Assuring a Secure Energy Future

Energy Research: Future Challenges and Opportunities

NANOTECHNOLOGY: THE NEW GENERATION
Embassy of France, Washington DC

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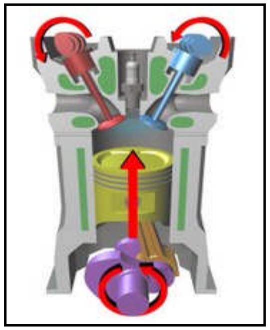
Under Secretary for Science
U.S. Department of Energy
July 8, 2008
www.science.doe.gov

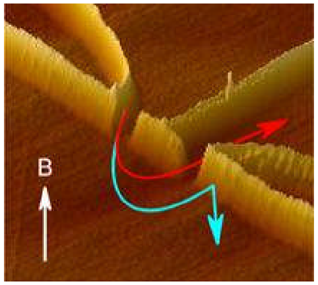
Essential Role of Basic Science

- **Today's energy technologies and infrastructure are rooted in 20th Century technologies and 19th Century discoveries—internal combustion engine, incandescent lighting.**
- Current fossil energy sources, current energy production methods, and current technologies cannot meet the energy challenges we now face.
- Incremental changes in technology will not suffice. We need **transformational discoveries** and **disruptive technologies.**
- **21st Century technologies will be rooted in the ability to direct and control matter down to the molecular, atomic, and quantum levels.**

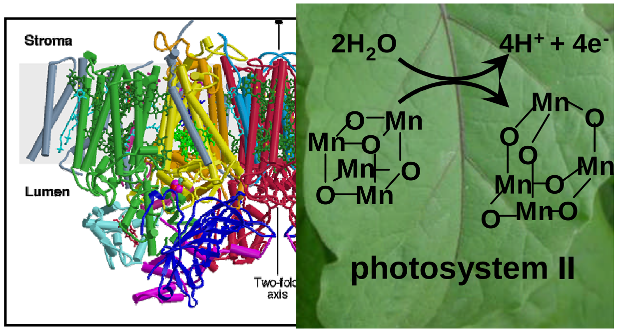

Watt Steam Engine, 1782


Four-stroke combustion engine, 1870s

Quantum Control of Electrons



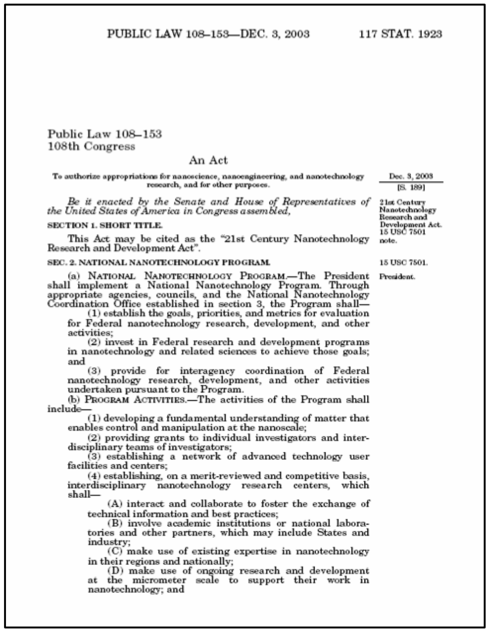
Separating electrons by their spin for "spintronics" and other applications of electron control.



Bio-inspired nanoscale assemblies – self-repairing and defect-tolerant materials and selective and specific chemical reactivity.

National Nanotechnology Initiative

- The NNI is an interagency program that coordinates Federal nanoscale research and development activities and related efforts among various participating entities (currently 25)
- The NNI began in 2001 and its activities were codified and further defined in the 21st Century Nanotechnology Research and Development Act (Dec. 2003)
- Estimated federal NNI funding is nearly $1.5 billion in FY 2008



PUBLIC LAW 108–153—DEC. 3, 2003 117 STAT. 1923

Public Law 108–153
108th Congress

An Act

To authorize appropriations for nanoscience, nanoengineering, and nanotechnology research, and for other purposes.

Dec. 3, 2003
[S. 189]

Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled,

21st Century Nanotechnology Research and Development Act. 15 USC 7501 note.

SECTION 1. SHORT TITLE.

This Act may be cited as the "21st Century Nanotechnology Research and Development Act".

SEC. 2. NATIONAL NANOTECHNOLOGY PROGRAM.

15 USC 7501.

President.

(a) NATIONAL NANOTECHNOLOGY PROGRAM.—The President shall implement a National Nanotechnology Program. Through appropriate agencies, councils, and the National Nanotechnology Coordination Office established in section 3, the Program shall—

(1) establish the goals, priorities, and metrics for evaluation for Federal nanotechnology research, development, and other activities;

(2) invest in Federal research and development programs in nanotechnology and related sciences to achieve those goals; and

(3) provide for interagency coordination of Federal nanotechnology research, development, and other activities undertaken pursuant to the Program.

(b) PROGRAM ACTIVITIES.—The activities of the Program shall include—

(1) developing a fundamental understanding of matter that enables control and manipulation at the nanoscale;

(2) providing grants to individual investigators and interdisciplinary teams of investigators;

(3) establishing a network of advanced technology user facilities and centers;

(4) establishing, on a merit-reviewed and competitive basis, interdisciplinary nanotechnology research centers, which shall—

(A) interact and collaborate to foster the exchange of technical information and best practices;

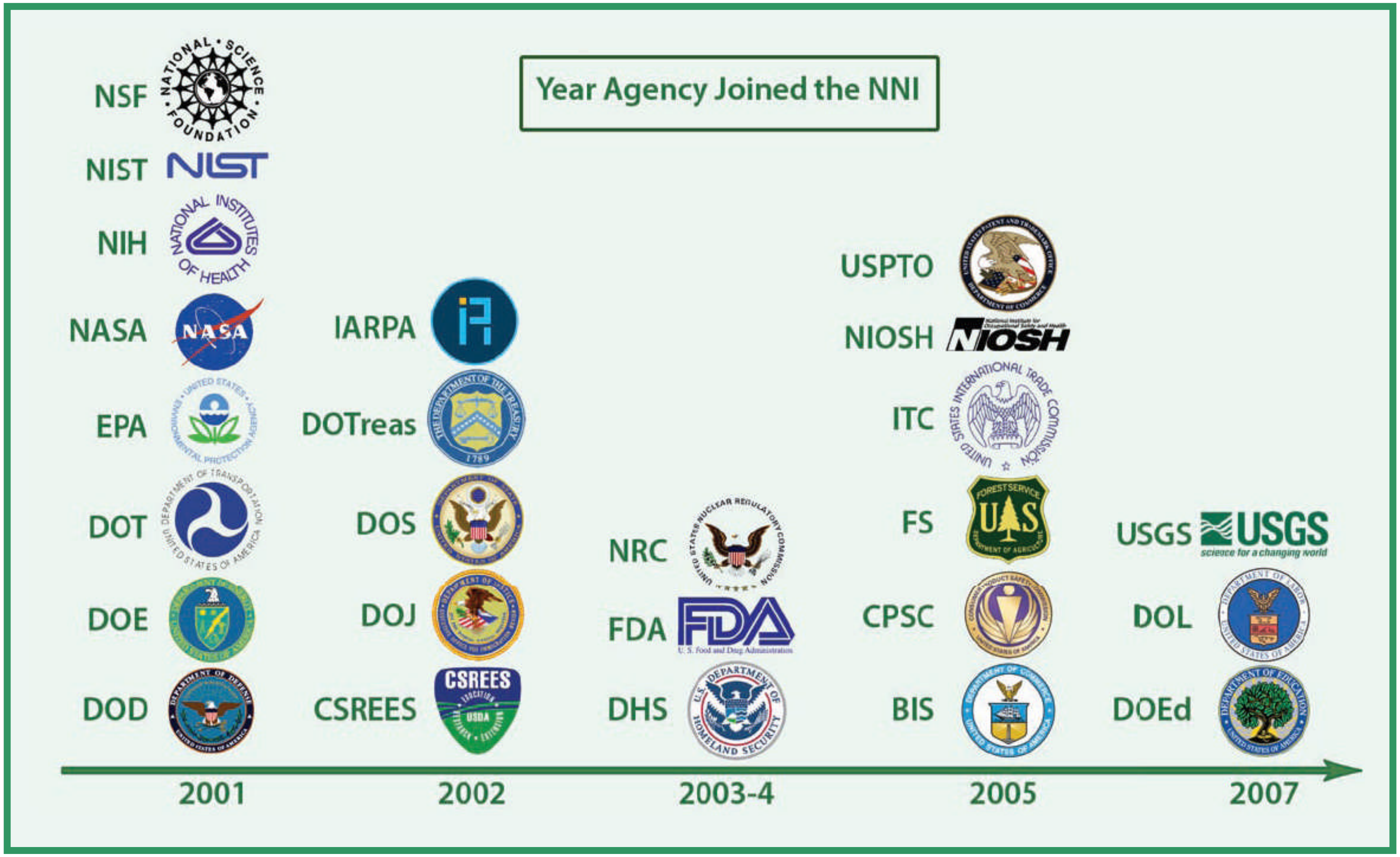
(B) involve academic institutions or national laboratories and other partners, which may include States and industry;

(C) make use of existing expertise in nanotechnology in their regions and nationally;

(D) make use of ongoing research and development at the micrometer scale to support their work in nanotechnology; and

Participating Agencies in the NNI

- *Six agencies developed original 2001 NNI proposal*
- *Now have 25 NSET Subcommittee member agencies*



NSET: Nanoscale Science, Engineering, and Technology

FY 2009 NNI Budget Request

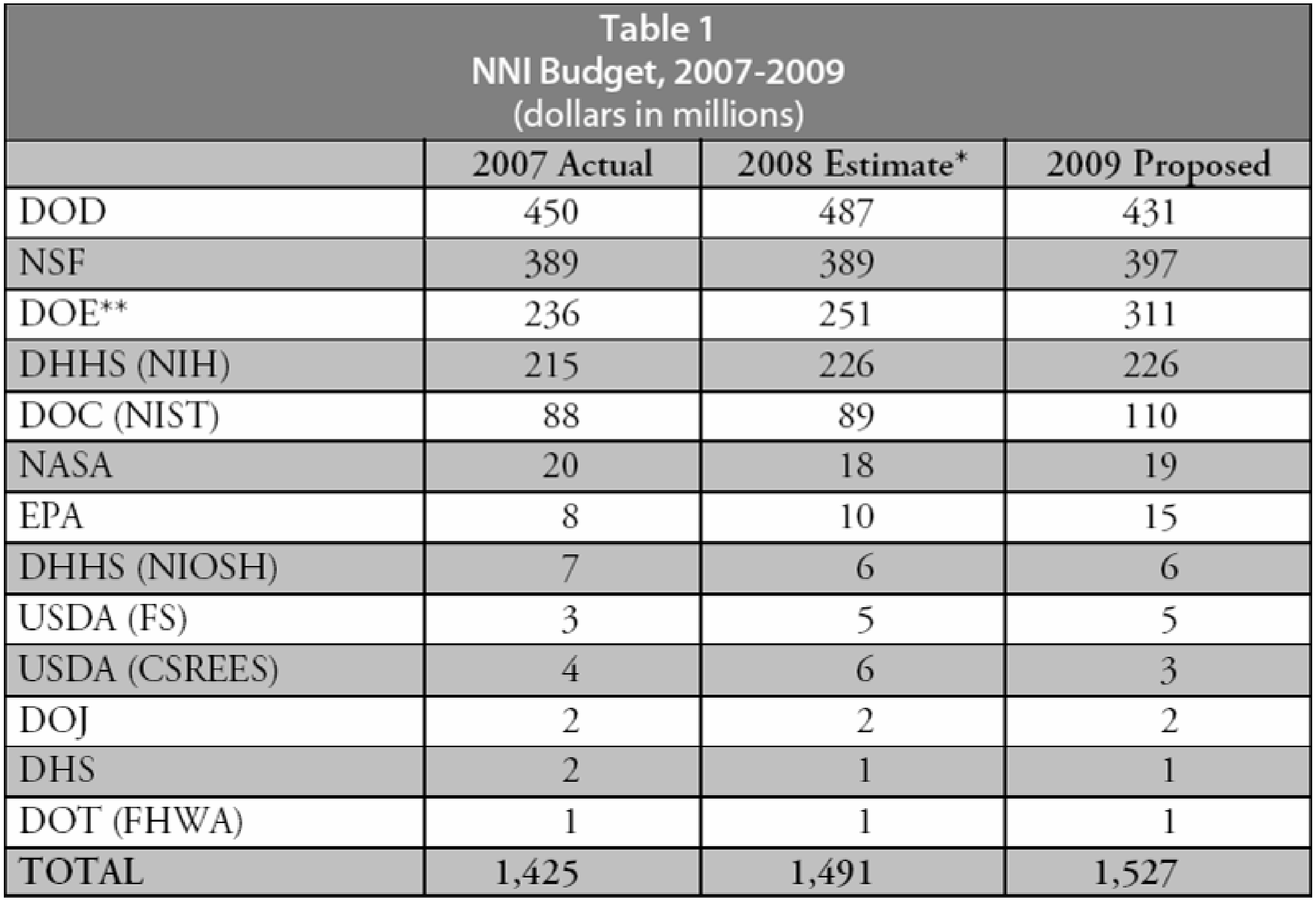


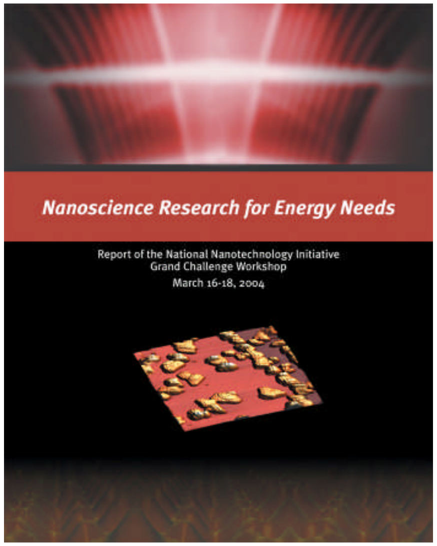
Table 1
NNI Budget, 2007-2009
(dollars in millions)

	2007 Actual	2008 Estimate*	2009 Proposed
DOD	450	487	431
NSF	389	389	397
DOE**	236	251	311
DHHS (NIH)	215	226	226
DOC (NIST)	88	89	110
NASA	20	18	19
EPA	8	10	15
DHHS (NIOSH)	7	6	6
USDA (FS)	3	5	5
USDA (CSREES)	4	6	3
DOJ	2	2	2
DHS	2	1	1
DOT (FHWA)	1	1	1
TOTAL	1,425	1,491	1,527

**Some congressionally directed expenditures are included in the 2007 actual and 2008 estimate values above. The NNI requests for FYs 2007 and 2008, as originally published in the President's FY 2007 and 2008 Budgets, were $1,277 million and $1,447 million, respectively.*

From http://www.nano.gov/html/about/funding.html

Nanoscience Research for Energy Needs



Nanoscience Research for Energy Needs

Report of the National Nanotechnology Initiative
Grand Challenge Workshop
March 16-18, 2004

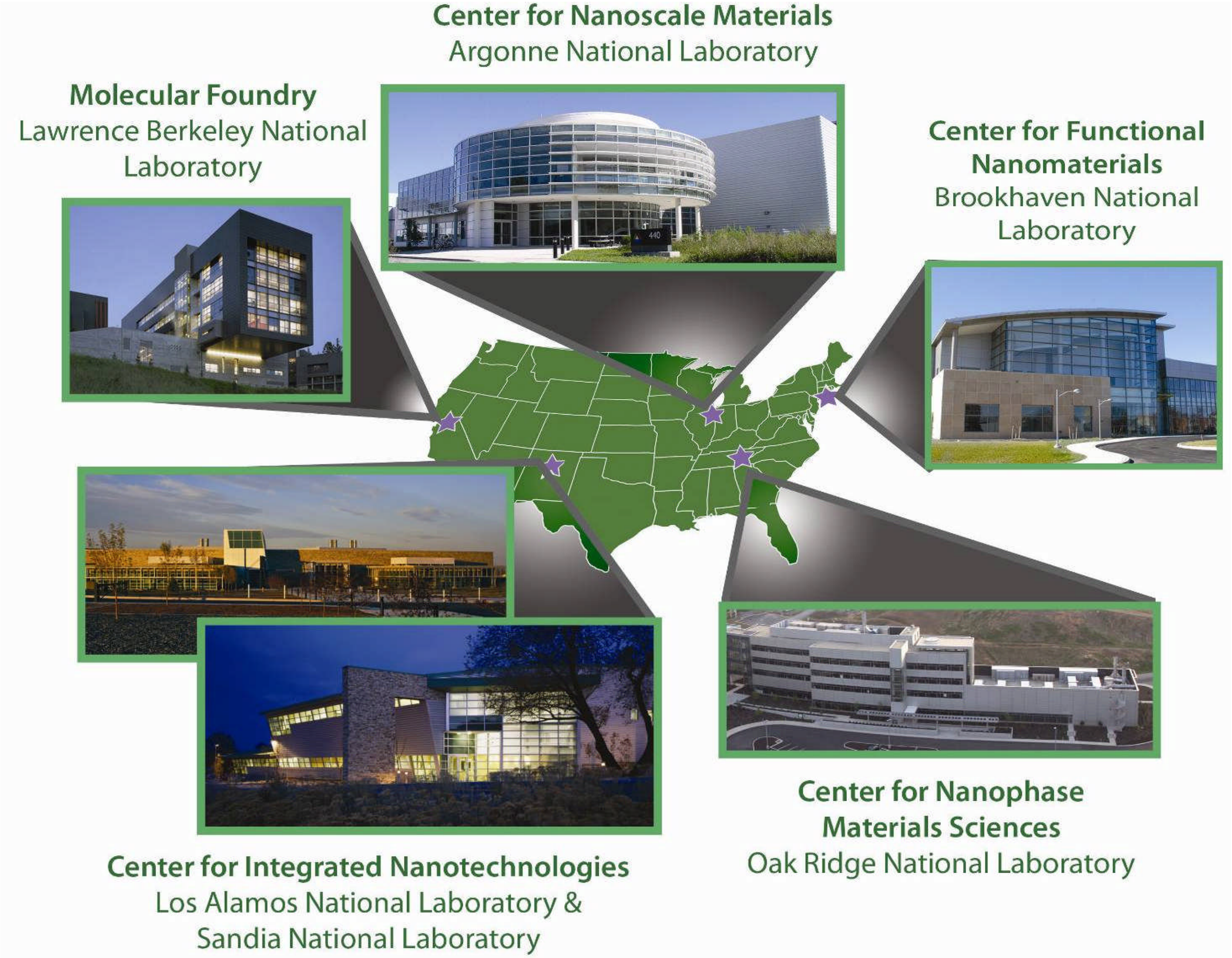
"All the elementary steps of energy conversion take place on the nanoscale. Thus, the development of new nanoscale materials, as well as the methods to characterize, manipulate and assemble them, creates an entirely new paradigm for developing new and revolutionary energy technologies."

The workshop identified nine key areas of energy technology in which nanoscience is expected to have a substantial impact:

- **Scalable methods to split water with sunlight for hydrogen production**
- **Reversible hydrogen storage materials operating at ambient temperatures**
- **Harvesting of solar energy with 20 percent power efficiency and 100 times lower cost**
- **Solid-state lighting at 50 percent of the present power consumption**
- **Highly selective catalysts for clean and energy-efficient manufacturing**
- **Super-strong light-weight materials to improve efficiency of cars, airplanes, etc.**
- **Power transmission lines capable of 1 gigawatt transmission**
- **Low-cost fuel cells, batteries, thermoelectrics, & ultra-capacitors built from nanostructured materials**
- **Materials synthesis and energy harvesting based on the efficient and selective mechanisms of biology**

Five Nanoscale Science User Facilities

DOE/SC's Signature Contribution to the National Nanotechnology Initiative



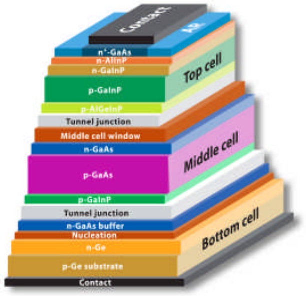
The DOE Nanoscale Science Research Centers

Solar Energy

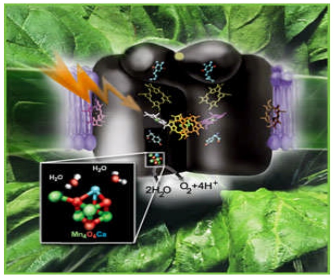
Science Transforming Energy Technologies

Imagine:
- Solar photovoltaics exceeding thermodynamic efficiency limits
- Direct conversion sunlight to chemical fuels

- Sunlight provides by far the largest of all carbon-neutral energy sources – more energy from sunlight strikes the Earth in one hour (4.6×10^{20} joules) than all the energy consumed on the planet in a year.
- Despite the abundance, less than 0.1% of our primary energy derives from sunlight.
- The three routes for using solar energy – conversion to electricity, fuels, or thermal heat – exploit the functional steps of capture, conversion, and storage. They also exploit many of the same electronic and molecular mechanisms.
- The challenge: reducing the costs and increasing the capacity of converting sunlight into electricity or fuels that can be stored or transported (solar electricity, solar fuels, solar thermal systems).
- Silicon: The top commercial solar cells (single crystal silicon) have reached conversion efficiencies of 18%; triple-junction cells with Fresnel lens concentrator technology are approaching efficiencies of 40%. Cost-effective improvements in efficiency dependent on our ability to understand and control phenomena at the nanoscale.
- Photosynthesis: Borrowing nature's design for capturing sunlight – bio-inspired nanoscale assemblies to produce fuels from water and CO_2.



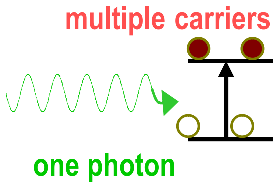
A multi-layered triple-junction solar cell designed to absorb different solar photons.



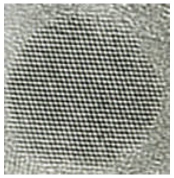
Photosystem II uses solar energy to break two molecules of water into one oxygen molecule plus four hydrogen ions, meanwhile freeing electrons to drive other reactions.

Basic Research Needs for Solar Energy Utilization

The physical, chemical, and biological pathways of solar energy conversion meet at the nanoscale. The ability to create nanoscale structures coupled with advanced characterization, theory, and computational tools suggest that understanding and control of efficient solar energy conversion are within reach.

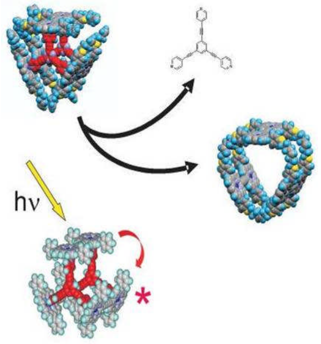


- **Photovoltaics exceeding thermodynamic efficiency limits**
  New concepts, structures, and methods of capturing the energy from sunlight without thermalization of carriers are required to break through the Shockley-Queisser efficiency barrier (32%). Multiple-exciton generation from a single photon is a prime example.
- **Easily manufactured, low-cost polymer and nanoparticle photovoltaic structures**
  “Plastic” solar cells made from molecular, polymeric, or nanoparticle-based structures could provide flexible, inexpensive, conformal solar electricity systems.



Si nanocrystals (7 nm diameter)

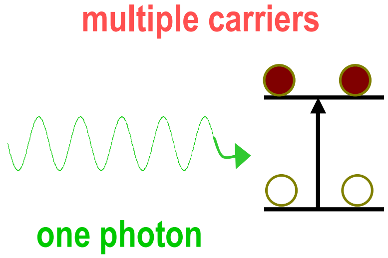
- **Efficient photoelectrolysis**
  Solar fuels generation involves coupling photo-driven single electron steps with fuel-forming, multi-electron processes. No man-made systems approach the performance of naturally found enzymes. Practical solar fuel formation requires construction of new catalyst systems to form hydrogen and oxygen from water and to efficiently reduce carbon dioxide from the air.
- **Defect-tolerant and self-repairing systems**
  Understanding the defect formation in photovoltaic materials and self-repair mechanisms in photosynthesis will lead to defect tolerance and active self-repair in solar energy conversion devices, enabling 20+ years operation.
- **Bio-inspired molecular assemblies systems**
  The design and development of light-harvesting, photoconversion, and catalytic modules capable of self-ordering and self-assembling into an integrated functional unit to realize an efficient artificial photosynthetic system for solar fuels.
- **New experimental and theoretical tools**
  Development of experimental and theoretical tools that could enable the theoretical prediction of optimally performing structures.

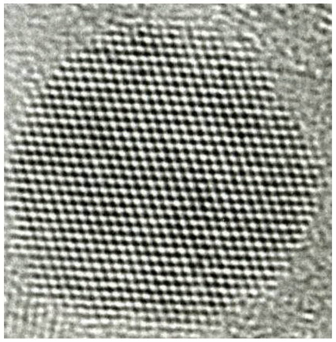


A prism-shaped assembly of three porphyrin molecules that displays enhanced light harvesting capability

Exceeding Today’s Thermodynamic Limits for PV through Multiple Exciton Generation (MEG)

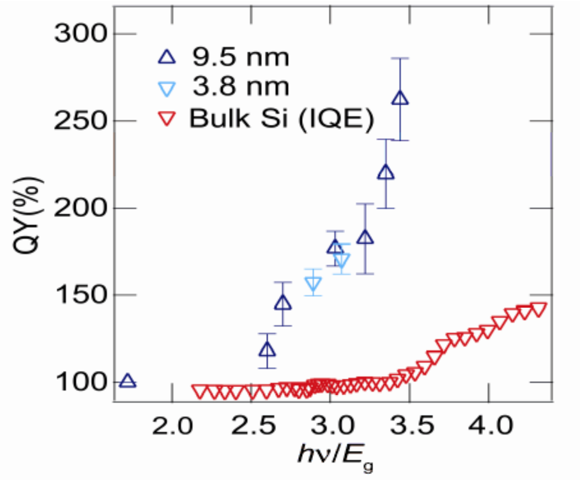
- In a normal PV solar cell, a single solar photon generates a single carrier of electric current – an electron-hole pair, or exciton – in a bulk semiconductor crystal. This process is inefficient because much of the energy of the solar photon is lost as excess heat.
- Nanocrystalline semiconductor samples have been shown to exhibit a remarkable effect, known as multiple exciton generation (MEG), in which a single photon can generate 2, 3, 4 or more excitons. MEG has been demonstrated in a wide range of nanostructured semiconductors; most recently in pure silicon, which is abundant, non-toxic, and currently utilized for over 90% of the PV market.
- The fundamental mechanism of MEG is not well understood and further work, comparing experimental results with the latest theoretical models is required.
- Critical issues remain before MEG can be harnessed in a real solar cell, including the efficient separation and harvesting of the charge carriers to produce electrical current. But current estimates indicate that if realized, an MEG PV cell might achieve 50% efficiency – a revolutionary advance in our ability to harness renewable energy from the sun.





Si nanocrystals (7 nm diameter)

MEG has the potential to dramatically increase PV efficiency. With 2 charge carriers per photon in silicon, efficiency can be raised to over 40%.

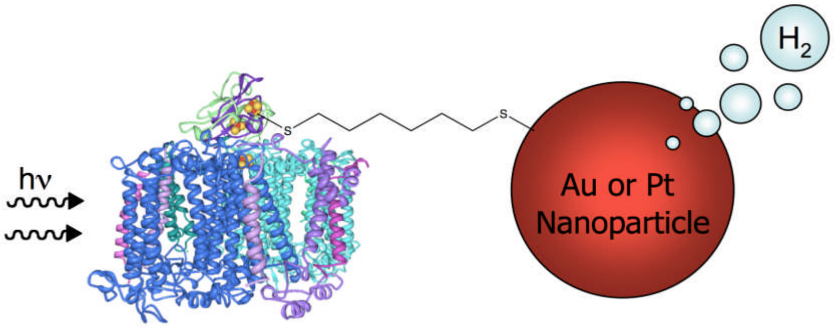


A. Nozik et al., NREL; V. Klimov et al., LANL

Efficient Solar Hydrogen Production by a Hybrid Photo-catalyst System

Molecular Wire

Delivers the highly reducing electrons to the catalyst rapidly and efficiently



Photosystem I

Efficient solar absorber which generates a stable charge-separated state, a source of highly reducing electrons.

Catalyst

Uses the photo-generated electrons to reduce protons from solution into hydrogen (H_2).

R. A. Grimme, C. E. Lubner, D. A. Bryant and J. H. Golbeck, *J. Am. Chem. Soc.*, 2008, *130*, 6308-6309

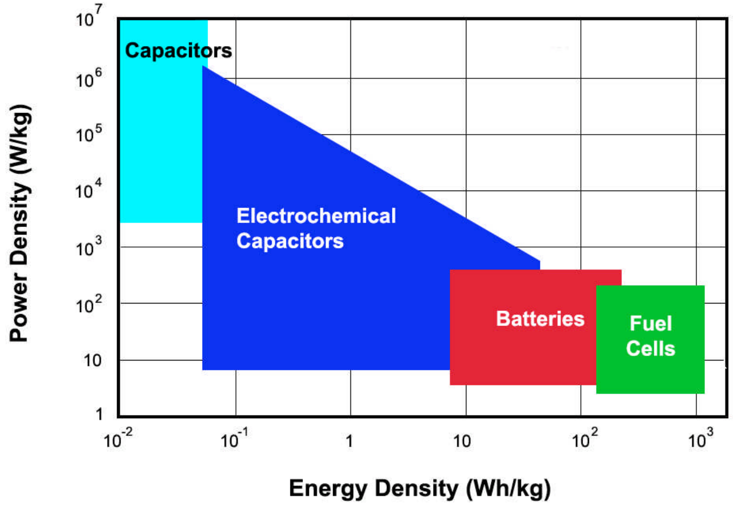
- Solar energy is an attractive source for large scale hydrogen production. Robust, inorganic catalyst systems such as platinized TiO_2 have been used to generate hydrogen from sunlight, but efficiency is low because they can only use the UV portion of the solar radiation. Natural photosynthetic systems such as Photosystem I (PS I) can absorb ~45% of solar spectrum, but are coupled indirectly and inefficiently to a non-robust, oxygen-sensitive hydrogenase to generate hydrogen.
- In a novel strategy that combines the best of both worlds, a synthetic molecular wire, consisting of a Fe_4-S_4 cluster and an organic dithiol, is used to covalently link PS I with the Au or Pt nanoparticles. This provides a rapid, efficient pathway for shuttling photo-generated electrons to the inorganic nanocatalyst.
- Upon illumination, the PS I-Molecular Wire-Nanocatalyst hybrid system generates 8 H_2 per PS I per second over a period of 12-16 hours (with cytochrome c_6 as electron donor).
- This represents a new benchmark in the efficiency of hydrogen production by use of modified or hybrid photosynthetic systems. To compare, a genetically engineered PS I-hydrogenase gene fusion generates 0.0045 H_2 per PS I per second, and platinized chloroplasts generate 0.045 H_2 per PS I per second.

Electrical Energy Storage

Science Transforming Energy Technologies

Imagine:
- Solar and wind providing over 30% of electricity consumed in U.S.
- The number of all-electric/plug-in hybrid vehicles on the road exceeding gasoline-powered vehicles

- Many renewable energy sources such as wind and solar are *intermittent* — To make these energy sources truly effective and integrate them into the electrical grid, we need significant breakthroughs in electrical energy *storage* technologies.
- Electrical energy storage (EES) devices with substantially higher energy and power densities and faster recharge times are needed if all-electric/plug-in hybrid vehicles are to be deployed broadly.
- EES devices: batteries—store energy in chemical reactants capable of generating charge; electrochemical capacitors—store energy directly as charge.
- Fundamental gaps exist in understanding the atomic- and molecular-level processes that govern operation, performance limitations, and failure of these devices.

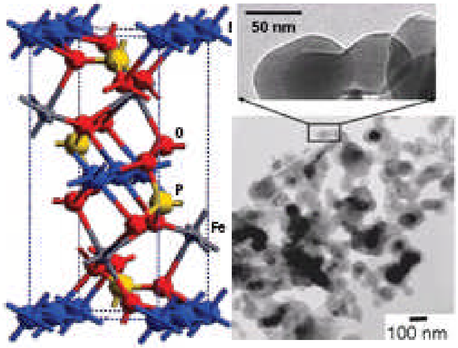


Energy and power densities of various energy storage devices. Electrochemical capacitors bridge between batteries and conventional capacitors.

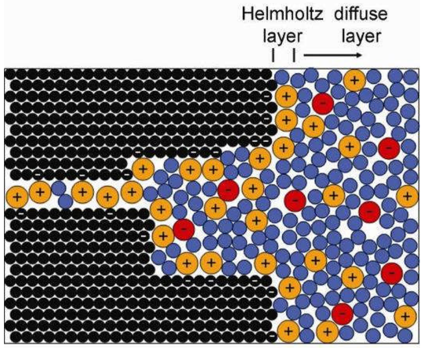
Basic Research Needs for Electrical Energy Storage

Knowledge gained from basic research in chemical and materials sciences is needed to surmount the significant challenges of creating radical improvements for electrical energy storage devices for transportation use, and to take advantage of large but transient energy sources such as solar and wind.

- **Nanostructured electrodes with tailored architectures**
  Fundamental studies of the electronic conductivity of $LiFePO_4$ led to the discovery of doping-induced conductivity increases of eight orders of magnitude. This research discovery led to the development of high power-density Li-ion batteries by A123 Systems to power electric vehicles such as the Chevy Volt and the Th!nk.
- **The promise of higher battery power via conversion reactions**
  Current batteries operate with slightly less than one electron per redox center with typical electrode materials. New research on conversion reactions is looking at advanced materials to yield up to six electrons per redox center, allowing a large increase in battery power density. An example of such a reaction using cobalt is: $\mathbf{CoO_2 + 2\,e^- + 2\,Li^+ \leftrightarrows CoO + Li_2O}$. Other reactions using sulfides, phosphides and flourides are being investigated.
- **Multifunctional material architectures for ultracapacitors:**
  Basic research in materials for capacitors is enabling the development of multi-functional nanoporous structures and facilitating the understanding of charge storage mechanisms at surfaces. Ultracapacitors complement battery power by allowing very rapid charge and discharge cycles and the high surface area of nanostructures yields high charge storage capacity.
- **Understanding behavior in confined spaces:**
  The behavior of electrolytes as a function of pore size in electric double layer capacitors is not well understood but crucial to enabling higher charge densities. Nanometer-scale pores offer high surface areas but create an increased importance of the Helmholz layer in the overall capacitance and affect the dynamics of the charge cycle.



$LiFePO_4$ structural model and nanostructure

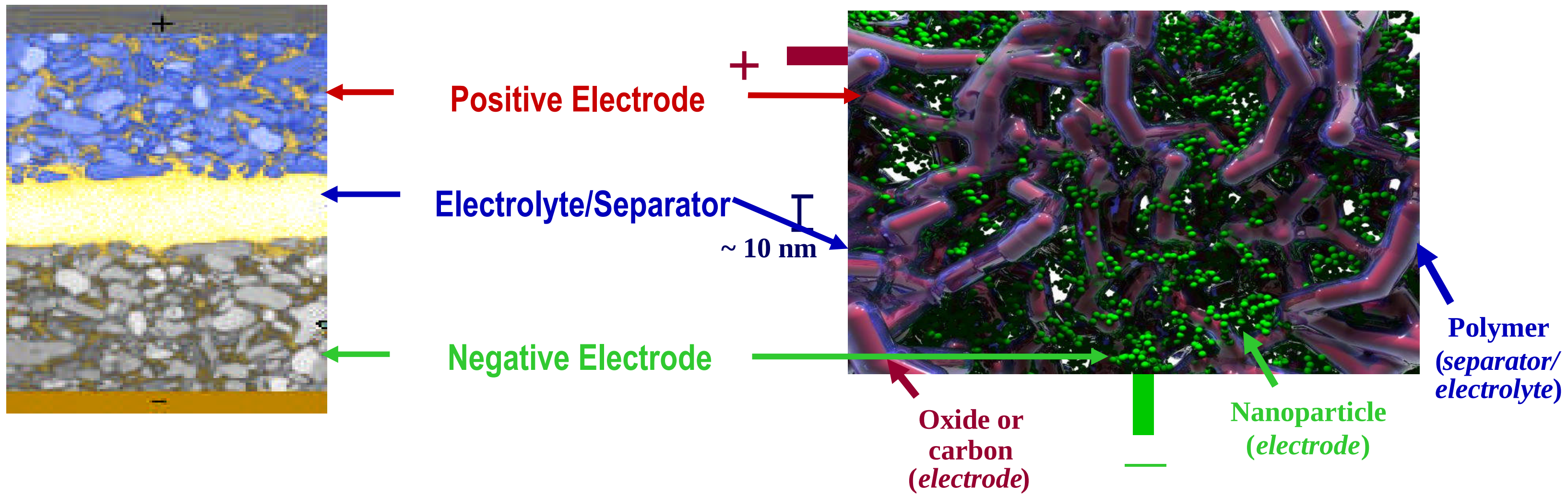


Ion solvation changes with pore size during electric double layer charging (electrode, black; solvent, blue; cation, orange; anion, red)

Nanomaterials are Key to Improved Battery and Capacitor Storage

Current Battery Structure

3-D Nanoscale Electrochemical Battery Cell Structure



- Current battery consists of 2-dimensional structures of electrodes separated by electrolytes in a planar geometry. Nanostructured architectures for power storage (batteries, fuel cells, ultracapacitors, photovoltaics) provide many advantages over existing technologies to minimize power losses, improve charge/discharge rates and enhance energy densities.
- Three-dimensional structures can further revolutionize the ability of these devices to accumulate, store and release charge at unprecedented levels. Electrodes in these architectures will consist of interconnected ~10nm domains and mesopores (10-50nm). Ultrathin, conformal and a pinhole-free separator/electrolyte are electrodeposited onto the electrode nanoarchitecture. Low melting point metals (mp<200°C) or colloids fill the remaining mesoporous volume. These designs have the potential for higher performance by separating the length scales for electronic and ionic transport, thereby accessing previously unachievable power and energy densities.
- In addition, new nanoscale materials could be produced by self-assembly. Nature uses self-assembly to produce materials with specific functionality. These bio-inspired concepts have potential for the development of novel nanomaterials and architectures to enhance the development of chemical energy storage systems. The ability to apply these techniques to the fabrication of battery electrodes could be revolutionary.

Long et al., *Chem. Rev* **104**, 4463–4492, 2004; Fischer et al., *Nano Letters*, 7, 281, 2007

Bioenergy

Science Transforming Energy Technologies

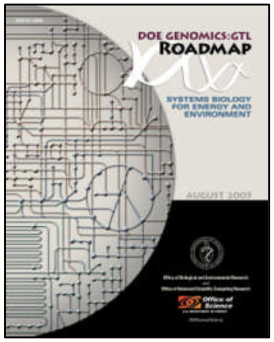
Imagine: • A sustainable, carbon-neutral biofuels economy that meets over 30% of U.S. transportation fuel needs (cars and trucks) without competing with food, feed, or export demands.

- The development of biofuels—especially lignocellulose biofuels—represents a major scientific opportunity that can strengthen U.S. energy security and protect the global environment.
- Biofuels can be essentially carbon-neutral or even carbon-negative – as plant feedstocks grow, they reabsorb the carbon dioxide emitted when biofuels are burned, and they can store carbon dioxide in their roots.
- To produce lignocellulosic biofuels, or biofuels from plant fiber, cost-effectively on a commercial scale will require transformational breakthroughs in basic science focused on both plants and microorganisms and processing methods.
- The challenge is the recalcitrance of the plant cell wall – plant fiber has evolved over the millennia to be extremely resistant to breakdown by biological or natural forces.
- Many scientists believe we are within reach of major breakthroughs in developing cost-effective methods of producing liquid fuels from lignocellulose in the near- to mid- term.
- The environmental sustainability aspects associated with bioenergy derived from feedstock crops – water, soil quality, land-use changes, genetically altered plants, carbon balance – must be addressed proactively.

DOE Bioenergy Research Centers

Grand Science Challenges:

- Using a systems biology approach, understand the principles underlying the structural and functional design of living systems — plants and microorganisms.
- Develop the capability to model, predict, and engineer optimized enzymes, microorganisms, and plants — bioenergy and environmental applications.

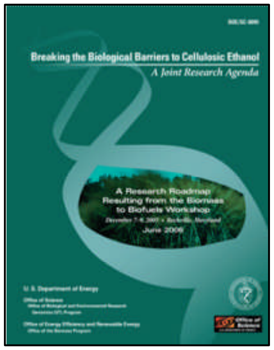


DOE GENOMICS:GTL
ROADMAP
SYSTEMS BIOLOGY FOR ENERGY AND ENVIRONMENT
AUGUST 2005
Office of Science

“Basic Research Needs” for cellulosic ethanol (and other biofuels) production:

The emerging tools of systems biology are being used to help to overcome current obstacles to bioprocessing cellulosic feedstocks to ethanol and other biofuels– metagenomics, synthetic biology, high-throughput screening, advanced imaging, high-end computational modeling.

- **DOE BioEnergy Science Center** – led by Oak Ridge National Laboratory, includes 9 partnering institutions. This center focuses on the resistance of plant fiber to breakdown into sugars and is studying the potential energy crops poplar and switchgrass.
- **DOE Great Lakes Bioenergy Research Center** – led by University of Wisconsin-Madison in partnership with Michigan State University, includes 6 other partnering institutions. This center is studying a range of plants and is exploring plant fiber breakdown and how to increase plant production of starches and oils, which are more easily converted to fuels. This Center also focuses on sustainability, examining the environmental and socioeconomic implications of moving to a biofuels economy.
- **DOE Joint BioEnergy Institute** – led by Lawrence Berkeley National Laboratory, includes 5 other partnering institutions. This center focuses on “model” crops of rice and *Arabidopsis thaliana* in the search for breakthroughs in basic science and is exploring microbial-based synthesis of fuels beyond ethanol.



Breaking the Biological Barriers to Cellulosic Ethanol
A Joint Research Agenda
A Research Roadmap Resulting from the Biomass to Biofuels Workshop
June 2006
U. S. Department of Energy
Office of Science

Nanoscale Science for Biofuel Production

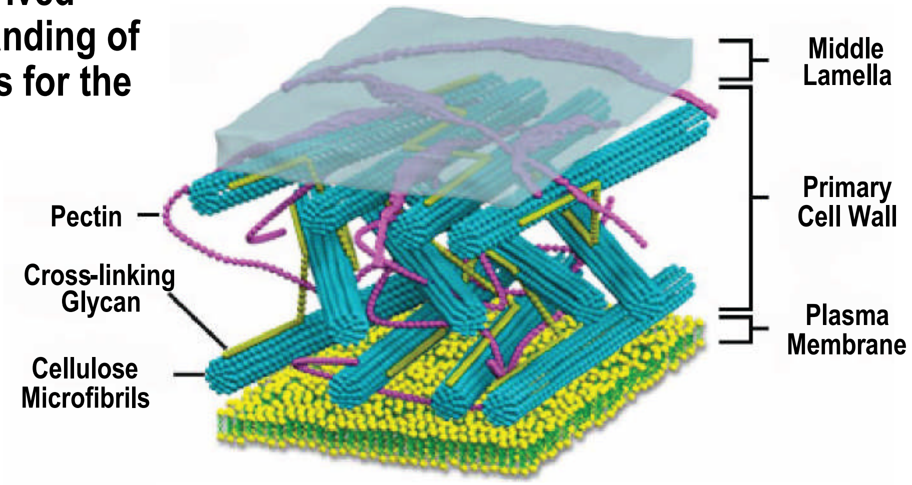
The biochemical or catalytic conversion of biological derived feedstocks into chemical fuels requires greater understanding of the structure of the plant cell wall and design of catalysts for the deconstruction of cellulose and lignin at the nanoscale.

- **The plant cell wall on the nanoscale**

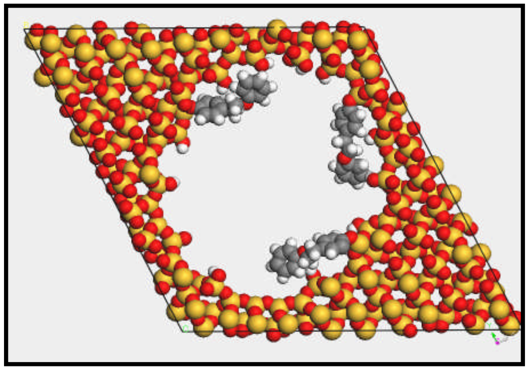
  The detailed structure of the plant cell wall is not well understood at the nanoscale. Applications of the tools of the physical sciences (x-ray and neutron scattering, laser spectroscopies, imaging microscopies, etc.) are needed to characterize the complex physical and chemical structure of the cell wall in order to attack the recalcitrance problem.

- **Design of catalysts for biofuels production**

  The catalytic route to biofuels seeks to design advanced catalysts on the nanoscale that will deconstruct cellulose and lignin into smaller chemical building blocks that can then be reformed into a broad range of fuels, both alcohols and hydrocarbon fuels (gasoline and diesel). There is a critical need to design and understand reactions that remove oxygen and increase the hydrogen-carbon ratio - new classes of nanoscale catalysts are needed for both these types of conversions.



A plant cell wall, which is the raw material for biofuels, is a complex nanostructure of polymers not well understood at the molecular scale.

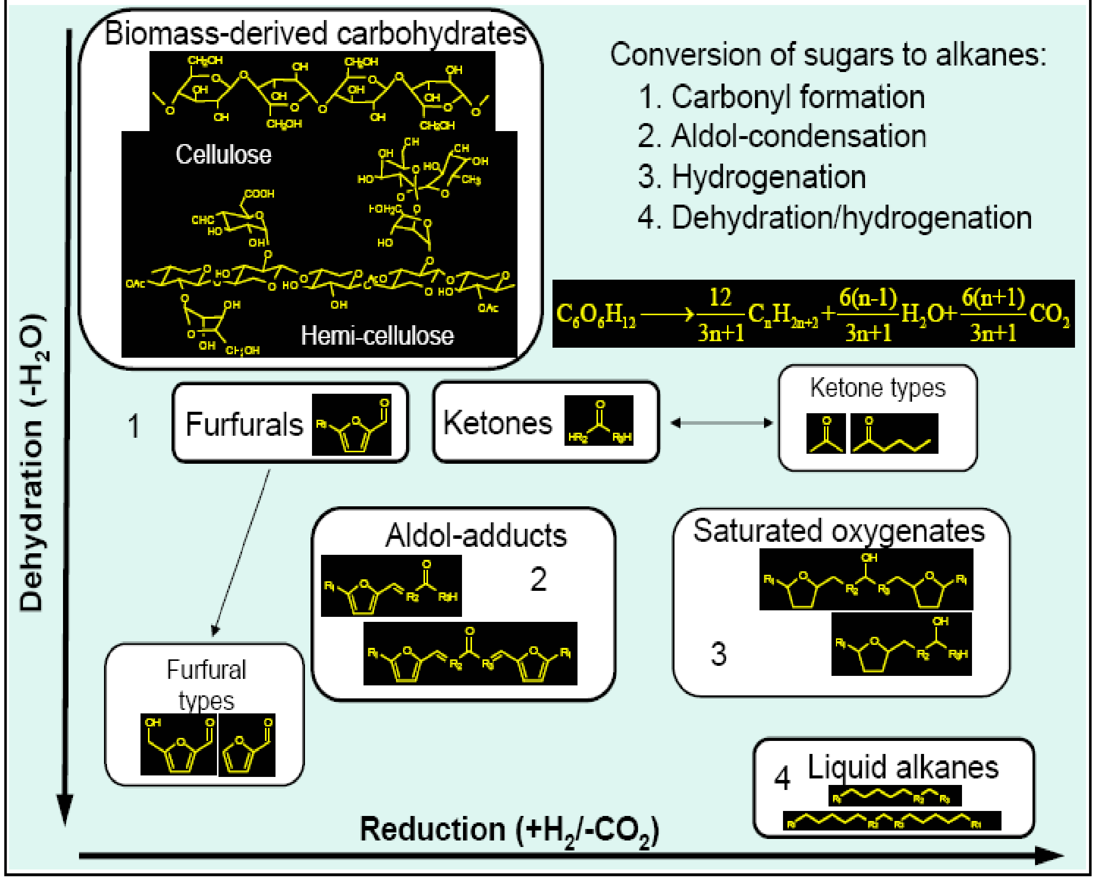


Nanoscale confinement of model compound for lignin within mesoporous silica, which can serve as a support for nanoscale deconstruction catalysts.

Nanoscale Catalysts for Plant-derived Fuels

Efficient conversion of biomass into energy products is being pursued through the development of new nanoscale catalysts and improved methods for converting plant biomass into the next generation of fuels.

Process and Discovery Chemical Catalysis for Biofuels Production



Biomass-derived carbohydrates

Cellulose

Hemi-cellulose

Conversion of sugars to alkanes:

1. Carbonyl formation
2. Aldol-condensation
3. Hydrogenation
4. Dehydration/hydrogenation

$$C_6O_6H_{12} \longrightarrow \frac{12}{3n+1} C_nH_{2n+2} + \frac{6(n-1)}{3n+1} H_2O + \frac{6(n+1)}{3n+1} CO_2$$

1 Furfurals

Ketones

Ketone types

Furfural types

Aldol-adducts 2

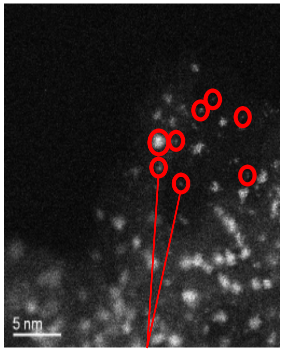
Saturated oxygenates 3

4 Liquid alkanes

Dehydration ($-H_2O$)

Reduction ($+H_2/-CO_2$)

- Biomass-derived carbohydrates and the oxygenated components of bio-oils contain excess functionality (e.g., C-OH and/or C=O groups) for use as fuels and chemicals.
- The design of new catalysts will enable control of this the functionality in the final product, to create a variety of desired next generation fuels..



Pt-Re bimetallic alloys

High-resolution TEM of Nano-particles of Pt-Re on a high surface area carbon support (~300 m^2/g). Pt-Re and Pt-Ru biometallic alloys† on carbon supports have enabled low-temperature catalytic routes for conversion to synthesis gas suitable for Fischer-Tropsch synthesis of alkanes with targeted structure and molecular weight.

Agnew. Chem. Int. Ed. **46**: 7164-83 (2007)

Nuclear Energy

Science Transforming Energy Technologies

Imagine:
- Abundant fossil-free power with zero greenhouse gas emissions
- A closed fuel cycle

- Good for both energy security and the environment:
  - Reduces Nation’s dependence on fossil fuels and imports
  - No carbon dioxide or toxic emissions
- Currently provides 20% of nation’s electricity and could provide much more
- Key challenge is handling spent fuel – and related problem of proliferation
- Advances in science and engineering can provide major reduction in spent fuel by “closing” fuel cycle:
  - Recycling spent fuel and burning it in fission reactors
  - Reducing storage requirements by up to 90%
  - Can extend fuel supplies 100X; energy remaining in “spent” fuel
  - New recycling technologies could reduce nuclear materials proliferation concern

Performance of materials and chemical processes under extreme conditions is a limiting factor in all areas of advanced nuclear energy systems

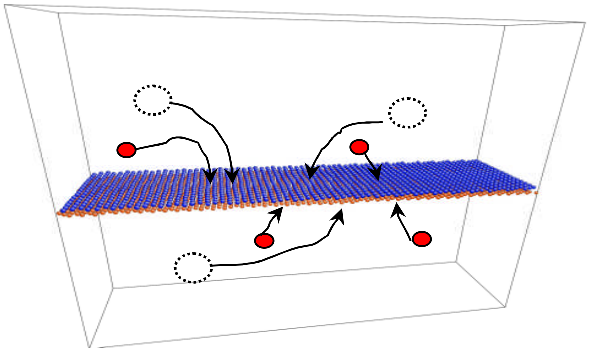
Basic Science for Advanced Nuclear Energy Systems

Fundamental Challenge: To understand and control chemical and physical phenomena in complex systems from femto-seconds to millennia, at temperatures to 1000 ^{o}C and for radiation doses to hundreds of displacements per atom.

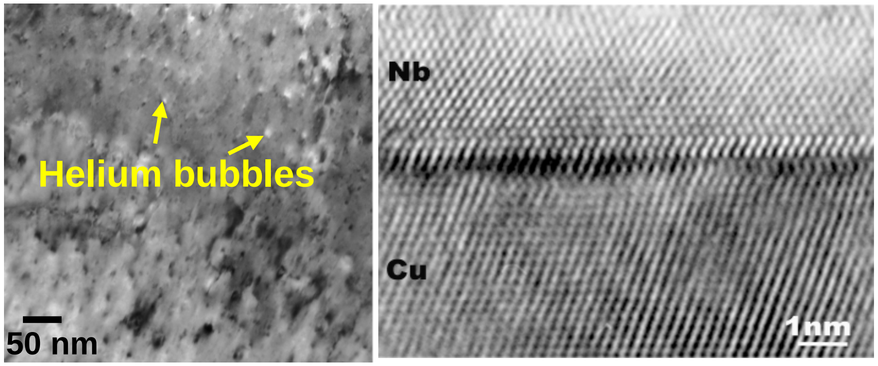
Basic Science:

- Research in Basic Energy Sciences
  - Materials and chemistry under extreme temperature, pressure, corrosive, and radiative environments; chemistry at interfaces and in complex solutions; separations science; advanced actinide fuels; nanoscale synthesis and characterization for design of materials and interfaces with radiation, temperature and corrosion resistence; predictive modeling and simulation
  - Workshop: Basic Research Needs for Advanced Nuclear Energy Systems, July 31-August 2, 2006.
- Research in Nuclear Physics
  - Nuclear measurements (neutron and charged particle beam accelerator experiments, cross-section measurements), nuclear data (cross-section evaluation, actinide nuclear data), nuclear theory and computation
  - Nuclear Physics and Related Computational Science R&D for Advanced Fuels Cycles Workshop, August 10-11, 2006.
- Research in Advanced Scientific Computing
  - Developing and scaling next-generation multiscale and multiphysics codes; advanced modeling and simulation to improve future reactor designs; reactor core simulations; fluid flow and heat transfer; and radiation induced microstructural evolution of defects.
  - Workshop on Simulation and Modeling for Advanced Nuclear Energy Systems, August 15-17, 2006.

Interface-Moderated Radiation Resistance for Advanced Nuclear Energy Systems



Molecular simulations showed that the interfaces in Cu/Nb layered structures possess a strong affinity for defects, thereby catalytically removing them from the bulk of the material.



Pure Cu

5 nm layer thickness Cu-Nb multilayer

Room temperature helium implantation to a maximum concentration of 8 at.%

- The clustering of vacancies and interstitials following prolonged irradiation leads to permanent damage of structural metals.
- Using computer modeling it was discovered that certain interfaces have the ability to “sweep up” point defects and heal the damage.
- To verify this observation, nanolayered Cu-Nb laminates with closely-spaced, tailored interfaces were produced and subjected to high doses of radiation. As predicted, these structures demonstrate a remarkable resistance to radiation damage.
- In pure Cu irradiated with He+ ions, helium bubbles quickly form and the material swells. On the contrary, the Cu-Nb nanolayered laminate remains structurally intact with no bubbles.
- The interfaces in nanolayered composites attract, absorb and annihilate radiation-induced point defects, thereby making these materials stable under extreme irradiation conditions.

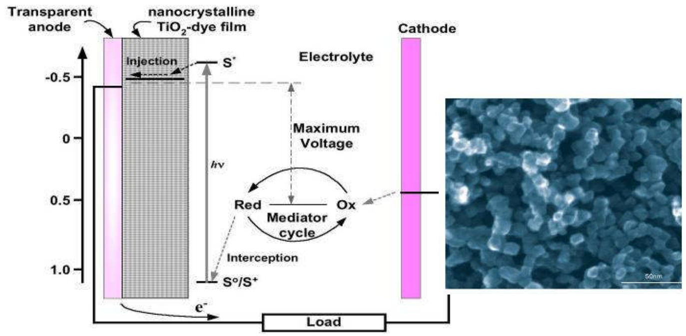
A. Misra and R.G. Hoagland, LANL

Hydrogen Economy

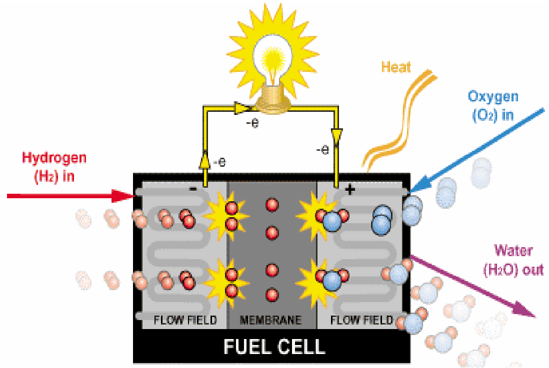
Science Transforming Energy Technologies

Imagine:
- A hydrogen economy that provides ample and sustainable energy, flexible interchange with existing energy technologies, and a diversity of end uses to produce electricity through fuel cells.

- The hydrogen economy is a compelling vision, as it provides an abundant, clean, secure and flexible energy carrier. However, it does not operate as an integrated network, and it is not yet competitive with the fossil fuel economy in cost, performance, or reliability.
- There have been significant accomplishments in basic and applied hydrogen research in the past years leading to major advances in hydrogen production, storage, and fuel cell technologies.
- Specifically, hydrogen production from natural gas has met its 2010 target of $3/gge (gallon of gasoline equivalent); hydrogen storage capacities have been increased by 50%; and fuel cells costs have been decreased by 60%.
- But fundamental science breakthroughs are needed in order to meet the longer-term (2015 and beyond) technological readiness requirements.



Dye-Sensitized photoelectrochemical cells for solar hydrogen production via water electrolysis. The cell consists of a highly porous thin layer of titanium dioxide nanocrystal aggregates.

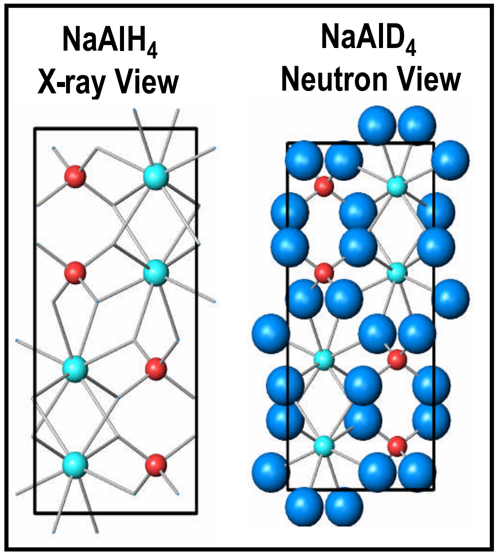


$2H_2 + O_2 \rightarrow 2H_2O$ + electrical power + heat

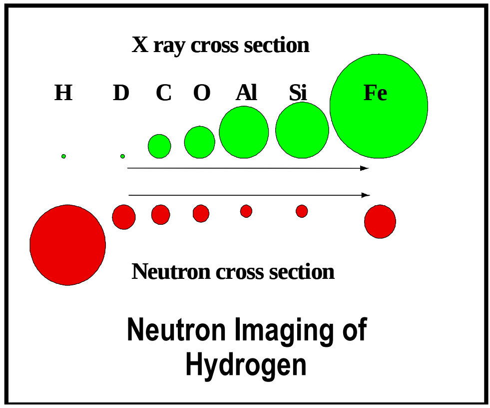
Basic Research Needs for Hydrogen Production, Storage and Use

The hydrogen economy offers a vision for energy management in the future. Research needs are quintessentially *nano*: catalysis, hydrogen storage materials, and electrode assemblies for fuel cells all depend on nanoscale processes and architecture to achieve high performance.

- **Hydrogen Production**
  - **Fossil Fuel Reforming:** Catalytic mechanisms and design, high temperature gas separation
  - **Solar Photoelectrochemistry/Photocatalysis:** Light harvesting, charge transport, chemical assemblies, bandgap engineering, interfacial chemistry, catalysis, organic semiconductors, theory and modeling
  - **Bio- and Bio-inspired H_2 Production:** Microbes & component redox enzymes, nanostructured 2D & 3D hydrogen/oxygen catalysis, sensing, energy transduction, biological and biomimetic H_2 production systems
  - **Nuclear and Solar Thermal Hydrogen:** Thermodynamic data and modeling for thermochemical cycle (TC), high temperature materials: membranes, TC heat exchanger materials, gas separation, improved catalysts
- **Hydrogen Storage**
  - **Metal Hydrides and Complex Hydrides:** Degradation, thermophysical properties, effects of surfaces, processing, dopants, and catalysts in improving kinetics, nanostructured composites
  - **Nanoscale/Novel Materials:** Finite size, shape, and curvature effects on electronic states, thermodynamics, and bonding, heterogeneous compositions and structures, catalyzed dissociation and interior storage phase
  - **Theory and Modeling:** Model systems for benchmarking against calculations at all length scales, integrating disparate time & length scales, first principles methods applicable to condensed phases
- **Fuel Cells**
  - **Electrocatalysts and Membranes:** Oxygen reduction cathodes, minimize rare metal usage in cathodes and anodes, synthesis and processing of designed triple percolation electrodes
  - **Low Temperature Fuel Cells**: 'Higher' temperature proton conducting membranes, degradation mechanisms, functionalizing materials with tailored nano-structures
  - **Solid Oxide Fuel Cells:** Theory, modeling and simulation, validated by experiment, for electrochemical materials and processes, new materials-all components, novel synthesis routes for optimized architectures, advanced in-situ analytical tools

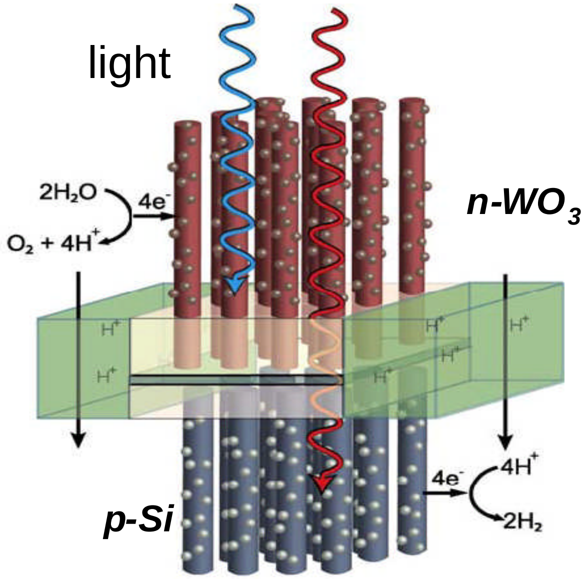

$NaAlH_4$ X-ray View

$NaAlD_4$ Neutron View



Neutron Imaging of Hydrogen

Sunlight Driven Hydrogen Formation

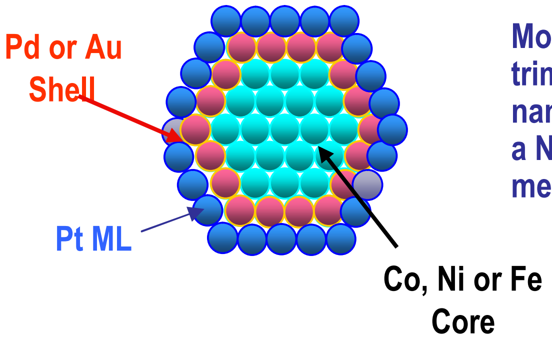


Solar powered water splitting scheme incorporating two separate semiconductor rod-array photoelectrodes that sandwich an electronically and ionically conductive membrane.

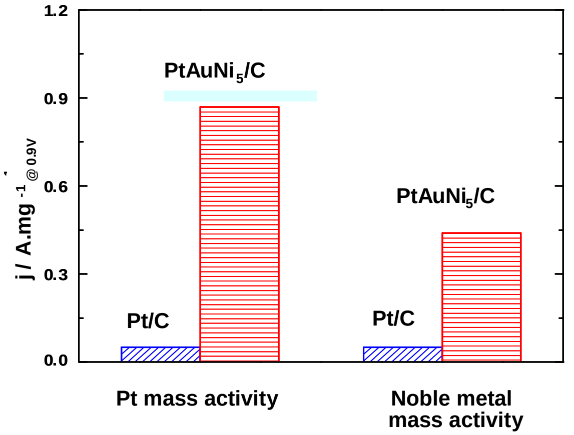
- Traditional photoelectrochemical water splitting is limited by a cumbersome planar, two electrode configuration for light absorption and H_2 and O_2 generation. Current generation of semiconductors used for absorbing visible solar spectrum are intrinsically unstable. Precious metals (Pt, Pd) are needed for H_2 evolution.
- One key constraint in photon absorbers for solar energy conversion is that the samples need to be thick enough for sufficient absorption, yet pure enough for high minority carrier length and photocurrent collection.
- New nanorod configuration was recently developed to orthogonalize the directions of light absorption and charge carrier collection, i.e. it separates longitudinal light absorption from transverse carrier diffusion to reactive surface.
- The short diffusion paths to reaction broadens usable materials to include earth abundant, resistive semiconductors. Opposing nanorod configuration with conductive ion membrane allows for compact device with inherent separation of O_2 and H_2 gas.
- High surface-to-volume ratio of nanostructure decreases current density and permits use of broad range of new metals as sites for H_2 and O_2 evolution.

Spurgeon JM, Atwater HA, Lewis NS, *Journal of Physical Chemistry C,* 112, 6186-6193 (2008).

Tri-Metallic-Decorated Surface Alloys: A New Catalytic Paradigm



Model structure of a trimetallic layered nanoparticle showing a Ni core and noble metal shell.



The activity measurements show trimetallic particles being about 20x more active than monometallic ones (on a Pt-mass basis.)

M.H. Shao, K. Sasaki, R.R. Adzic, *J. Am. Chem. Soc.* 128 (2006) 3526-3527.
M. H. Shao, K. Sasaki, P. Liu, R.R. Adzic, *Z. Phys. Chem.* 221 (2007) 1175-1190.

- A conceptual search for stable electrocatalytic alloys for both anodes (hydrogen oxidation) and cathodes (oxygen reduction) in fuel cells led to the development of novel catalyst nanostructures containing three components: a non-noble metallic core, a palladium or gold shell, and a platinum top monolayer.
- Theoretical electronic structure calculations supported the hypotheses that these new structures would present novel properties, particularly higher activity for both hydrogen and oxygen reactions. Empirical know-how projected that the stability of the tri-metallic particle would be larger than a mono or bimetallic particle, but the challenge was to synthesize and maintain the electrocatalytic functions during the cathodic reduction.
- Recent results successfully confirmed the predictions, providing evidence that the three-layered catalysts can be synthesized and that their activity is 20 times higher than that of regular Pt catalysts. The stability under cathodic reduction is better than initially expected (XANES data show a smaller extent of Pt oxidation in trimetallic particles than in monometallic ones). The concept of interlayer Au to suppress oxidation of Pt can be applied to other alloys of non-Pt electrodes, potentially eliminating in the future the need for such noble metal in electrocatalysts.

Energy Frontier Research Centers

Engaging the Nation’s Intellectual and Creative Talent

Innovative basic research to accelerate scientific breakthroughs needed to create advanced energy technologies for the 21st century

The DOE Office of Science announced the Energy Frontier Research Centers (EFRCs) program. EFRC awards are $2–5 million/year for an initial 5-year period. Universities, labs, and other institutions are eligible to apply.

Energy Frontier Research Centers will pursue fundamental basic research in areas such as:

- Solar Energy Utilization
- Catalysis for Energy
- Electrical Energy Storage
- Solid State Lighting
- Superconductivity
- Biofuels
- Geosciences for Nuclear Waste and CO2 Storage
- Advanced Nuclear Energy Systems
- Combustion of 21st Century Transportation Fuels
- Hydrogen Production, Storage, and Use
- Materials Under Extreme Environments

Concluding Remarks

“To keep America competitive into the future, we must trust in the skill of our scientists and engineers and empower them to pursue the breakthroughs of tomorrow . . . This funding is essential to keeping our scientific edge.”

President George W. Bush
State of the Union Address
January 28, 2008

The only truly unlimited resource we have is our ideas.