Solar Photochemistry

Portfolio Description
This activity supports molecular-level research on solar energy capture and conversion in the condensed phase and at interfaces. These investigations of solar photochemical energy conversion focus on the elementary steps of light absorption, electrical charge generation, and charge transport within a number of chemical systems, including those with significant nanostructured composition. Supported research areas include organic and inorganic photochemistry and photocatalysis, photoinduced electron and energy transfer in the condensed phase and across interfaces, photoelectrochemistry, and artificial assemblies for charge separation and transport that mimic natural photosynthetic systems. Capital equipment funding is provided for items such as ultrafast laser systems, scanning tunneling microscopes, fast Fourier transform infrared and Raman spectrometers, and computational resources.

Unique Aspects
This activity is the dominant supporter of solar photochemistry research in the United States. Solar photochemical energy conversion is an important long-range option for meeting future energy needs. An attractive alternative to semiconductor photovoltaic cells, solar photochemical and photoelectrochemical conversion processes produce fuels, chemicals, and electricity with minimal environmental impact and with closed renewable energy cycles. Artificial photosynthesis can be coupled to chemical reactions for generation of fuels such as hydrogen, methane, or complex hydrocarbons. The activity also provides unique support for radiation science via specialized electron pulse radiolysis facilities at Notre Dame and BNL, which serve the academic research community, industrial users, and other DOE national laboratories. Research in radiation sciences investigates fundamental physical and chemical effects produced by the absorption of energy from ionizing radiation. Fundamental studies of radiation science are of importance in understanding chemical reactions that occur in radiation fields of nuclear reactors, including in their fuel and coolants, and in the processing, storage, and remediation of nuclear waste. This research is required for effective nuclear waste remediation, fuel-cycle separation, and for design of next-generation nuclear reactors.

Relationship to Other Programs
The Solar Photochemistry research effort interfaces with several activities in BES as well as within DOE.

- Within BES, research efforts are coordinated with Photosynthetic Systems activities in biochemical aspects of photosynthesis; Chemical Physics in theoretical calculations of excited states and computational modeling; Physical Biosciences and Catalysis Science in investigations of electron transfer reactions in homogeneous and microheterogeneous solutions and advanced catalytic materials; and the Materials Sciences and Engineering Division efforts in fundamental photovoltaics research.
- This research activity sponsors – jointly with other BES research activities as appropriate – program reviews, principal investigators' meetings, and programmatic workshops.
- Many projects within solar photochemistry coordinate efforts with the Joint Center for Artificial Photosynthesis Energy Innovation Hub, as well as with the many relevant Energy Frontier Research Centers active in solar energy research.

- The work of solar photochemistry is relevant to the DOE Office of Energy Efficiency and Renewable Energy (EERE) activities in its Solar Energy Technologies program on photovoltaics and its Fuel Cells Technologies program.
- The radiation sciences activity in the Solar Photochemistry program is closely coordinated with the BES Condensed Phase and Interfacial Molecular Sciences in the physical and chemical aspects of radiolysis.
- There are also important interfaces between the radiation sciences activity and the DOE Office of Environmental Management activities in waste remediation and Office of Nuclear Energy activities on nuclear reactors, and nuclear waste processing and storage.

Significant Accomplishments
Significant advances in this program are found in the understanding and control of the fundamental processes for harvesting the energy from sunlight. These include the light harvesting of solar photons, the subsequent separation of charge through electron transfer, and the generation of electric power or the catalytic production of fuels.

- Many of these advances result from past investigations of model photosynthetic systems and their emulation. Researchers have discovered unexpected quantum coherence in energy transfer within the light absorbing antenna complexes of natural photosynthetic systems, which enables the absorbed light to spread out and sample the physical space of the chromophores and find the right place for electron transfer charge separation.
- In research on quantum dot nanoparticles, scientists have predicted and confirmed the generation of two electron hole pairs through absorption of a single photon. A vision for a new generation of solar cells has been envisioned, labeled “third generation,” that will exceed the Shockley-Queisser limit on present solar cell efficiencies.
- In systems for artificial photosynthesis, investigators have developed molecular models for light to chemical energy conversion. This work has refined the models of electron transfer and charge transport in organic complexes that are the backbone of advances in organic and polymeric “plastic” solar cells.
- Advances in homogeneous catalysis of photo- induced water splitting have led to the synthesis of many thousand inorganic catalysts within the past several years. A new field in photon driven fuel production has been created with the study of molecules located at solid surfaces where new pathways exist for charge transfer-induced catalysis.
- Many novel nanostructures of semiconductor electrodes have been developed for the photoelectrolysis of water and reduction of CO_2 to multi-carbon compounds. This research in Solar Photochemistry has formed the basis of the Joint Center for Artificial Photosynthesis Energy Innovation Hub and of a half dozen Energy Frontier Research Centers focused on solar photoconversion.

Mission Relevance
Solar photochemical energy conversion is an important option for generating electricity and chemical fuels and therefore plays a vital role in DOE’s development of solar energy as a viable component of the nation’s energy supply. Photoelectrochemistry provides an alternative to semiconductor photovoltaic cells for electricity generation from sunlight using closed, renewable energy cycles. Solar photocatalysis, achieved by coupling artificial photosynthetic systems for light harvesting and charge transport with the appropriate electrochemistry, provides a direct route to the generation of fuels such as hydrogen, methane, and complex hydrocarbons. Radiation

chemistry methods are of importance in solving problems in environmental waste management and remediation, nuclear energy production, and medical diagnosis and radiation therapy.

Scientific Challenges

The major challenges in solar photoconversion have been outlined in a BES workshop on *Basic Research Needs for Solar Energy Utilization*. Among these challenges, knowledge gained in charge separation and transport needs to be applied to activation of small molecules such as CO_2 and H_2O via photocatalytic cycles to transform them into fuels. The principles of this research are being extended to the problem of nitrogen fixation. The major scientific challenge for photoelectrochemical energy conversion is that semiconductors capable of absorbing solar photons are susceptible to oxidative degradation in water, whereas oxide semiconductors resistant to oxidative degradation absorb too little of the solar spectrum. Ongoing research activities include multibandgap, multilayer cascade-type semiconductors, photosensitized nanoparticulate solids, and the study of multiple exciton generation within nanoparticles. Experimental and theoretical studies on quantum coherence in light antenna complexes should lead to efficient and robust artificial light-collecting molecular assemblies. Computational chemistry methods incorporating recent advances in calculation of excited states should be developed and applied in design of photocatalysts and molecular dynamics simulations in artificial photosynthesis. There are also challenges in fundamental understanding of energy transfer and the generation, separation, and recombination of charge carriers in organic-based molecular semiconductors, which can lead to a new type of inexpensive and flexible solar cell. A workshop on *Basic Research Needs for Advanced Nuclear Energy Systems* identified new directions, connections, and roles for radiation chemistry in the nuclear energy systems of the future. A common theme is the need to explore radiolytic processes that occur across solid-liquid and solid-gas interfaces, where surface chemistry can be activated and changed by radiolysis. These interfaces abound in nuclear reactors and high level radioactive wastes. A more fundamental understanding of radiolytic reactions in heterogeneous media is needed in order to predict and control radiation chemical transformations in complex environmental systems.

Projected Evolution

An increased emphasis on solar fuels production will require new semiconductor and molecular systems for photoconversion. Of emphasis are new hybrid systems that feature molecular catalysis at surfaces and new nanoscale structures for the photochemical generation of fuels. Novel quantum size structures, such as hybrid semiconductor/carbon nanotube assemblies, fullerene-based linear and branched molecular arrays, and semiconductor/metal nanocomposites, must be examined. Unresolved basic science issues in photocatalysis will be explored in coupling photoinduced charge separation to multielectron, energetically uphill redox reactions. Photoconversion systems will be investigated that are based on organic semiconductors and conducting polymers, which are inexpensive and easy to manufacture. In these efforts, an enhanced theory and modeling effort is needed for rational design of artificial solar conversion systems. In radiation chemistry, electron pulse radiolysis methods will investigate reaction dynamics, structure, and energetics of short-lived transient intermediates in the condensed phase. Fundamental studies on reactivity of nitrogen oxides in aqueous solution are pertinent to understanding radiolytic degradation of nuclear tank waste.