

## The Emerging Technology of Solar Fuels

The production of transportation fuels from sunlight, at costs that will be competitive with petroleum-based fuels in a future carbon-constrained economy, is one of the most important and daunting challenges facing chemists today. The use of carbon-based fuels, following current trends, will double the current level of atmospheric CO<sub>2</sub> in this century,<sup>1</sup> possibly leading to disastrous environmental and economic consequences.<sup>2</sup> The usable capacity of solar power is estimated to be 600 TW,<sup>3</sup> an order of magnitude larger than the projected energy needs of the entire world in 2050, and most of the solar spectrum is delivered at energies that (thermodynamically) can drive water splitting or CO<sub>2</sub> reduction. Transforming the world's energy economy boils down to technological problems that are largely chemical: how to design molecules and materials that efficiently absorb light and separate charge and then drive uphill redox reactions at low overpotential.

How hard can this problem be? Very hard because electron–hole recombination, fuel–oxidant recombination, and unwanted side reactions are energetically favorable and fast relative to fuel-forming and water oxidation reactions. To put it into perspective, solar water splitting has been actively researched since 1972, when Fujishima and Honda first demonstrated it in an UV light-driven photoelectrochemical cell.<sup>4</sup> The first example of photocatalytic water splitting with visible light did not come for another 29 years.<sup>5</sup> Almost a decade later, the best photocatalytic water splitting systems still use only the blue edge of the visible spectrum, and their efficiency is quite low, but important advances have been made in controlling the catalytic reactions. Visible-light-driven CO<sub>2</sub> reduction is at an even earlier stage of development than water splitting, with no known photocatalysts that can simultaneously reduce CO<sub>2</sub> and oxidize water. However, in both cases, our mechanistic understanding of the loss processes is now much clearer. Furthermore, in both cases, the synthesis of photocatalytic molecules and materials is becoming increasingly sophisticated.

The Perspectives in this issue give a snapshot of the current status of solar fuels research and describe recent progress in the authors' laboratories. Maeda and Domen have addressed one of the trickiest problems in the photocatalysis of thermodynamically uphill reactions, preventing the (downhill) catalytic reaction of the strongly oxidizing and reducing chemical products.<sup>6</sup> This is done by encapsulating the noble metal catalyst particles in a 2 nm thick shell of Cr<sub>2</sub>O<sub>3</sub>, which allows protons and H<sub>2</sub> molecules to pass through but inhibits the access of O<sub>2</sub> molecules. Remarkably, the evolution of hydrogen by oxynitride semiconductors coupled to these core–shell catalyst particles is insensitive to the oxygen pressure in the system, despite the 1.23 V driving force for the hydrogen–oxygen reaction. Maeda and Domen also describe clever Z-scheme designs in which two separate semiconductor particles perform water oxidation and reduction, linked by a redox shuttle that is compatible with the products made in both reactions. In this Perspective and the following one by Maggard and co-workers,<sup>7</sup> new strategies for tuning the band

gap and controlling the synthesis of semiconductor photocatalyst particles are described. The particle size and surface microstructure can strongly affect the relative rates of recombination and catalytic reactions and thus the efficiency of water splitting. Maeda and Domen note that with oxide and oxynitride semiconductors, the dominant loss mechanism is electron–hole recombination within the particle. This conclusion is consistent with mechanistic studies of TiO<sub>2</sub> photoelectrodes.<sup>8</sup> Recent work on single-crystal nanoparticle photocatalysts reinforces this conclusion by demonstrating high quantum efficiencies for light-driven hydrogen evolution in solutions of sacrificial electron donors.<sup>9,10</sup> These studies show that semiconductor photocatalysts can be designed so that electron transfer to noble metal nanoparticles is faster than charge recombination. It remains a challenge to integrate these efficient “half-cell” photocatalysts with photosystems for water oxidation without introducing other pathways for back electron transfer, fuel oxidation, or catalyst photodecomposition.

To realize carbon-containing solar fuels, it is necessary to react CO<sub>2</sub> catalytically with solar hydrogen or to reduce it directly. The Perspective by Grills and Fujita<sup>11</sup> explains why the photocatalytic reduction of CO<sub>2</sub> to CO and other carbon-containing compounds has been a more difficult problem than water splitting. They describe progress in designing molecular donor–acceptor systems that combine the functions of light-induced charge separation and two-electron, two-proton reduction of CO<sub>2</sub> to CO. A bottleneck in the catalytic cycle of CO<sub>2</sub> reduction is the displacement of a polar solvent molecule in the coordination sphere of a transition metal, such as Re(I), with a weakly coordinating CO<sub>2</sub> molecule. Grills and Fujita show that supercritical CO<sub>2</sub> and biphasic CO<sub>2</sub>/ionic liquid systems are effective media for increasing the turnover rate in these systems.

For both photocatalytic water splitting and CO<sub>2</sub> reduction, the cost, activity, and stability of molecules and catalysts that contain noble metals are important practical issues. The current cost of a mole of Pt (Rh, Ir, Pd, Re, ...) is roughly a million times the cost of a mole of H<sub>2</sub>. Thus, to break even on the cost of metals alone, turnover numbers (TON) in excess of 10<sup>6</sup> would be needed. For a realistic system life (~20 years), this number approaches 10<sup>9</sup>. Turnover frequencies (TOF) should also be very fast, 10<sup>3</sup> s<sup>-1</sup> or more, to compete effectively with back electron transfer reactions and photocatalyst decomposition. Grills and Fujita explain that the current state of the art is many orders of magnitude away from either target.<sup>11</sup>

A simple way to accelerate catalytic reactions is to increase the temperature. However, there is a problem with using temperature to increase the TOF or TON in either molecular- or semiconductor-based photocatalytic systems. Increasing

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the temperature also accelerates thermally activated excited-state decay and charge recombination processes. In semiconductor p–n junction devices, this effect is responsible for the loss of photovoltage with increasing temperature, and it is the reason why concentrator solar cells must be actively cooled.

An interesting way around this problem and also the ubiquitous problem of the poor utilization of red and near-infrared light in artificial photosynthesis is to split the functions of light-induced charge separation and catalysis into low- and high-temperature stages. This approach has a number of important advantages. The high quantum efficiency of charge separation in excitonic or p–n junction solar cells can be exploited, and decomposition pathways associated with semiconductor–liquid junctions are eliminated. The need for noble metal catalysts and the TOF problem are greatly relaxed by increasing the temperature of catalytic cycles by hundreds of degrees. Licht has recently shown in a proof-of-concept system that this approach could result in very efficient solar fuel generation.<sup>12</sup> The short-wavelength part of the solar spectrum is directed to an efficient multijunction photovoltaic cell. The long-wavelength part of the spectrum, along with waste heat from the solar cell, is concentrated to heat a molten carbonate electrolyte for electrolysis of CO<sub>2</sub>, which is powered by the electrical output of the solar cell. Although the cost of materials (especially the concentrator photovoltaic cell) is high, one can imagine variations on this theme that would involve much lower cost components.

Given the scientific progress on several parallel paths that are highlighted in this issue, it is no longer unreasonable to use the word “technology” in the same breath as “solar fuels.” It will be interesting to see how these lines of research continue to develop and what other creative ideas will be brought to bear on this important problem in the coming decade.

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