

Visible Light Water Splitting Using Dye-Sensitized Oxide Semiconductors

W. JUSTIN YOUNGBLOOD,[†] SEUNG-HYUN ANNA LEE,
KAZUHIKO MAEDA,[‡] AND THOMAS E. MALLOUK*

Department of Chemistry, The Pennsylvania State University, University Park,
Pennsylvania 16802

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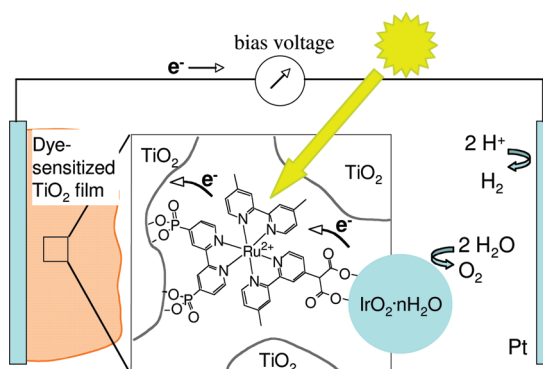
CONSPECTUS

Researchers are intensively investigating photochemical water splitting as a means of converting solar to chemical energy in the form of fuels. Hydrogen is a key solar fuel because it can be used directly in combustion engines or fuel cells, or combined catalytically with CO₂ to make carbon containing fuels. Different approaches to solar water splitting include semiconductor particles as photocatalysts and photoelectrodes, molecular donor-acceptor systems linked to catalysts for hydrogen and oxygen evolution, and photovoltaic cells coupled directly or indirectly to electrocatalysts.

Despite several decades of research, solar hydrogen generation is efficient only in systems that use expensive photovoltaic cells to power water electrolysis. Direct photocatalytic water splitting is a challenging problem because the reaction is thermodynamically uphill. Light absorption results in the formation of energetic charge-separated states in both molecular donor-acceptor systems and semiconductor particles. Unfortunately, energetically favorable charge recombination reactions tend to be much faster than the slow multi-electron processes of water oxidation and reduction. Consequently, visible light water splitting has only recently been achieved in semiconductor-based photocatalytic systems and remains an inefficient process.

This Account describes our approach to two problems in solar water splitting: the organization of molecules into assemblies that promote long-lived charge separation, and catalysis of the electrolysis reactions, in particular the four-electron oxidation of water. The building blocks of our artificial photosynthetic systems are wide band gap semiconductor particles, photosensitizer and electron relay molecules, and nanoparticle catalysts. We intercalate layered metal oxide semiconductors with metal nanoparticles. These intercalation compounds, when sensitized with [Ru(bpy)₃]²⁺ derivatives, catalyze the photoproduction of hydrogen from sacrificial electron donors (EDTA²⁻) or non-sacrificial donors (I⁻). Through exfoliation of layered metal oxide semiconductors, we construct multilayer electron donor-acceptor thin films or sensitized colloids in which individual nanosheets mediate light-driven electron transfer reactions. When sensitizer molecules are "wired" to IrO₂ · nH₂O nanoparticles, a dye-sensitized TiO₂ electrode becomes the photoanode of a water-splitting photoelectrochemical cell.

Although this system is an interesting proof-of-concept, the performance of these cells is still poor (~1% quantum yield) and the dye photodegrades rapidly. We can understand the quantum efficiency and degradation in terms of competing kinetic pathways for water oxidation, back electron transfer, and decomposition of the oxidized dye molecules. Laser flash photolysis experiments allow us to measure these competing rates and, in principle, to improve the performance of the cell by changing the architecture of the electron transfer chain.



Introduction

Visible light water splitting is a long-standing problem in photochemistry.^{1,2} Efficient photocatalytic water-splitting systems could have practical value

for solar energy conversion, particularly if they could be coupled to higher temperature catalytic reactions for making liquid fuels.³ In addition, the lessons learned from the design and study of

water-splitting catalysts would be relevant to other energy-related problems, including fuel cell catalysis and the photocatalytic synthesis of higher value chemicals from carbon dioxide.

In principle, direct water splitting is possible with both visible and near-infrared light, because the difference between the potentials of the $\text{H}_2/\text{H}_2\text{O}$ and $\text{H}_2\text{O}/\text{O}_2$ half-cell reactions is only 1.23 V. Bolton et al.⁴ considered the thermodynamics of photochemical water splitting in detail and concluded that it is possible to store about 12% of the incident solar energy in the form of hydrogen, allowing for reasonable losses (a total of 1.0 eV) in the electron transfer steps and the catalytic reactions of water oxidation and reduction. The catch is that their calculations assume a quantum yield of 100%. In practice, there have been very few reports of photocatalytic water splitting using visible light,^{5–7} and the best reported quantum yield is so far about 6% at 420 nm,⁸ meaning that the best solar power conversion efficiency is still below 0.5%.

In contrast to photocatalytic systems, photoelectrochemical cells based on semiconductor p–n junctions and semiconductor–liquid junctions can be quite efficient. The difference is that charge recombination in a p–n junction is inhibited by the electric field that separates the light-generated minority and majority carriers. Photon-to-electron quantum yields approaching unity and power conversion efficiencies up to 18% have been reported with single crystal photoelectrodes.⁹ As noted above, photocatalytic water splitting would become similarly efficient if charge recombination reactions could be made sufficiently slow.

Photoinduced electron transfer reactions in molecular donor–acceptor dyads and in sensitizer–semiconductor dyads are now well understood processes. High quantum yields for *transient* photochemical charge separation are very often found, and when these systems are coupled to sacrificial electron donors or acceptors, hydrogen or oxygen can be made in good quantum yield.^{10,11} One must be careful not to brag about the “efficiency” of these sacrificial systems in the context of practical energy conversion, because the overall reaction (e.g., persulfate to oxygen and sulfate) is usually downhill thermodynamically. However, sacrificial donors such as EDTA or methanol, or acceptors such as persulfate, are useful in mechanistic studies because they remove the complication of back electron transfer and allow one to examine a light-driven half cell reaction (water oxidation or reduction) in isolation. For example, the oxidation of photoexcited Ru(II) polypyridyl complexes by persulfate provides a photogenerated oxidant with a well-defined potential for studying the kinetics of oxygen evolution by different catalysts.¹¹ The quantum yield of hydro-

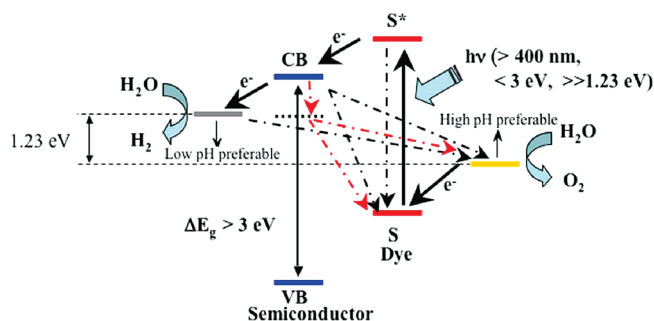


FIGURE 1. Kinetic scheme illustrating forward electron transfer (solid lines) and possible recombination pathways (dotted lines) in sensitized semiconductor nanosystems containing hydrogen and oxygen evolving catalysts.

gen or oxygen evolution in sacrificial half cycles is also an effective method for rapidly screening new photosensitizers or catalysts.¹⁰

The high quantum yields obtained in sacrificial half cycles imply that the essential components (photosensitizers, electron relays, and catalysts) are already in hand for overall water splitting, at least at the proof-of-concept level. The problem is to combine them in such a way that reverse reactions, electron transfer short-circuits and hydrogen–oxygen recombination, do not dominate kinetically. Back electron transfer in even the simplest such systems (e.g., a sensitized oxide semiconductor particle, loaded with a hydrogen evolving catalyst and linked through a sensitizer to an oxygen evolving catalyst, Figure 1) is however quite complex. At each branch point in the chain, a high quantum yield can result only if the forward electron transfer rate (solid arrows) is faster than the sum of all the reverse rates from the same point in the system. For example, in Figure 1, the forward electron transfer from the semiconductor to the hydrogen evolving catalyst must compete effectively with back transfer to the oxidized dye, and also with electron transfer to the catalyst for water oxidation. In general, the reverse pathways have much greater driving forces than the forward ones, and this makes the reverse reactions fast. However, because electron transfer rates are also strongly distance-dependent, it should be possible to arrange the molecules in space in such a way that the forward pathway becomes kinetically competitive or even dominant. Photosynthesis is living proof of this principle, which is the general theme of the research described in this Account.

Assembly of Nanostructures for Light-Induced Charge Separation

Layer-by-Layer Assembly of Multicomponent Electron Transfer Chains. Layer-by-layer (LBL) assembly offers a simple way to control the distances between electroactive mole-

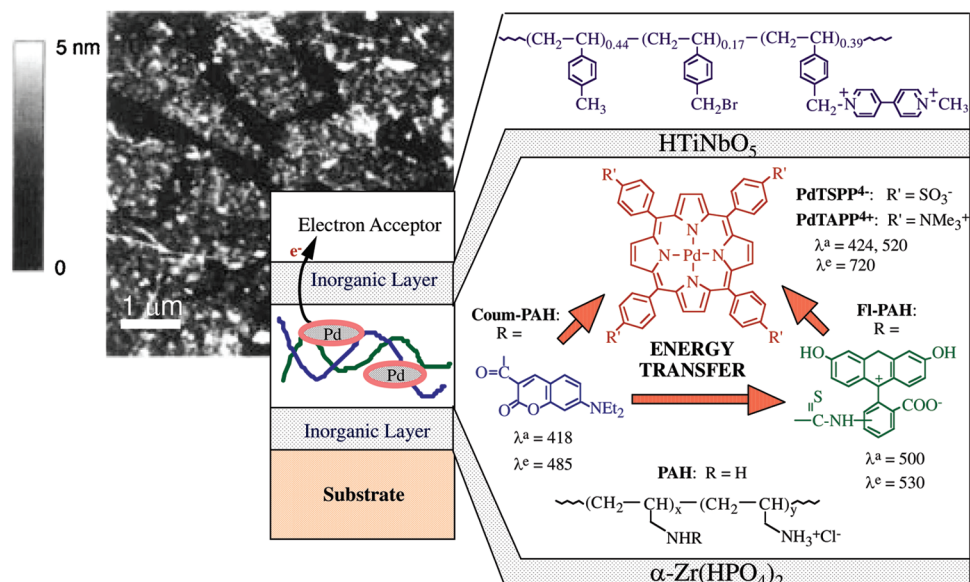


FIGURE 2. Cascade of energy/electron transfer reactions in a multilayer LBL assembly. Polycation chains containing coumarin and fluorescein groups are sandwiched with porphyrin sensitizer molecules between anionic sheets. Electron transfer from the porphyrin to the viologen polymer in the top layer occurs rapidly ($1\text{--}2\ \mu\text{s}$ time scale) because of the intermediacy of the semiconducting titanoniobate layer, but back electron transfer is slow ($\sim 900\ \mu\text{s}$). A tapping mode AFM image of titanoniobate sheets on the top surface of a three-layer LBL film is shown at the left.

cules, at least in the stacking direction of a multilayer film. With this idea in mind, we developed schemes for growing layered metal–organic solids on surfaces by sequential adsorption of the constituent metal ions and ligands.^{12–14} The first of these was the metal phosphonate LBL method, in which Zr^{4+} or other multiply charged metal ions were alternately adsorbed with diphosphonic acids.¹² The phosphonate ligands could contain electroactive or photoactive groups, and early experiments by Katz et al. explored the photochemistry of zirconium phosphonate films that contained porphyrin sensitizers and viologen electron acceptors in different layers.¹⁵ Two problems with the metal phosphonate method were the need to derivatize the electroactive molecules with phosphonic acid groups and the long adsorption times needed to grow ordered films. In 1991, Decher and Hong discovered the electrostatic layer-by-layer assembly method, which overcame both problems.¹⁶ However, LBL deposition of linear polyelectrolytes results in “fuzzy” multilayers in which there is strong mixing of successive layers.¹⁷ For artificial photosynthesis, one needs well stratified structures to prevent back electron transfer reactions.

A modification of the LBL method uses two-dimensional sheets, which are made by exfoliating layered solids, in place of organic polyanions.^{18–20} This results in a “lasagna” architecture that separates the electroactive components into well-defined layers. We showed by using fluorescent resonant energy transfer (FRET) that there was minimal layer interpen-

etration in such structures.²¹ Several different kinds of sheets could be used, but the most relevant to artificial photosynthesis were insulating 1 nm thick sheets made from zirconium phosphate ($\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$)²² and wide band gap semiconductor sheets made by exfoliation of layered metal oxide semiconductors (LMOS).²³ In the assembly shown schematically in Figure 2, there are five photoactive/electroactive components organized by the LBL method. Visible photons are absorbed by the coumarin and fluorescein molecules, and energy is transferred efficiently to the porphyrin sensitizer (PdTSPP^{4-}) in the same layer. The porphyrin triplet excited state is quenched by forward electron transfer to the titanoniobate sheets, which then transfer the electron to the viologen polymer. The overall quantum yield for this multistep cascade is 0.6, and the lifetime of the porphyrin–viologen charge-separated state is long (0.9 ms), because back electron transfer reaction from the viologen to the LMOS sheet is energetically uphill.²⁴

Hydrogen Evolution from Sensitization of Layered Metal Oxide Semiconductors. While it is possible to achieve long-lived transient charge separation by organizing redox molecules into assemblies like that shown in Figure 2, permanent charge separation requires catalysis of the water oxidation and/or reduction reactions. The LMOS sheets that are the primary electron acceptors in Figure 2 can be functionalized with catalytic particles for hydrogen evolution. Using this idea, we were able to demonstrate photochemical hydrogen evo-

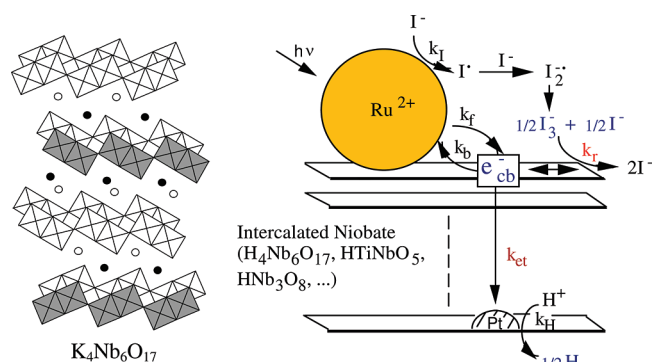


FIGURE 3. Scheme for visible light evolution from aqueous I^- , a nonsacrificial electron donor. Electron transfer to the hydrogen-evolving Pt catalyst (k_{et}) occurs on a time scale of tens of milliseconds. The idealized structure of the LMOS $\text{K}_4\text{Nb}_6\text{O}_{17}$ is shown at the left.

lution from water using iodide, a nonsacrificial donor.²⁵ The photolysis of HI at sensitized LMOS particles is shown schematically in Figure 3. The layered architecture of an LMOS, such as $\text{K}_4\text{Nb}_6\text{O}_{17}$, allows for selective internal platinization²⁶ such that the hydrogen evolving Pt catalyst sites are segregated by charge exclusion from the triiodide that accumulates in solution.

HI photolysis is the “poor man’s” water splitting, because the standard potential for the reaction is only +0.535 V. It allows one to take a realistic look at the competition between forward and back electron transfer rates in a thermodynamically uphill photoreaction. The segregation of catalyst sites allowed this system to function with a *nonsacrificial* electron donor in contrast to earlier photocatalytic systems that depended on sacrificial donors. A stringent test of the compartmentalization of the catalyst for the hydrogen half reaction was the inability of these materials to catalyze the thermodynamically downhill reaction of H_2 and I_3^- in the dark.²⁷

The rate of hydrogen evolution decreases, approaching zero, as the concentration of triiodide builds up. Since no dark reaction was observed between hydrogen and triiodide, the cause of the rate decay was identified as charge recombination between oxidized electron donor species and the LMOS. Transient spectroscopy showed that the rate of back electron transfer was 3 orders of magnitude slower than the forward electron injection. However, percolation of the injected electrons to catalytic Pt sites was hindered by the low interlayer conductivity of the LMOS. Accordingly, the rate of hydrogen evolution was correlated to the interlayer spacing, which could be modulated by cation exchange.

Because back electron transfer from the semiconductor to I_3^- was responsible for the low quantum yield in this system,

subsequent experiments focused on insulating the semiconductor from the triiodide ions, by using anionic surface modifiers to repel negatively charged I_3^- and I_2^- .²⁸ Dye-sensitized LMOS particles treated with either $[\text{TiNbO}_5]_n^{n-}$ polyanions (derived from exfoliated KTiNbO_5) or poly(styrenesulfonate) showed 3- to 5-fold improvement in the hydrogen evolution rate. This dramatic improvement resulted from a 10-fold decrease in the rate of back electron transfer from the LMOS to triiodide. With these anionic surface modifiers, the lifetime of charge separation in the iodide–sensitizer–LMOS triad was in the millisecond range, and initial quantum yields of 30% were obtained for HI photolysis. It follows that efficient coupling of such a system to oxygen evolving catalysts (to replace the iodide donor) would require electron transfer from the catalyst to the oxidized sensitizer on a time scale of hundreds of microseconds. The turnover rate for oxygen evolution should also be sufficiently fast to keep up with the photon flux at solar irradiance levels. We will revisit these key issues in the context of water splitting using dye-sensitized solar cells below.

Photocatalytic Water Reduction with Nanosheets and Nanoscrolls. In a dye-sensitized semiconductor photosystem like that illustrated in Figure 1, the semiconductor particle mediates electron transfer between the dye and a particle (typically Pt or Rh) or molecule that catalyzes hydrogen evolution. For the hydrogen evolution reaction to be efficient, the rate of electron transfer to this catalyst should be fast relative to back electron transfer to the oxidized dye or electron donor. The dynamics of these processes have been studied for many years, especially with colloidal TiO_2 particles.^{29,30} Oxide nanosheets, which are obtained by exfoliation of LMOS compounds, make particularly good electron transfer mediators. We recently observed external quantum yields of 20–25% for hydrogen evolution from EDTA^{2-} solutions with niobate nanoscrolls and nanosheets catalyzed by Pt and sensitized by a phosphonated $[\text{Ru}(\text{bpy})_3]^{2+}$ derivative (Figure 4).³¹ Taking into account light scattering, the low extinction coefficient of the dye, and the charge injection efficiency, this system has >50% internal quantum yield for hydrogen evolution from photoinjected electrons. This high internal quantum yield shows that the single crystal oxide nanoscrolls and sheets are good mediators of electron transfer between the dye molecules and Pt particles. Most interestingly, we found that electron transfer from EDTA^{2-} to Ru^{3+} was the slowest step in the overall reaction, implying that one could replace the sacrificial electron donor with a nonsacrificial donor if the Pt catalyst could be compartmentalized to eliminate the back reaction with H_2 . Domen and co-workers have shown that

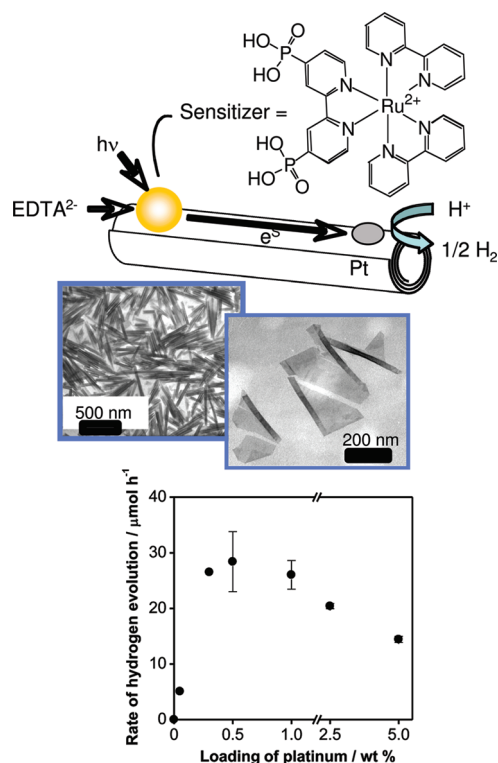


FIGURE 4. (top) Schematic representation of photoinduced electron transfer from a phosphonated $[\text{Ru}(\text{bpy})_3]^{2+}$ sensitizer to Pt catalyst particles, mediated by LMOS nanoscrolls derived from $\text{H}_4\text{Nb}_6\text{O}_{17}$. (center) TEM images of the scrolling of individual nanosheets (right) and of nanoscrolls precipitated from a suspension of exfoliated $\text{H}_4\text{Nb}_6\text{O}_{17}$ (left). (bottom) The dependence of the rate of hydrogen evolution on Pt loading and the high quantum yield establish that electron transfer from EDTA^{2-} to Ru^{3+} is the slowest step in the overall process.

$\text{Rh}-\text{Cr}_2\text{O}_3$ core-shell particles on oxynitride semiconductor particles can catalyze the forward reaction of hydrogen evolution even in the presence of molecular oxygen,³² so this appears to be a promising avenue to pursue with exfoliated nanosheets.

Catalysis of the Water Oxidation Reaction

The oxidation of water is arguably the most difficult problem in artificial photosynthesis. Because it is a four-electron process, water oxidation at moderate overpotential (100–300 mV) is slow even with the best catalysts. A related problem is that molecules that can oxidize water tend to be unstable at the very positive potentials needed to drive the reaction. As noted above (see Figure 1), water oxidation catalysts must deliver electrons to oxidized photosensitizer molecules rapidly, because the time scale for back electron transfer is fast, typically microseconds to milliseconds. Despite much recent progress in the design of molecular water oxidation catalysts,^{33–39} such fast turnover rates have not been achieved.

Transition metal oxides have been known for many years to be good catalysts for water oxidation.⁴⁰ Harriman and co-workers surveyed a number of such catalysts, including IrO_2 , RuO_2 , and Co_3O_4 , and found that IrO_2 was both stable and very active in the sacrificial half-cycle of water oxidation from persulfate ($\text{S}_2\text{O}_8^{2-}$) and photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$.¹¹ Several groups have now studied water oxidation by $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ nanoparticles in both electrochemical and photochemical systems.^{41–44} With these amorphous, hydrated nanoparticles, O_2 turnover rates of $\sim 40 \text{ s}^{-1}$ per surface Ir atom were measured under photochemical conditions at pH 5.7, where the overpotential for water oxidation by $[\text{Ru}(\text{bpy})_3]^{3+}$ is 370 mV.⁴¹ Murray and co-workers found electrochemical turnover rates of 5–6 s^{-1} per Ir atom (of which about 50% are on the surface) at 250 mV overpotential with mesoporous films of 2 nm $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ particles.⁴⁴ Considering the difference in overpotentials, the electrochemical data are consistent with the photochemical measurements.

Another important finding in the photochemically driven reaction between $[\text{Ru}(\text{bpy})_3]^{3+}$ and $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ was that the H/D kinetic isotope effect (KIE) is 1.0.⁴¹ Because most of the ensuing reaction steps involve proton and electron transfer, the lack of a KIE means that the initial electron transfer between Ir(IV) and Ru(III) is the slow step in the overall process at low overpotential. Outer-sphere electron transfer rates are strongly distance-dependent, and this suggested to us a strategy of directly coupling the sensitizer to the nanoparticles to increase the rate. We found that the alkaline hydrolysis of IrCl_6^{2-} in the presence of dicarboxylic acids, especially succinate and malonate derivatives, gave stable 1–2 nm diameter capped particles. These particles could be linked to $[\text{Ru}(\text{bpy})_3]^{2+}$ derivatives through the capping ligands.⁴⁵ In these covalently linked sensitizer– $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ dyads, the first-order electron transfer rate from Ir(IV) to Ru(III) was $8 \times 10^2 \text{ s}^{-1}$, corresponding to electron transfer on the millisecond time scale. This is comparable to the charge-separated state lifetime in some of the LMOS-based photosystems described above (Figures 2 and 3), and so it suggested that sensitizer-capped $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ clusters could be integrated with oxide semiconductors for overall water splitting.

Overall Water Splitting in a Dye-Sensitized Solar Cell

The simplest system for exploring the idea of visible light water splitting with a sensitized oxide semiconductor is a photoelectrochemical cell. In an electrochemical cell, one can avoid the possible complication of H_2 – O_2 recombination by making H_2 in a physically separated cathode compartment. A

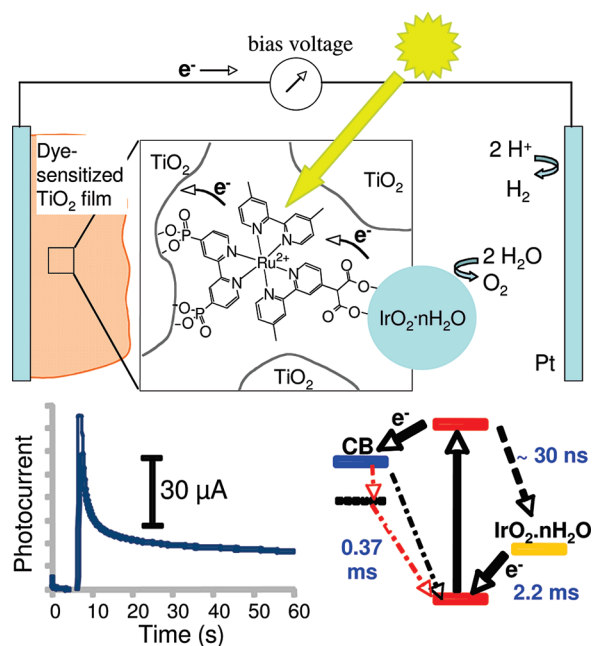


FIGURE 5. (top) Schematic diagram of a water-splitting dye-sensitized solar cell. The inset illustrates a sensitizer-capped IrO₂·nH₂O catalyst particle in the mesopores of the TiO₂ electrode film. (bottom left) Current transient obtained under visible light illumination. (bottom right) Energy level diagram showing the rates of forward and back electron transfer from and to the sensitizer molecule.

schematic of such a cell is shown in Figure 5.⁴⁶ Here the photoanode is a mesoporous TiO₂ electrode, as in a dye-sensitized solar cell (DSSC).⁴⁷ The dye is a monolayer of sensitizer-capped IrO₂·nH₂O particles. The [Ru(bpy)₃]²⁺ sensitizer is modified with both phosphonate and malonate ligands in the 4-positions of the 2,2'-bipyridyl ligands in order to adsorb strongly to TiO₂ and IrO₂·nH₂O, respectively. The cathode is a Pt wire electrode. Because the potential of electrons in trap states below the anatase conduction band is not sufficiently negative to reduce water, a bias voltage (≥330 mV) must be applied for water splitting to occur in this cell.

In a conventional DSSC, the anode and cathode are connected by the I⁻/I₃⁻ redox couple, which very rapidly regenerates the Ru(II) state of the sensitizer following electron injection into the TiO₂ anode film. In the case of our water-splitting DSSC, the electron donor is Ir(IV), and thus the oxidized sensitizer is reduced on a much slower time scale. The rate of this electron transfer was found by flash photolysis to be 2.2 ms, which unfortunately cannot compete effectively with the fast (0.37 ms) charge recombination reaction between the photoinjected electron and Ru(III). Also, each IrO₂·nH₂O particle is capped with 10–20 sensitizer molecules, of which only a few are likely also to bind the TiO₂ surface. The rest undergo rapid (~30 ns) excited state quenching by electron

transfer to Ir(IV). The combination of these two effects makes the steady-state quantum efficiency of this cell about 1%.

Although this system is inefficient, it represents a proof-of-concept of overall water splitting in a sensitizer-based photo-system. The low quantum efficiency can be understood in terms of three problems that can be addressed by design at the molecular level. The simplest of these is to make catalyst particles that are connected to only one sensitizer molecule, so that each sensitizer can bind both TiO₂ and IrO₂·nH₂O. A second problem is to slow down the back electron transfer reaction, for example, by changing the distance between redox partners, and a third is to speed up the electron transfer from Ir(IV) to Ru(III). Speeding up the latter reaction is also important for improving the turnover number of the sensitizer, which is now poor (<20) because the Ru(III) form is unstable in water. The photocurrent transients in this system (Figure 5) show an initial spike which decays over a time scale of seconds, indicating polarization of the mesoporous TiO₂ electrode. Because the oxygen evolution reaction generates protons, the current decay may result from a local pH drop in the TiO₂ film, which decreases the overpotential for water oxidation. A simple solution to this problem would be to find more effective buffers that can penetrate into the porous film. The importance of local buffering in water oxidation catalysis has been suggested by recent experiments on cobalt phosphate⁴⁸ and cobalt oxide⁴⁹ catalysts, in which phosphate groups or a porous silica support can strongly enhance the catalyst turnover rate.

Future Prospects for Solar Water Splitting Nanosystems

The development of efficient and durable catalysts for visible light water splitting is still a challenging problem. For sensitizer-based systems to be competitive with existing technologies, such as photovoltaic cells coupled to electrolyzers, the quantum yield will need to increase to near unity and the turnover number to about 10⁹. Both of these problems have already been overcome for electrical power generation in DSSCs,⁴⁷ so there is reason to be cautiously optimistic about the use of sensitized oxide semiconductors in water-splitting systems. In the DSSC, the oxidized sensitizer is reduced on the nanosecond time scale by I⁻. Similarly fast reduction of Ru(III) will be needed to achieve high turnover numbers in water-splitting cells. One strategy for speeding up this reaction is to insert a fast mediator between the sensitizer and the oxygen evolution catalyst. It is worth noting that in Photosystem II of green plant photosynthesis, there is such a mediator (tyrosine-Z) between the "sensitizer" (P680) and the

CaMn₃O₄ cluster that catalyzes oxygen evolution.⁵⁰ Even in that case, however, the molecules are subject to destruction by side reactions at the very positive potential of water oxidation. Sophisticated shunting and repair mechanisms are therefore essential to oxygenic photosynthesis.

An alternative approach to water splitting exploits the built-in electric field of nanoscale and microscale semiconductor p–n junctions. Lee and co-workers have reported very interesting photocatalyst particles in which charge separation at an oxide heterojunction inhibits recombination and increases the quantum yield for making hydrogen or oxygen.⁵¹ Liquid junction semiconductor nanowire solar cells have now been studied by several groups. These cells can contain dye-sensitized oxide nanowire arrays⁵² or arrays of narrow band gap semiconductor nanowires (e.g., Si and InP).^{53–59} With Si and InP wires, current rectification has been observed at the semiconductor–liquid junction and in both radial and axial p–n junctions. In principle, it should be possible to make nanostructures in which the photovoltages of these junctions add in series. This would provide architectures difficult to achieve in molecular systems (but expected to have higher efficiency⁴), in which two (or more) photons are absorbed per electron transferred. With silicon wires, a series of 3–4 p–n junctions should develop enough driving force to split water, using appropriate catalysts at the reducing and oxidizing ends of the series photodiode. It will be interesting to see if these microengineered solar cells, which contain no molecules and address the problem of charge recombination with built-in electric fields, can outrun the molecular approach to achieving efficient and durable visible light water splitting.

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BIOGRAPHICAL INFORMATION

W. Justin Youngblood received his B.S. degree from Washington and Lee University (1994) and his Ph.D. in Chemistry from North Carolina State University (2005). He was a postdoctoral fellow at Penn State (2005–2008), and is now an Assistant Professor of Chemistry at the University of North Texas. His current research involves the design and synthesis of new organic materials and supramolecular arrays for organic photovoltaics.

Seung-Hyun Anna Lee received her B.S. (2002) and M.S. (2005) degrees in Chemistry from Purdue University. She is currently

working toward her Ph.D. in Chemistry at Penn State. Her research interests include dye-sensitized solar cells, electrochemistry, and electrocatalysis.

Kazuhiko Maeda received his B.S. degree from Tokyo University of Science (2003), his M.S. degree from Tokyo Institute of Technology (2005), and his Ph.D. from the University of Tokyo (2007). As a graduate student and postdoctoral fellow with Prof. Kazunari Domen, he developed visible light water splitting catalysts based on zinc oxide–gallium nitride semiconductor particles. He was a postdoctoral fellow at Penn State (2008–2009), and is currently an Assistant Professor at the University of Tokyo, where his research interests are photocatalytic and photoelectrochemical water splitting using semiconductor particles of (oxy)nitrides and inorganic metal-oxide nanosheets.

Thomas E. Mallouk received his Sc.B. degree from Brown University (1977) and his Ph.D. in Chemistry from the University of California, Berkeley (1983). He was a postdoctoral fellow at MIT (1983–1985). His research focuses on the synthesis, assembly, and applications of nanoscale inorganic materials.

FOOTNOTES

*To whom correspondence should be addressed. E-mail: tom@chem.psu.edu.

†Current address: Department of Chemistry, University of North Texas, Denton, TX 76203.

‡Current address: Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

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