Solar Photochemistry

Portfolio Description

This program supports fundamental, 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, charge separation, and charge transport within a number of chemical systems, including those with significant nanostructured composition. Supported research areas include organic and inorganic photochemistry, catalysis 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. Enhanced theory and modeling efforts form an integral part of the rational design of these artificial solar conversion systems.

Scientific Challenges

The major challenges in solar photoconversion have been outlined in a BES workshop on *Basic Research Needs for Solar Energy Utilization* (report link). 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 photosensitized nanoparticulate solids and the study of multiple exciton generation within nanoparticles and structured organic complexes. 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 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* (report link) 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

Advancing the science underpinning 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.

The Solar Photochemistry program does not fund research on device development or optimization.

Significant Accomplishments

Significant advances in this program follow from the understanding and control of the fundamental processes for harvesting energy from sunlight. These include the light harvesting of solar photons, the subsequent separation of charge through electron transfer to produce current, which can be directed to catalysis of chemical reactions for energy storage.

- Researchers 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 and charge separation.
- In research on quantum dot nanoparticles and organic dyes, scientists predicted and confirmed the generation of two electron-hole pairs through absorption of a single photon. A new generation of solar cells is envisioned, labeled “third generation,” that will exceed the Shockley-Queisser limit on present solar-cell efficiencies.
- In systems for artificial photosynthesis, investigators developed molecular models for light-to-chemical energy conversion. This work 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 led to the synthesis of many thousands of inorganic catalysts within the past several years. A new field in photochemistry has been created with the study of molecules located at solid surfaces where new pathways exist for charge-transfer-induced catalysis for chemical energy storage.
- Many novel nanostructures of semiconductor electrodes were developed for the photoelectrolysis of water and reduction of CO_2 to multi-carbon compounds. This research in Solar Photochemistry formed the basis of the Joint Center for Artificial Photosynthesis Energy Innovation Hub and a number of Energy Frontier Research Centers focused on the science of solar photoconversion.

Unique Aspects

This activity is the dominant supporter of solar photochemistry research in the United States. The research explores the fundamental science of solar photochemical energy conversion, which is an important long-range option for meeting future energy needs. An attractive alternative to semiconductor photovoltaic cells, solar photochemical and photoelectrochemical conversion processes create the potential to produce fuels, chemicals, and electricity with minimal environmental impact and with closed renewable energy cycles. Artificial photosynthesis can be coupled to chemical reactions for energy storage in the form of hydrogen, methane, or complex hydrocarbons. The activity also provides unique support for radiation science, investigating 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 design of next-generation nuclear reactors.

Mission Relevance

The research supported by this program produces fundamental knowledge that underpins DOE missions in energy production and environmental management. 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.

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 and Physical Biosciences activities in bio-inspired and biomimetic systems and components, Catalysis Science in aspects of catalysis and photocatalysis 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 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 Cell Technologies program.
- The radiation sciences activity in the Solar Photochemistry program is closely coordinated with the BES Condensed Phase and Interfacial Molecular Sciences program 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 on nuclear waste processing and storage.