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Forum

Preface: Overview of the Forum on Solar and Renewable Energy

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Inorganic Chemistry is pleased to present a Forum on Solar and Renewable Energy. The contributions that follow represent a sampler of cutting edge research that deals with different aspects of the science related to our Forum theme from the considered perspective of chemistry and, most especially, inorganic chemistry. The Articles are authored by leaders in the field and represent accounts of research in their respective laboratories ranging from dye-sensitized solar cells (DSSCs) and the photophysics of irradiated semiconductors to hydrogen generation and design considerations for artificial photosynthetic systems. They represent some of the science on which tomorrow's technology for energy generation will be built. There is no more serious challenge facing society today than energy for sustainable development.

In 1957, Charles David Keeling started a life-long series of measurements of global CO_2 levels. The activity was initiated as part of the International Geophysical year and was performed at Mauna Loa, HI, to remove local biases in the data and provide a reliable and reproducible baseline measurement of CO_2 in the atmosphere. The initial measurements revealed a surprising and unexpected annual oscillation that arose from different levels of photosynthetic activity between winter and summer in a world where most of the land mass is in the northern hemisphere. It was said that Keeling was observing the planet breathing. However, what was even more striking than the annual CO_2 oscillation of a living planet was the relentless upward bias in the baseline value of atmospheric CO_2 from year to year. The average baseline level of CO_2, which in 1957 was 316 ppm, has increased to 370 ppm in 2003. It has been estimated that the average global CO_2 level at the dawn of the industrial revolution was 280 ppm based on trapped air analyzed in ice cores, meaning that, since the latter part of the 19th century, this value has increased by 32%. These numbers are facts. Data through 1999 along with primary references up to that point may be found in the *World Energy Assessment*,[1] which is available online (http://www.undp.org/seed/eap/activities/wea/). The growth in the atmospheric CO_2 inventory tracks the increase in global burning of fossil fuel over the past 150 years. Detailed analysis of relative carbon isotope abundances confirms that the observed CO_2 increase comes from fossil fuels. The rate of CO_2 increase, which itself is accelerating, is by far the largest for any comparable period of time and reflects a world of both growing population and industrialization as people conduct all manner of activities associated with the functioning of modern societies: transportation, agriculture, manufacturing, construction, and heating, lighting, and cooling of homes and businesses. All of these activities consume energy.

In 1998, global annual energy consumption was 402 exajoules (12.7 TW), with the United States portion of that amount corresponding to approximately 25%. Of that global amount, 80% was generated from fossil fuels with a consequent annual emission of nearly 7 Gt C ($1\ \text{Gt} = 10^{12}$ kg) (see Chapter 3 of ref 1). Different scenarios have been proposed for future global annual energy needs with values of 837−1041 exajoules (26.4−32.9 TW) estimated for middle to high growth by 2050 and 1464−1859 exajoules (46.3−58.7 TW) by 2100. In an analysis of these numbers and their implications for the future, many projections of annual emissions and atmospheric inventory of CO_2 have been made.[2,3] The resultant numbers vary widely depending on the assumed composition of energy sources, the efficiency of energy production and consumption, the global economy, and different intervention scenarios to control CO_2 levels. Modestly stringent interventions are based on stabilizing atmospheric CO_2 in the 550−650 ppm range with substantially higher values projected ($>$750 ppm) if the present mix of global energy sources is maintained.

Clearly, CO_2 levels will continue to increase well into the future. It is important to recognize, at least briefly, what this means from an environmental standpoint. Records already

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(1) *World Energy Assessment: Energy and the Challenge of Sustainability*; United Nations: New York, 2000.

(2) Wigley, T. M. L.; Richels, R.; Edmonds, J. A. *Nature* **1996**, *379*, 240−243.

(3) Hoffert, M. I.; Caldeira, K.; Jain, A. K.; Haites, E. F.; Harvey, L. D.; Potter, S. D.; Schlesinger, M. E.; Wigley, T. M. L.; Wuebbles, D. J. *Nature* **1998**, *395*, 881−884.

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indicate that we are in a period of global warming, with a further rise in temperature to be expected. Climate sensitivity is a parameter that can be used to estimate that increase and is defined as the change in the mean global temperature resulting from a doubling of atmospheric CO_2.[4] While the range of values estimated for climate sensitivity may not appear large (1.5−4.5 °C), the consequences will be substantial, and if actual climate sensitivity lies in the upper half of the estimated range, the results may be devastating, at least for some regions, habitats, and species. Temperature increases alone tell only a fraction of the story. Higher temperatures lead to increased cycling of water and water vapor, higher levels of atmospheric water vapor (also a greenhouse gas), changing and more severe weather patterns, and rising sea levels from thinning polar icecaps. While these consequences are predicted and not guaranteed, what is certain is that we are perturbing the planet on a scale never done before by any of its inhabitants with consequential effects that are unquestionably serious and possibly catastrophic. It is thus imperative that the global community moves, and moves quickly, to a more CO_2-neutral energy production profile.

If we consider where the world stands today in terms of energy use and where it will be in 2050 assuming continued economic development, we are faced with a daunting challenge of where that energy will come from if our energy profile is to be more CO_2-neutral. It is likely, in fact, that reserves of readily accessible oil will be declining over this century, and while coal is abundant, it offers a host of environmental problems in addition to large-scale CO_2 generation that must be addressed (coal is the least hydrogen-rich of fossil fuels, meaning that more carbon is oxidized to CO_2 per gram of fuel). We need to look beyond something incremental because *the additional energy needed is greater than the total of all of the energy currently produced*. To demonstrate the challenges confronting the world in finding an additional 14−20 TW by 2050, consider the *total* amounts that may be possible for each as presented in the WEA and summarized on the webpage of one of the Forum contributors (Nathan S. Lewis, http://nsl.caltech.edu/energy.html): *biomass*, 7−10 TW available from the entire agricultural land mass of the planet (excluding the area required to house a population of 9 billion people); *wind on land*, 2.1 TW from saturating the entire class 3 (the wind speed required for sustainable energy generation, 5.1 m/s at 10 m above the ground) global land mass with wind mills; *nuclear*, 8 TW of nuclear energy requiring the construction of 8000 new nuclear power plants (to generate this energy, one new nuclear power plant needs to be built every 2 days until 2050); and *hydroelectric*, 1.5 TW left to tap by damming all available rivers. These unrealistic energy scenarios highlight that the additional energy needed per year by 2050 over the current 12.8 TW fossil fuel energy base is simply not attainable from these much discussed sources: the global appetite for energy is simply too great. While, in the short term, an "energy mix" will most likely be employed as a stop-gap measure to satisfy the world's growing need for energy, the answer to this dilemma over the long term must be solar energy, which is the theme of this Forum.

Solar energy is an inexhaustible (at least for several billion years) and freely available energy source. More energy comes from the sun in 1 h each day than is used by all humankind activities in 1 year. The challenge today is to capture and utilize solar energy for sustainable development on a grand scale. There are different manifestations of solar energy conversion, of which one relies fundamentally on chemistry for its scientific underpinnings, namely, the conversion of light into stored chemical energy in the form of fuel. We all know that photosynthesis powers life on the planet, and we can be inspired by the elaborate constructions of light-harvesting assemblies and photosynthetic reaction centers coupled with the multistep sequences that lead to the conversion of CO_2 and H_2O to carbohydrates and O_2. There is still much that remains to be understood about natural photosynthesis, particularly with regard to the oxidation of water to O_2, which may be a Forum subject in the future.

The execution of natural photosynthesis for energy (as opposed to food, clothing, and shelter) corresponds to obtaining energy from biomass. While large scale programs have been adopted in Brazil and are advocated in pilot projects here for ethanol as a biomass fuel, questions exist about the amount of net energy obtained in such an approach, and for the conversion of corn to ethanol in the United States, whether the energy balance overall is positive enough to merit use of this strategy for the long term. An analysis of corn-to-ethanol conversion needs to take into account the work done and energy consumed in planting, growing, fertilizing, harvesting, processing, and fermenting the corn.

Photosynthesis need not be limited to what is done in nature. The light-driven splitting of water into its constituent elements is one such example. Hydrogen and oxygen can then be run through a fuel cell to reform the water and give electrical energy with greater efficiency than was possible with conventional electrical generators. The sequence of water splitting and constituent element recombination is the essential linchpin of the much-discussed hydrogen economy. The development of a photosynthetic system that would accomplish the front end of this task using a large portion of the solar spectrum in a cost-effective way would be a major advance in energy production and the critical breakthrough in moving the hydrogen economy toward reality. The design of such a system can be guided by the key steps and requirements of natural photosynthesis such as the efficient capture of visible light photons, electron/hole separation through electron transfer to give energetic oxidizing and reducing equivalents, charge accumulation for the energy storing steps that follow, and catalysis of those reactions. Some of the efforts in these directions are chronicled in the Articles appearing in this Forum.

In the approaches being followed with respect to artificial photosynthesis and water splitting, one can find molecular, supramolecular, semiconductor, and hybrid systems being formulated, fabricated, and studied. The activity is at the cutting edge of architecture and engineering at the nanometer and sub-nanometer (i.e., molecular) scales. Scientists, and chemists foremost among them, are creating new molecules and materials with the specific focus of satisfying each

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(4) Caldeira, K.; Jain, A. K.; Hoffert, M. I. *Science* **2003**, *299*, 2052−2054.

criterion for photosynthesis in ways that vary from what has been done before. When successful, the chemistry and science will form the basis on which new technologies for energy production can be built. This is truly a "grand challenge", using sunlight and water to produce clean, environmentally friendly energy for sustainable development on a massive scale.

Another important line of attack in solar energy utilization—and one that is closer to widespread commercial implementation—is the direct conversion of light to electrical energy. Photovoltaic devices have been around for decades and are widely known for their use in space programs. However, their cost of production and their efficiency of operation have limited their utilization to special cases such as remote locations in which less expensive electrical energy is not available. On the basis of costs for turnkey (or complete) installations, electrical energy from photovoltaic devices was 6−10 times more expensive in 1999 than electrical energy generated using coal or oil. While the efficiency of photovoltaic panels has been improving, further development is necessary to make such systems economically viable on a larger scale with a more favorable energy payback time (that is, the time to recoup the complete costs of the installation).

An alternative approach to the photovoltaic device for the direct conversion of sunlight to electrical energy is the DSSC, in which an irradiated sensitizer transfers an electron to a wide band-gap semiconductor electrode, leading to photocurrent. The oxidized sensitizer or dye is then regenerated using a solution redox couple that also serves to accept electrons from the external circuit. The device is really a light-driven electrochemical cell with a dye-sensitized photoanode. The most successful and extensively studied DSSC is the Grätzel cell, which Michael Grätzel describes in his Forum contribution. The Grätzel cell is based on mesoscopic metal oxide, most notably TiO_2, thin films that are sensitized by surface-bound metal complexes and function through the agency of a redox couple in a fluid eletrolyte. The cell is elegantly conceived, as well as durable and robust. Gerald Meyer writes in his Forum Article about specific considerations regarding the photoanode in DSSCs and, in particular, about the thermodynamics, kinetics, and dynamics of interfacial charge separation in such systems.

A recent report from the U.S. Department of Energy based on a workshop held in Washington, DC, in April 2005 on Solar Energy (*Chem. Eng. News* **2005**, *82* (No. 22), 30) has identified a number of fundamental research needs that have to be addressed for the development of new solar energy based technology. While the entire report is available on the web at http://www.sc.doe.gov/bes/reports/abstracts.html#SEU, we highlight just a few of those needs that should be of interest to readers of *Inorganic Chemistry*:

(i) The development of structured assemblies that allow organization of the active units (light harvesting, charge conduction, and catalytic) for optimum coupling for efficient fuel production. This includes the further development of synthetic methods to accomplish the needed coupling between components contained in the assemblies.

(ii) The synthesis of new semiconductor nanocrystals containing p−n homo- and heterojunctions and their study for light-driven charge separation.

(iii) The development of novel methods for compartmentalizing oxidizing and reducing sites by nanostructure design and the development of nanoscale pore architectures that steer reaction intermediates to desired fuel products.

(iv) The design, synthesis, and study of efficient, high-turnover catalysts for the splitting of water and the reduction of carbon dioxide. To effect these reactions, robust ligands, multimetallic active sites and secondary environments will need to be designed and synthesized. The functioning of the new catalysts will rely on complex mechanisms that incorporate multielectron, atom, and proton-coupled electron-transfer reactions. The new catalysts will serve as components to be integrated into the higher order assemblies of part i.

(v) To design better interfacial catalysts for fuel formation and water oxidation, the detailed understanding developed for these reactions on the molecular level will need to be translated to surface-bound molecular and colloidal catalysts.

The Forum Articles cover ongoing research on different aspects of these highlighted needs. In addition to the Grätzel and Meyer contributions on DSSCs, Nathan Lewis discusses charge transfer and recombination at semiconductor−solution interfaces as well as chemical modification of semiconductor surfaces to modify and control interfacial reactions, while Arthur Nozik covers photoconversion efficiencies in semiconductor quantum dots with special focus on impact ionization that yields more excitons than photons absorbed. New approaches such as Nozik's offer the promise of greatly increasing the efficiency of solar cells. From the laboratory of Thomas Mallouk, efforts directed to the construction and utilization of integrated assemblies for catalytic hydrogen and oxygen evolution are described, including a novel layer-by-layer approach to achieve efficient light-driven charge separation with the ultimate goal of splitting water with visible sunlight. A contribution by Thomas J. Meyer and coworkers describes in depth approaches to artificial photosynthesis based on functional elements and modular components using ruthenium(II) tris diimine complexes as sensitizers in various constructions. Finally, the authors of this overview have written in separate contributions about (1) light-driven H_2 production and multielectron processes, notably water oxidation to O_2, that rely on proton-coupled electron transfer (Nocera) and (2) the design and synthesis of molecular systems having platinum(II) chromophores with covalently linked components for photoinduced charge separation (Eisenberg).

Clearly, the challenge for the 21st century is energy, and the answers to that challenge lie mainly in chemistry, with the discipline of inorganic chemistry playing a central role. What chemists do to address this challenge will have impact reaching far beyond our laboratories and institutions.

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