# Antenna molecule drives solar hydrogen generation

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It would be convenient if gigantic reservoirs of molecular hydrogen $H_{2(g)}$ existed in the earth's crust that could be safely tapped as an energy source. Instead, most hydrogen found near the earth's surface is bound up in water as protons, $H^+(aq)$ that must be reduced before utilization as a fuel (1). When the electrons for proton reduction come from the oxidation of water to $O_{2(g)}$, this redox chemistry is commonly referred to as "water splitting":

$$2H_2O_{(aq)} \rightarrow 2H_{2(g)} + O_{2(g)} \quad (\Delta G° = 4.92\,eV).$$
$$[1]$$
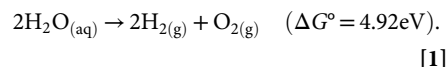
As shown in Eq. **1**, water splitting is thermodynamically uphill and hence provides a means for storing energy in chemical bonds. The reverse reaction produces water and energy. The identification of an inexpensive scalable process for water splitting has been a "holy grail" of science for decades that could one day enable a "hydrogen economy" (2). Electrolysis accomplishes water splitting, but practical utility requires an inexpensive source of electrical power that ideally would not involve greenhouse gas formation from fossil fuel combustion. Electricity generated from wind or photovoltaic panels could be used for this purpose, but this does not yet appear to be cost-effective. Approaches that integrate solar energy harvesting and catalysis

are particularly attractive as they afford the real possibility for inexpensive production of $H_{2(g)}$. In 1972, Fujishima and Honda (3) reported sustained water splitting from a relatively simple photoelectrochemical cell based on TiO_2 and Pt electrodes separated by a membrane (Fig. 1). The drawback was that sunlight absorption was limited to the UV region, comprising less than 3% of the solar spectrum. Since that time, alternative semiconductor materials have been identified that effectively harvest sunlight and split water more efficiently (4, 5); however, the associated costs are not economically competitive with today's fossil fuels. In a step toward simple low-cost approaches to solar hydrogen generation, Zheng et al. (6) report sustained $H_{2(g)}$ generation over periods of 12 d with ~40,000 turnovers by a dye molecule anchored to TiO_2/Pt particles in an aqueous suspension. The turnover numbers are unprecedented for solar fuel production and may enable practically useful molecular approaches to solar hydrogen production.

Light absorption by "dyads" drives the newly discovered hydrogen generation (6). The particular dyad that proved to be the most efficient is shown in Fig. 1 and referred to herein as the "Zheng dyad." It is composed of an organic dye molecule (Bodipy) covalently linked to a transition metal complex

(PtN_2S_2). The transition metal complex absorbs light across much of the visible region, but only weakly. In contrast, the organic Bodipy dye has a sharp intense absorption band in the green region with an extinction coefficient that is about two orders of magnitude larger. When linked together in the dyad, the optical and redox properties were well modeled as sum of the two individual parts, indicative of weak electronic coupling. Nevertheless, rapid energy transfer from the excited organic dye to the transition metal complex was observed to occur on a picosecond timescale. The Bodipy dye molecule hence serves as an antennae to effectively harvest sunlight and transfer energy to an inorganic complex capable of interfacial electron transfer to TiO_2/Pt catalytic sites where hydrogen gas evolution occurs. The dyads were found to be far more effective at $H_{2(g)}$ generation in pH 4 water than were the transition metal complex or organic dye molecules alone. Hence, energy transfer was credited for the tremendous success of the dyads.

The use of dyads that undergo energy transfer and the remarkably high turnover numbers accrued represent important advances toward the realization of a hydrogen economy. Although a single Bodipy dye was used for energy transfer, one could envision an ensemble of dyes much like in nature's antennae complex for photosynthesis where an array of organic pigments broadens the spectral range of light absorption and transfers that energy to the reaction center where electron transfer takes place (7). The studies reported were fundamental in nature yet have implications for practical solar energy, provided that alternative materials can be identified and this reduction chemistry can be integrated with an oxidation reaction that does not involve sacrificial reagents.

These two points, sacrificial reagents and materials chemistry, represent hurdles in reaching a practical device.

The hydrogen evolution data reported were acquired with ascorbic acid (or vitamin C)
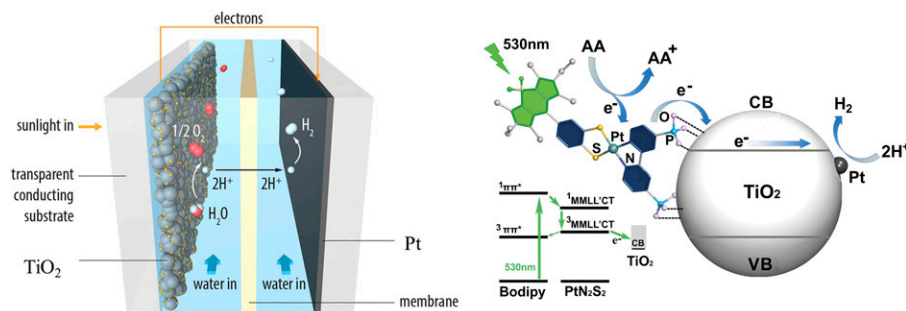
Fig. 1. The left-hand side shows a photoelectrochemical cell for water splitting based on Fujishima and Honda: an illuminated TiO_2 electrode oxidized water, the protons released diffuse through a membrane, and the electrons are transported through an external circuit for proton reduction at a Pt electrode. The right-hand side shows the Zheng dyad that sensitizes hydrogen evolution to visible light at a particulate Pt/TiO_2 interface. Right-hand image courtesy of Richard Eisenberg (University of Rochester, Rochester, NY).

dissolved in the aqueous suspension as a "sacrificial" electron donor. Ideally, sacrificial reagents simply provide redox equivalents to the light-driven reactions and do nothing else. In such a case, their use enables optimization of proton reduction without addressing the oxidation chemistry. However, in practice, sacrificial reagents may not be innocent and can participate in other ways. For example, ascorbic acid is often used in fluorescence microscopy to prevent dye photobleaching; illuminated dyes are not as stable in its absence (8). Hence, as the authors correctly point out, the use of different sacrificial reagents and experimental conditions preclude a determination of how the Zheng dyads would perform in a complete water-splitting cell or why these dyads are so stable relative to others that have been reported in the literature (6). A critical step toward practical application will be to successfully integrate the light-driven $H_{2(g)}$ formation with a nonsacrificial oxidation half-reaction.

If the hydrogen generated were to be burned on a global scale, then water would seem to be the necessary source of the electrons; otherwise, a tremendous amount of oxidized products would accumulate as waste. On the other hand, if the hydrogen were used in fuel cells, then many alternative chemically reversible oxidation reactions could be utilized. Fuel cells are expensive yet are inherently more efficient as they avoid the Carnot efficiency limitations of irreversible combustion reactions. One possible source of electrons is from halide ions. For example, iodide oxidation is far more kinetically rapid and thermodynamically favorable than is water oxidation (9). Indeed, if iodide were used in place of ascorbic acid in the reported dyad assembly, prior work suggests that $H_{2(g)}$ and I_2 would be generated under solar illumination that could later be recombined to generate electrical power (10). Note that related HBr splitting in photoelectrochemical cells with inorganic photovoltaic materials was investigated by Texas Instruments in the 1970s but was abandoned due to corrosion issues associated with bromine storage (11).

Both the oxidation and the reduction reactions occurred in the same suspension in this trial of the Zheng dyad. In future embodiments of this approach, it may well be optimal to separate the two reactions into individual cells so that the reaction products can be more easily separated. This could be accomplished with an ohmic contact to a TiO_2 electrode rather than a suspension of particles. This would enable physical separation of the TiO_2 and Pt with a wire for selective transport of the injected electrons away from the dyad/TiO_2 to a separate compartment much like in the original Fujishima and Honda experiment (Fig. 1). The rutile TiO_2 reported in their classical study would not provide adequate surface area for attachment of the Zheng dyad as far more sunlight light would be transmitted than would be absorbed. Monolayers of even the most strongly absorbing pigments are not generally useful for solar light harvesting on planar materials (12). However, the mesoporous nanocrystalline TiO_2 thin films used in dye-sensitized solar cells (13, 14) circumvent this issue and would provide a surface area for the Zheng dyad that is ~1,000 times that of a planar material. In fact, such a high surface area would not be necessary for the Zheng dyad as the antennae Bodipy chromophore would likely enable the use of thinner films or materials with inherently lower surface areas.

The energetics of the TiO_2 must be considered. Unlike in this report where the Pt and TiO_2 are fused together, it is known that, when electrons are removed from TiO_2 (or other semiconducting binary oxides) to a separate metal electrode, they do not have the potential required for proton reduction (15). This remains an issue even for the original Fujishima and Honda report; most experimentalists apply a small potential or a pH gradient to raise the Fermi energy of the electrons in the counterelectrode. Even ternary materials like $SrTiO_3$ whose conduction band edge is appropriate for unassisted water splitting are far more efficient when a bias is applied (16). Although the band edge positions of semiconductors are not fixed in energy and can be widely tuned through pH, ion adsorption, light absorption, or surface dipoles, the fact that unassisted water splitting has not yet been achieved at oxide surfaces despite thousands of investigations is worrisome. It may signal that efficient unassisted water splitting with metal oxide materials is not possible. Alternative semiconductor materials or the use of tandem solar cells (with light absorption at both electrodes) may be necessary.

From a more purely fundamental point of view, the behavior of the Zheng dyad provides a number of new molecular insights into light-driven interfacial chemistry that would be difficult to garner from the study of solid-state materials alone. For example, the position of the link between the transition metal complex and the Bodipy in the dyad was found to directly influence the energy transfer dynamics and hence $H_{2(g)}$ production. Likewise, the chemical identity of the functional groups that bind the dyad to the TiO_2 surface were shown to be critically important. The role of spin on the Bodipy was also of keen interest, with the singlet states undergoing rapid picosecond energy transfer to the inorganic complex, while the population of triplet states was unproductive. Although the details go beyond what would be of interest to nonspecialists, many additional insights were provided. Suffice it to say that, with continued molecular-level studies of solar fuel production, like those described for the Zheng dyad, a body of knowledge will grow that will one day make it possible to rationally optimize water splitting and solar fuel production, providing a sustainable energy source for future generations.

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