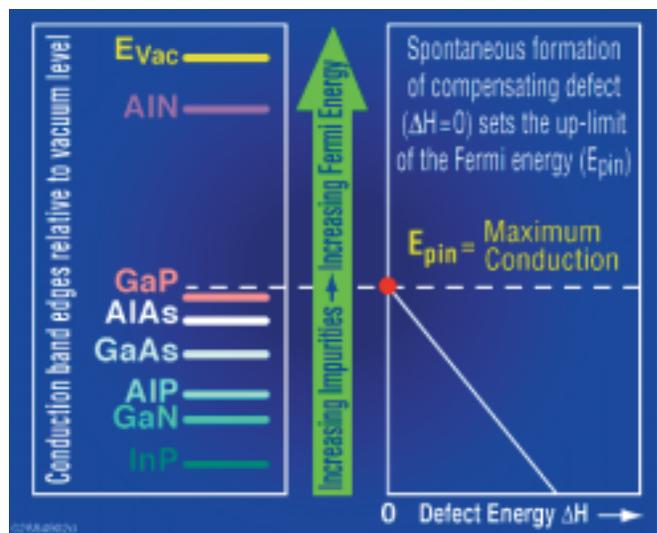
these materials. They then investigated the intrinsic electrochemical behavior of the materials and determined the Li diffusion coefficient as a function of Li content and charge and discharge cycling.

Researchers will continue their research on cathode materials for Li batteries, extending their investigations to include the technologically important MnO-based systems. They will also expand their research to other areas, including:

- Transparent conductors, including p-type oxides such as CuAlO_2 and SrCu_2O_2 and co-doped or substitutionally doped oxides like ZnO
- Ferroelectric and dielectric materials, such as the $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) system and composite films of MgO/BST, which have promising properties for use in microwave circuits
- Combinatorial materials growth, as a method to quickly discover and optimize new materials – most notably transition metal oxides – that will be suitable as absorber layers in photovoltaics, transparent conductors, and lithium batteries.

Solid-state theory. The solid-state theory group uses fast computers and quantum mechanical strategies to search for new, stable electronic materials, and it investigates the theoretical foundations of photovoltaic materials, quantum nanostructures, and order-disorder phenomena. To look for new materials, the group is developing an approach called LEGO (Linear Expansion of Geometric Objects), which is based on the recognition that complex crystal structures can be viewed as a collection of simple geometric objects. For photovoltaic materials, theorists use first-principles electronic structure theory to explain and predict material properties and electronic structure of materials and to explain why some semiconductor materials exhibit long-range order. For quantum nanostructures, scientists use pseudopotential many-body theory to predict optical and transport properties of semiconductor quantum dots, including "colloidal/freestanding" dots of Si, CdSe, and InP, as well as "self-assembled" dots of InAs/GaAs.

Overcoming doping bottlenecks. Many semiconductors cannot be doped to desired levels, particularly those with wide band gaps. Recent rapid progress in semiconductor research mandates that these limitations be overcome in order to tune semiconductors for precisely required properties. In this project, researchers are investigating doping bottlenecks using first-principles, total-energy calculations.



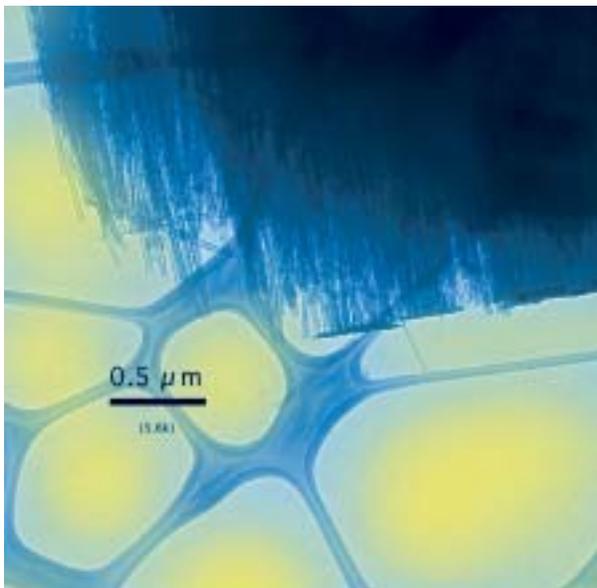
First-principles, total-energy calculations reveal that equilibrium n-type doping is limited by the spontaneous formation of closed-shell defects: the (3-) charged cation vacancy in III-V semiconductors.

The bottlenecks are caused by dopant solubility that is too low, donor/acceptor levels that are too deep, or the formation of intrinsic defects. The defect formation enthalpies depend on the Fermi energy, and thus always act to negate the effect of doping under equilibrium. NREL researchers are testing systematically the various microscopic defect models to understand the physics of doping. They have also identified bottleneck intrinsic defects as the cation vacancies for n-type materials. Researchers are proposing new strategies for overcoming the equilibrium doping bottlenecks. And to increase the dopant solubility, they are proposing surface enhancement of stability and molecular doping by design at low-growth temperatures.

Using carbon nanotubes for CO₂ removal. Because of concerns associated with global warming, improved methods are needed for removing CO₂ from the hydrogen produced by steam reformers and partial oxidation reactors. NREL scientists are researching two areas: membranes fabricated using carbon nanotubes that either block or selectively transmit CO₂; and using carbon nanotube powders that discriminate between different molecules by competitive reactions during pressure swing adsorption.

This research capitalizes on:

- Tunable properties of both the membranes and powders, which bestow unique behaviors and advantages
- Synergies with an NREL project funded by the Office of Energy Efficiency and Renewable Energy (EERE), as well as a Cooperative Research and Development Agreement with Honda R&D Americas that focuses on hydrogen storage in single-wall carbon nanotubes (winner of a *Discover* magazine award in 1997).



NREL's research on carbon nanotube membranes focuses on the transport of gases through well-defined arrays of small, aligned, graphitic pores. Such pores are produced by forming carbon nanotubes within alumina templates using chemical vapor deposition, or by manipulating and arranging single-wall carbon nanotubes made by laser vaporization.

Chemical Sciences

NREL's investigations in chemical sciences involve the research areas of dye-sensitized photochemical solar cells; photon conversion using quantum dots and quantum dot arrays; synthesis and characterization of III-V quantum dots; interfacial photochemical processes; pho-

toconversion processes in molecular semiconductors; and basic research in C₁ electrocatalysis.

Fundamental studies of dye-sensitized photochemical solar cells. The photochemical solar cell is a potentially low-cost, efficient solar cell based on dye-sensitized nanocrystalline films of titanium dioxide (TiO₂). This device contains a photoelectrode made of a nanocrystalline film of TiO₂ particles. Dye molecules are adsorbed onto the surface of the TiO₂ particles so that, when exposed to light, they inject electrons into the semiconductor material, which are collected as current. After traversing the external circuit, electrons are injected back into the electrolyte and become part of a series of reactions that restore the oxidized dye molecules to their original state to complete the energy conversion cycle.

The research in this project focuses on:

- Understanding the charge carrier dynamics and other basic mechanisms involved in charge generation, separation, transport, and energy conversion in these cells
- Understanding the influence of light intensity and photoinjected electron concentration on the recombination kinetics
- Clarifying the factors affecting the photostability of dye-sensitized nanocrystalline TiO₂ solar cells
- Investigating how quantum dots can be used to sensitize TiO₂.

Photon conversion using quantum dots, quantum dot arrays, carrier dynamics, and quantization effects at semiconductor-molecule interfaces. Quantum dots are semiconductor particles that typically have a radius that ranges from 2 to 25 nanometers. They exhibit extremely interesting optical, electronic, and photoelectrochemical properties that are a function of their size. Quantum dot arrays – which are formed by assembling quantum dots into close-packed ordered or disordered structures – also have unique and important properties that may be useful as photoelectrodes in photon conversion systems.

In this project researchers are:

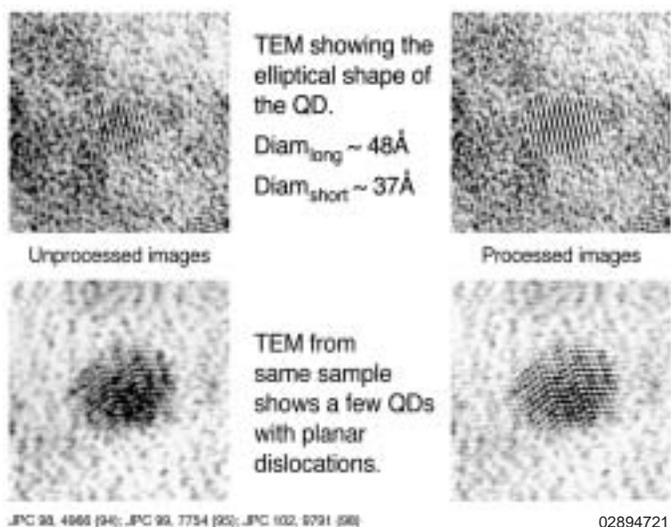
- Using a variety of spectroscopic and other techniques to study the fundamental properties of III-V quantum dots and quantum dot arrays
- Developing the basic science underpinning the use of quantum dots and arrays in quantum dot solar cells based on quantum dot-sensitized TiO₂ electrodes, quantum dot-organic semiconducting polymer structures, and quantum dot solids with inter-quantum dot electron and hole transport
- Conducting theoretical and experimental studies on the electronic coupling between quantum dots, and

on the dynamics of electron relaxation, transfer, and transport at semiconductor-molecule interfaces

- Exploring unique properties of quantum dots such as efficient anti-Stokes photoluminescence (up-conversion) and two-color photoluminescence blinking.

Synthesis and characterization of III-V quantum dots.

Semiconductor quantum dots represent a new class of materials between molecules and bulk solids. They are large enough to maintain the bulk crystal structure and small enough to produce quantization effects. These characteristics make them extremely promising for use in highly efficient photoconversion systems.



High-magnification TEM images of InP quantum dots (QDs).

In this project, NREL researchers are:

- Synthesizing quantum dots of a variety of III-V semiconductor materials, including InP, GaAs, GaP, GaN, and GaInP
- Investigating the influence of organic stabilizers and various matrices on electronic coupling between quantum dots
- Exploring the mechanisms of energy transfer of electronic excitation in three-dimensional ordered arrays of InP quantum dots
- Using transient absorption and photoluminescence to determine carrier dynamics in the quantum dots.

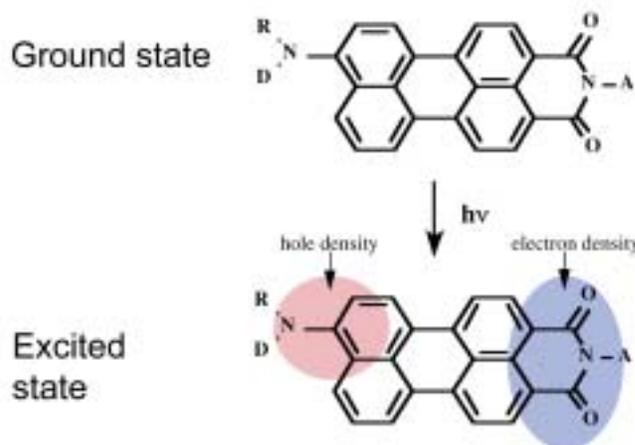
Interfacial photochemical processes: dye-sensitized nanoparticle electrodes. Chemically modifying the nanocrystalline TiO₂ electrodes of a photochemical solar cell improves the performance of the device and increases its photovoltage. The objective of this project is to understand how this happens by resolving issues involving the mechanics and kinetics of charge transport and recombination across the nanocrystalline/electrolyte interface, the separability of the ion and electron diffu-

sion process, the electrical potential distribution in the cell, the location of the charge separation, and the mechanism of photopotential generation. Researchers are addressing these issues through experimental studies using electrical impedance and optical modulation spectroscopy, and through theoretical approaches to provide an understanding of the effect of experimental parameters on electron-transport rate measurements.

Photoconversion processes in molecular semiconductors.

In this task, researchers seek to understand fundamental aspects of photoconversion processes in organic-based systems by studying energy transfer processes and the generation, separation, and recombination of charge carriers in molecular semiconductors and dye-sensitized solar cells. A particular focus involves studying these processes in self-organizing films of liquid crystalline molecular semiconductors. These compounds were synthesized in the belief that highly ordered films may reveal the intrinsic properties of molecular semiconductors more clearly than the usual amorphous or polycrystalline films deposited by thermal evaporation.

Recently, researchers have invented a procedure for correctly doping molecular semiconductors for the first time. The dopant is a reduced (for n-type) or oxidized (for p-type) derivative of the host molecule that has a covalently attached counter charge bound to the periphery of the molecule (not in conjugation with the chromophore). Researchers recently synthesized the first examples of this idea and showed that 0.3% dopant in the host lattice increases the conductivity by a factor of 10⁶. Since the low conductivity of molecular semiconductors is often a major factor limiting their photoconversion efficiency, NREL scientists are optimistic that this doping technique will eliminate this problem and thereby open a new area of research in the field of molecular semiconductors.



The photo excitation of a charge-transfer dye polarizes its electron density. One of the questions researchers are trying to answer is whether this polarization affects the efficiency of electron and hole transfer.

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Novel ordered semiconductors

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Photon conversion using quantum dots, quantum dot arrays, carrier dynamics, and quantization effects at semiconductor-molecular interfaces

O.I. Mičić, K.M. Jones, A. Cahill, and A.J. Nozik, "Optical, Electronic, and Structural Properties of Uncoupled and Close-Packed Arrays of InP Quantum Dots," *J. Phys. Chem. B* **102**, 9791 (1998).

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Interfacial photochemical processes: dye-sensitized nanoparticle electrodes

J. van de Lagemaat, N.-G. Park, and A.J. Frank, "Influence of Electrical Potential Distribution, Charge Transport and Recombination on the Photopotential and Photocurrent Conversion Efficiency of Dye-

Sensitized Nanocrystalline TiO_2 Solar Cells: A Study by Electrical Impedance and Optical Modulation Techniques," *J. Phys. Chem. B* **104**, 2044 (2000).

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NREL Center for Basic Sciences

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Cover Illustration

Three-dimensional electronic density map of core-shell quantum dots (QDs) of lattice-matched ZnCdSe_2 shells on InP cores:

(a) Hard-sphere representation of the atomic structure shown with a slice through the QD center perpendicular to the [001] direction.

Green = P, blue = In, red = Cd, yellow = Zn, and gray = Se.

(b) Electron-density isosurfaces of the same QD, with the rectangle outlining the outermost positions of the centers of the

core InP atoms. (c) A single electron-density isosurface for the full dot (not sliced).

