**Research Activity:** **Solar Photochemistry** (formerly Photochemistry and Radiation Research)
Division: Chemical Sciences, Geosciences, and Biosciences
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## Portfolio Description:

This activity supports photochemical studies relevant to capture and conversion of solar energy and fundamental studies in chemical and physical properties induced by ionizing radiation. The solar photochemistry research encompasses physical chemical aspects of natural photosynthesis, charge separation by donor-acceptor models and nanoscale inorganic/organic assemblies, photocatalytic fuel-forming reactions, photoelectrolysis of water for solar hydrogen production, and photoelectrochemistry. Bioinspired photosynthetic models seek to mimic the key aspects of photosynthesis: the antenna, reaction center, catalytic cycles, and product separation. Research in radiation sciences investigates fundamental physical and chemical effects produced by the absorption of energy from ionizing radiation. Highly reactive transient intermediates and the kinetics and mechanisms of their chemical reactions are explored in the liquid phase and at liquid/solid interfaces as are radiolytic reactions in ionic liquids. Specialized accelerator facilities for electron pulse radiolysis are supported at Brookhaven National Laboratory (BNL) and the Notre Dame Radiation Laboratory.

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. 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.

## Unique Aspects:

This activity is the dominant supporter of solar photochemistry research in the United States and 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 (DOE) national laboratories

## 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; 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 Hydrogen, Fuel Cells, and Infrastructure 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:

Stratospheric ozone depletion by chlorofluorocarbons was predicted by F. Sherwood Rowland of UC, Irvine, in 1974. Professor Rowland's research, solely supported by this activity, involved the chemistry of "hot" chlorine

atoms produced by nuclear recoil and complementary photolytic reactions. Rowland was awarded the Nobel Prize in 1995. Radiotracers for nuclear medicine were pioneered by Alfred Wolf at BNL. The "special pair" model for electron donor chlorophyll molecules in photosynthesis was introduced by Joseph Katz and James Norris of Argonne National Laboratory (ANL). Photosynthetic molecular models for light to chemical energy conversion were developed by Michael Wasielewski of ANL and by Professors Gust, Moore, and Moore of Arizona State University. The "inverted region" in Marcus electron transfer theory was verified in pulse radiolysis experiments by John Miller at ANL.

## Mission Relevance:

Solar photochemical energy conversion is a long-range option for meeting the world's future energy needs. An alternative to solid-state semiconductor photovoltaic cells, the attraction of solar photochemical and photoelectrochemical conversion is that fuels, chemicals, and electricity may be produced with minimal environmental pollution and with closed renewable energy cycles. A strong interface with EERE solar conversion programs exists at the National Renewable Energy Laboratory involving shared research, analytical and fabrication facilities, and a jointly shared project on dye-sensitized solar cells. 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 recent 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 "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

## Funding Summary:

**Dollars in Thousands**

| FY 2007 | FY 2008 | FY 2009 Request |
|---|---|---|
| 30,603 | 30,603 | 39,569 |

| Performer | Funding Percentage |
|---|---|
| DOE Laboratories | 53% |
| Universities | 47 % |

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

The program provides funding for approximately 55 university grants supporting about 100 graduate students and postdoctoral research associates, and partially supporting about 50 faculty. There are 10 programs at DOE national laboratories supporting about 45 senior staff and 50 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 BNL; in photoelectrochemistry at NREL, Notre Dame, and Pacific Northwest National Laboratory (PNNL); and in photosynthesis at 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. The radiation chemistry effort is centered at specialized electron pulse radiolysis facilities at Notre Dame and BNL.

## Projected Evolution:

In solar photochemistry, an increased emphasis on solar water splitting will explore new semiconductor, molecular, and hybrid systems for photoconversion. 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.