Introduction to Solar Photon Conversion

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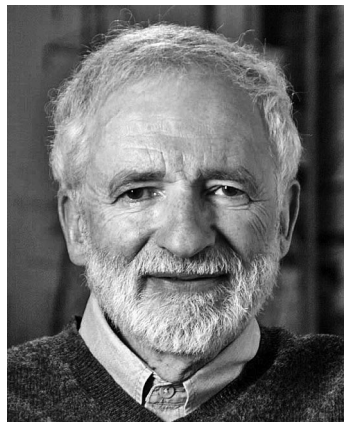

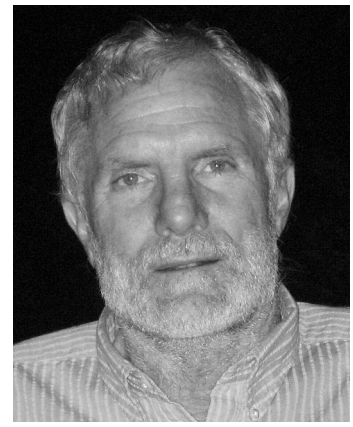

Dr. Arthur J. Nozik is a Senior Research Fellow at the U.S. DOE National Renewable Energy Laboratory (NREL), Professor Adjoint in the Department of Chemistry and Biochemistry at the University of Colorado, Boulder, and a Fellow of the NREL/University of Colorado Renewable and Sustainable Energy Institute. In 2009, Nozik was selected as Associate Director of a joint Los Alamos National Lab/NREL Energy Frontier Research Center for DOE called Center for Advanced Solar Photophysics. Between 2006 and 2009 he served as the Scientific Director of the Center for Revolutionary Solar Photoconversion under the Colorado Renewable Energy Collaboratory. Nozik received his BChE from Cornell University in 1959 and his Ph.D. in Physical Chemistry from Yale University in 1967. Before joining NREL in 1978, then known as the Solar Energy Research Institute (SERI), he conducted research at the Materials Research Center of the Allied Chemical Corporation (now Honeywell, Inc.). Dr. Nozik's research interests include size quantization effects in semiconductor quantum dots and quantum wells, including multiple exciton generation from a single photon; the applications of unique effects in nanostructures to advanced approaches for solar photon conversion; photogenerated carrier relaxation dynamics in various semiconductor structures; photoelectrochemistry of semiconductor−molecule interfaces; photoelectrochemical energy conversion; photocatalysis; optical, magnetic, and electrical properties of solids; and Mössbauer spectroscopy. He has published over 250 papers and book chapters in these fields, written or edited five books, holds 11 U.S. patents, and has delivered over 275 invited talks at universities, conferences, and symposia. He has served on numerous scientific review and advisory panels, chaired and organized many international and national conferences, workshops, and symposia, and received several awards in solar energy research, including the 2009 Science and Technology Award from the Intergovernmental Renewable Energy Organization associated with the United Nations, the 2008 Eni Award from the President of Italy, and the 2002 Research Award of the Electrochemical Society. Dr. Nozik has been a Senior Editor of The *Journal of Physical Chemistry* from 1993 to 2005 and is on the editorial advisory board of the *Journal of Energy and Environmental Sciences* and the *Journal of Solar Energy Materials and Solar Cells*. A Special Festschrift Issue of the *Journal of Physical Chemistry* honoring Dr. Nozik's scientific career appeared in the December 21, 2006 issue. Dr. Nozik is a Fellow of the American Physical Society and a Fellow of the American Association for the Advancement of Science; he is also a member of the American Chemical Society, the Electrochemical Society, and the Materials Research Society.

John R. Miller is a senior scientist and group leader of Thermal and Photoreactions in the Chemistry Department at Brookhaven National Laboratory. After his Ph.D. at the University of Wisconsin in 1971, he took a postdoc and then a staff position at Argonne National Laboratory, focusing on long distance electron transfer (electron tunneling and hole tunneling) reactions and then on the energy dependence of electron transfer, confirming the "inverted region" predicted by the Marcus theory. His main experimental tools have been electron accelerators and the radiation chemistry that enables their study of electron transfer. Recent work has focused on the extent to which long, conjugated molecules can serve as "molecular wires" that transport charges and excitons for improved solar photoconversion. He was a recipient of the University of Chicago Distinguished Performance Award.

The efficient and cost-effective direct conversion of solar photons into solar electricity and solar fuels is one of the most important scientific and technological challenges of this century. It is estimated that at least 20 terawatts of carbon-free energy ($1^1/_2$ times the total amount of all forms of energy consumed today globally), in the form of electricity and liquid and gaseous fuels, will be required by 2050 in order to avoid the most serious consequences of global climate change and to ensure adequate global energy supply that will avoid economic chaos. But in order for solar energy to contribute a major fraction of future carbon-free energy supplies, it must be priced competitively with, or perhaps even be less costly than, energy from fossil fuels and nuclear power as well as other renewable energy resources. The challenge of delivering very low-cost solar fuels and electricity will require groundbreaking advances in both fundamental and applied science. This Thematic Issue on Solar Photon Conversion will provide a review by leading researchers on the present status and prognosis of the science and technology of direct solar photoconversion to electricity and fuels. The topics covered include advanced and novel concepts for low-cost photovoltaic (PV) energy based on chemistry (dye-sensitized photoelectrodes, organic and molecular PV, multiple exciton generation in quantum dots, singlet fission), solar water splitting, redox catalysis for water oxidation and reduction, the role of nanoscience and nanocrystals in solar photoconversion, photoelectrochemical energy conversion, and photoinduced electron transfer.

The direct conversion of solar photons to electricity via photovoltaic (PV) cells is a vital present-day commercial industry, with PV module production growing at about 75%/year over the past 3 years. However, the total installed yearly averaged energy capacity at the end of 2009 was about 7 GW-year (0.2% of global electricity usage). Thus, there is potential for the PV industry to grow enormously in the

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future (by factors of 100−300) in order for it to provide a significant fraction of total global electricity needs (currently about 3.5 TW). Such growth will be greatly facilitated by, and probably even require, major advances in the conversion efficiency and cost reduction for PV cells and modules; such advances will depend upon advances in PV science and technology, and these approaches are discussed in this Thematic Issue.

Industrial and domestic electricity utilization accounts for only about 30% of the total energy consumed globally. Most (∼70%) of our energy consumption is in the form of liquid and gaseous fuels. Presently, solar-derived fuels are produced from biomass (labeled as biofuels) and are generated through biological photosynthesis. The global production of liquid biofuels in 2009 was about 1.6 million barrels/day, equivalent to a yearly output of about 2.5 EJ (about 1.3% of global liquid fuel utilization). The direct conversion of solar photons to fuels produces high-energy chemical products that are labeled as solar fuels; these can be produced through nonbiological approaches, generally called artificial photosynthesis. The feedstocks for artificial photosynthesis are H_2O and CO_2, either reacting as coupled oxidation−reduction reactions, as in biological photosynthesis, or by first splitting H_2O into H_2 and O_2 and then reacting the solar H_2 with CO_2 (or CO produced from CO_2) in a second step to produce fuels through various well-known chemical routes involving syngas, water gas shift, and alcohol synthesis; in some applications, the generated solar H_2 itself can be used as an excellent gaseous fuel, for example, in fuel cells. But at the present time, there is no solar fuels industry. Much research and development are required to create a solar fuels industry, and this Thematic Issue presents several reviews on the relevant solar fuels science and technology.

The first three manuscripts relate to the daunting problem of producing solar fuels. Lewis and colleagues present a comprehensive review of solar water splitting based on semiconductor electrodes. The semiconductor electrodes are either in direct contact with an aqueous electrolyte, creating a semiconductor−liquid junction, in which case this defines a true photoelectrochemical (PEC) configuration, or the semiconductors can form buried p−n junctions connected to metal anodes and/or cathodes, in which case various combination of PV and PEC cell configurations are possible. The issues of cell energetics, cell efficiency, photocorrosion, and electrocatalysis are discussed in detail. Nocera et al. first discuss the global energy problem and review the issues and technologies for solar energy storage. Then they focus on solar fuels as the best option for solar energy storage at sufficient scale to solve the looming energy crisis. As mentioned above, better and cheaper catalysts for H_2O oxidation and CO_2 reduction are critical to make advances in producing cost-effective solar fuels. Nocera et al. provide a detailed and comprehensive review of progress in the catalysis of both the oxygen evolving reaction (OER) and the hydrogen evolving reaction (HER) based on both solid-state and molecular catalysts, including the recent work from Nocera's group on a new Co-based OER catalyst that has self-healing characteristics. Chen et al. present a very extensive review of photocatalytic hydrogen generation based on water splitting that is focused on oxide semiconductors as photocatalytic particles. There has been a long and still ongoing search for the ideal semiconductors and architectures that can split water efficiently, without any external voltage applied, and are photostable. The many oxide materials described in this review can also be considered for PEC cells as photoelectrodes as well as photocatalytic particles.

Approaches to next-generation photovoltaics is the largest area covered in this issue. Eight reviews examine a range of exciting science with great potential to enhance the utilization and impact of solar electricity. Ginley et al. examine methods to produce low-cost inorganic PV cells via solution-based processing using various methods such as electrochemical/chemical bath deposition, spin/spray-coating, and direct-write inkjet printing. The issues of solution precursors (i.e., inks), as well as the formation of conducting contacts and dielectrics, are discussed toward the goal of a complete PV cell produced by solution processing. The comprehensive review of dye-sensitized (Grätzel) solar cells by Hagfeldt et al. describes their principal constituents, including dyes and redox couples, and the measurements to characterize these cells. Kamat et al. survey the performance of a wide range of nanostructured materials in solar cells. Complex composites and structures discussed in this review include inorganic and organic materials, molecular chromophores, quantum dots, and semiconductor−liquid junctions, all designed to enhance performance in these PV cells.

Gregg et al. and Durrant et al. describe solar cells based on molecular semiconductors. Gregg emphasizes discrete molecules such as phthalocyanines, porphyrins, and perlyene dimides in layered devices, while Durrant emphasizes conjugated polymers in bulk heterojunction cells (BHJ). Both reviews illuminate the challenges of obtaining good mobilities and charge separation/transport in these low dielectric materials, discussing energetics of charge transfer and Onsager escape. Guldi et al. describe photoinduced electron transfer in phthalocyanine light absorbers covalently linked to fullerenes or noncovalently attached to larger structures such as carbon nanotubes. The fascinating potential of these molecular assemblies for use in photovoltaics is examined in several specific systems. A most central issue for the potential of polymer-based solar photoconversion is the formation of the polymers. Synthesis is a principal focus of the review by Müllen et al., who describe polymer-based solar cells in flat heterojunction, bulk heterojunction, and inverted heterojunction configurations and the polymers that make them possible. In addition to many families of polymers, they discuss research to create and investigate low-bandgap polymers and polymers with attached traps.

Carbon nanotubes have special electronic properties with important potential applications. They can be inexpensively produced from various carbon sources using several techniques. They have structures formed from graphene sheets rolled into straight tubes with different chirality. Dillon reviews the nature and history of carbon nanotubes and describes their properties, progress in their synthesis, and their uses to enhance the active layers of bulk heterojunction solar cell, to serve as transparent electrodes in opto-electronic devices, and their roles in Li-ion batteries, supercapacitors, and hybrids of these two devices.

Sunlight consists of photons having a wide range of energies from 0.5 to 3.5 eV (infrared to UV), but current solar cells utilize a relatively small fraction (about $^1/_3$) of the total energy of the solar photons This is because photons with energies below the optical bandgap (i.e., HOMO−LUMO transition) are not absorbed and hence not utilized at all, while for high energy photons, the excess kinetic energy of the photogenerated electrons and holes (charge carriers) created above the bandgap (termed hot carriers) is lost as

heat through electron−phonon scattering, resulting in hot electron and hole cooling. Both of these losses lead to an upper bound on the thermodynamic efficiency of single-bandgap cells called the Shockley−Queisser limit; at 1 sun in the radiative limit, this limiting power conversion efficiency is 32%. Fundamental thermodynamic limits on conversion efficiency apply to both photovoltaics and solar fuels but with different values because the former produces instantaneous power without energy storage, while the latter produces stored energy in the chemical bonds of the fuel products.

Major increases (up to a factor of 2) in thermodynamic conversion efficiency can be achieved in solar photoconversion by reducing or eliminating the energy losses from the cooling of hot carriers or by enabling the absorption of sub-bandgap photons. These approaches have been termed "third-generation solar photon conversion". Nozik et al. describe how semiconductor quantum dots (QDs) can generate two or more excitons from hot excitons created by absorption of high-energy photons; this process is termed multiple exciton generation (MEG) and can in principle increase the conversion efficiency by $^1/_3$ in an ideal MEG cell system. Michl and Smith explore and review the basic science of the molecular analogue of MEG, a photochemical process termed "singlet fission", in which two triplets are produced from the first excited singlet. This requires uniquely designed molecules with special energetic configurations for the singlet and triplet states. The potential gain in conversion efficiency for solar cells based on singlet fission is the same as for MEG, generating two electron−hole pairs in a QD-based solar cell.

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