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. This activity, with its integration of physical and synthetic scientists devoted to solar photochemistry, is unique to DOE. 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.

The program provides funding for approximately 60 university grants supporting about 100 graduate students and postdoctoral research associates, and partially supporting about 80 faculty members. There are 10 programs at DOE national laboratories supporting about 25 senior staff and 30 graduate students and postdoctoral research associates. Programs at the laboratories are multi-investigator efforts on problems that require extensive participation by senior experienced scientists and postdoctoral associates. In photochemistry, major research groups are supported in inorganic photochemistry and electron transfer at Brookhaven National Laboratory (BNL); in photoelectrochemistry at the National Renewable Energy Laboratory (NREL), Notre Dame, and Pacific Northwest National Laboratory (PNNL); and in photosynthesis at Argonne National Laboratory (ANL) and Lawrence Berkeley National Laboratory (LBNL). Many of the research efforts at the DOE national laboratories involve strong collaborative interfaces with university and industrial communities. Research in radiation chemistry is centered at specialized electron pulse radiolysis facilities at Notre Dame and BNL.

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. Increasing worldwide demands for energy will need to be met with technologies such as solar photoconversion that do not produce greenhouse gases. 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 Department of Energy 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. Such understanding is required for effective nuclear waste remediation and for design of next-generation nuclear reactors that might employ special media, such as supercritical fluids as coolants. The radiation chemistry of ionic liquids is relevant to their use as fuel-cycle separation solvents.

Relationship to Other Programs

The solar photochemistry research effort interfaces with several activities in BES: 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. The research 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 is closely coordinated with the BES Condensed Phase and Interfacial Molecular Sciences in the physical and chemical aspects of radiolysis. The radiation science effort also coordinates with BES Catalysis Science in reaction kinetics in homogeneous solutions, and Mechanical Behavior and Radiation Effects in radiolytic damage to glasses and radiation-induced corrosion of structural materials. There are also important interfaces with 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

Research in Solar Photochemistry has made significant advances 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 are a consequence of past investigations of model photosynthetic systems and an emulation of how they perform these functions. Researchers have discovered unexpected quantum coherence in energy transfer within the light absorbing antenna complexes of natural photosynthetic systems. This coherence enables the absorbed light to spread out and sample the physical space occupied by numbers of light absorbing molecules in order to find the right place for the reaction for electron transfer charge separation. In research on quantum dot nanoparticles, scientists have predicted and confirmed the generation of two electron hole pairs through the absorption of a single photon. Concepts such as these have led to a vision for a new generation of solar cells, labeled “third generation,” that will exceed the Shockley-Queisser limit on the efficiency of present solar cells. 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 dozen inorganic catalysts within the past several years where the preceding decades had produced only one. A new field of catalysis for photon driven fuel production has been created with the study of molecules located at solid surfaces where charge transfer can induce catalytic action by either the solid or the molecule. Many novel nanostructures of semiconductor electrodes have been developed for the photoelectrolysis of water.

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. Fundamental concepts derived from studying highly efficient excited-state charge separation and transport in molecular assemblies is also applicable to future molecular optoelectronic device development. 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 long-distance electron transfer needs to be applied in a meaningful way to activation of small molecules such as CO_2 and H_2O via photocatalytic cycles to transform them into fuels. The major scientific challenge for photoelectrochemical energy conversion is that small band gap semiconductors capable of absorbing solar photons are susceptible to oxidative degradation, whereas wide band gap semiconductors, which are resistant to oxidative degradation in aqueous media, absorb too little of the solar spectrum. Ongoing research activities include multibandgap, multilayer cascade-type semiconductors, photosensitized nanoparticulate solids, and the study of the mechanism of multiple exciton generation (MEG) within nanoparticles. Experimental and theoretical studies on photosynthetic pigment-protein antenna complexes should lead to advances in design of 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 photoconversion processes – energy transfer and the generation, separation, and recombination of charge carriers – in organic-based molecular semiconductors, which could lead to a new type of inexpensive and flexible solar cell. Fundamental studies on photochemical reaction pathways offer opportunities for less energy intensive and more environmentally benign processing of specialty chemicals and high volume industrial intermediates.

A recent workshop on *Basic Research Needs for Advanced Nuclear Energy Systems* has 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. Solid-liquid interfaces abound in nuclear reactors and high level radioactive wastes. Colloidal particles participate in gas production, gas retention, and in organic degradation of high level 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

In solar photochemistry, an increased emphasis on solar water splitting will explore new semiconductor and molecular systems for photoconversion. Also of emphasis are new hybrid systems that feature molecular catalysis at surfaces and new nanoscale structures for the photochemical generation of fuels. Modern combinatorial techniques will broaden and accelerate the search for new semiconductor and molecular structures. Novel quantum size structures, such as multiexciton generating quantum dots, hybrid semiconductor/carbon nanotube assemblies, fullerene-based linear and branched molecular arrays, and semiconductor/metal nanocomposites, will be examined that will allow for more complete and efficient use of the solar energy spectrum. 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. An enhanced theory and modeling effort is needed for rational design of artificial solar conversion systems. Of particular interest is the calculation of factors controlling photoinduced long-range electron transfer, charge injection at the semiconductor/electrolyte interface, and photoconversion in biomimetic assemblies for solar photocatalytic water splitting.

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. Studies of solvent effects on free radical reaction rates in supercritical fluids are relevant to next-generation supercritical water-cooled nuclear power plants.