

# Chemical approaches to artificial photosynthesis

Javier J. Concepcion, Ralph L. House, John M. Papanikolas, and Thomas J. Meyer<sup>1</sup>

Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290

photoelectrochemical cell | photosystem II | water splitting | solar fuels | artificial photosynthesis

In the early 1970s, the works by Fujishima and Honda (1) and Honda et al. (2) reported on the results of a now famous experiment. They showed that band gap excitation of anatase TiO<sub>2</sub> in a photoelectrochemical cell with a Pt counter electrode and an applied bias resulted in water splitting into hydrogen and oxygen. The timing of the result was impeccable. In 1973, the Organization of the Petroleum Exporting Countries (OPEC) declared an embargo on oil imports to the West, resulting in gasoline shortages and long lines at gas pumps. Suddenly, there was a pressing need for energy independence and new ways of providing for the energy-hungry economies of Western Europe, Japan, and the United States. The international research community responded. There was a short lived explosion of interest in converting sunlight into high-energy molecules by what we now call artificial photosynthesis to make solar fuels. Target reactions were water splitting into hydrogen and oxygen (1) and light-driven reduction of CO<sub>2</sub> by water to give CO, other oxygenates, or hydrocarbons. Methane is shown as the product in equation 2, but the ultimate target is liquid hydrocarbons to power our existing energy infrastructure (1 and 2):



The oil crisis eased in the late 1970s, and with it, the surge in research and the interest in new energy technologies. Time has passed; the world is a different place. Significant increases in oil prices and demand, fueled by increased consumption and growth in the rapidly developing economies of China, other parts of East Asia, and India, are changing the energy landscape. There is increasing momentum for developing new energy technologies driven by cost, national security considerations, and concerns about environmental damage from the use of hydrocarbon fuels. Hydrocarbons—oil, natural gas, and coal—dominate the energy scene, accounting for 85–90% of current energy use internationally. Although new hydrocarbon sources continue to be found and exploited, production costs are rising, and they will not last forever.

There is also rising concern about environmental impact and global warming. Carbon emissions increased 5.9% in 2010 to the release of one-half of a billion tons of carbon. This jump was the largest in a single year since the Industrial Revolution and the largest percentage increase since 2003. Rising temperatures that lead to sea level rise pose an enormous economic risk, not just to isolated Pacific atolls but also to large stretches of the heavily populated US East Coast.

The dependence of the United States and world economies on hydrocarbons will extend into the future. It will be driven by a new mix of hydrocarbon sources that have been made economic by the increasing price of oil; natural gas and liquid fuels from fracking are the poster children of the moment. However, environmental concerns and longer-term access to adequate energy supplies on a continuing basis are problems that will not go away.

It is possible to look ahead to a new energy future: one that is driven by enhanced efficiencies and increasing use of renewable energy sources. It will be driven by higher costs, decreased availability of accessible hydrocarbons, and a growing recognition of the long-term economic impact of hydrocarbons on the environment. All sources of energy will play a role driven locally and regionally by availability and cost, with increasingly important roles for renewable energy sources—biomass, wind, and solar energy. When integrated with high-efficiency grid systems, they could bring the capacity to power the urban centers and industrial complexes of a growing world economy.

The ultimate renewable energy source should be the sun. It provides ~10,000 times our current energy needs on a continuing basis day after day. However, the sun as a power source has two limitations. First, it is diffuse. To meet current US power demands with a 10% efficient solar device or devices, a collection area of ~58,000 square miles would be required. At current semiconductor prices, that collection area would cost tens of trillions of dollars. It would also require a sophisticated grid system. In the United States, it is a long way from New York City to the high deserts of Nevada, New Mexico, and other western states, where there is sunshine in abundance. Even worse, the sun is intermittent, providing only ~6 h

of useful energy per day on the average worldwide. If solar energy is to become a primary energy source, it will have to be tied to energy storage during the day for power consumption at night at unprecedented scales.

The only reasonable solution is artificial photosynthesis with energy stored in chemical bonds as solar fuels. *The goal of artificial photosynthesis is to mimic the green plants and other photosynthetic organisms in using sunlight to make high-energy chemicals but with far higher efficiencies and simplicity of design for scale-up and large-scale production.*

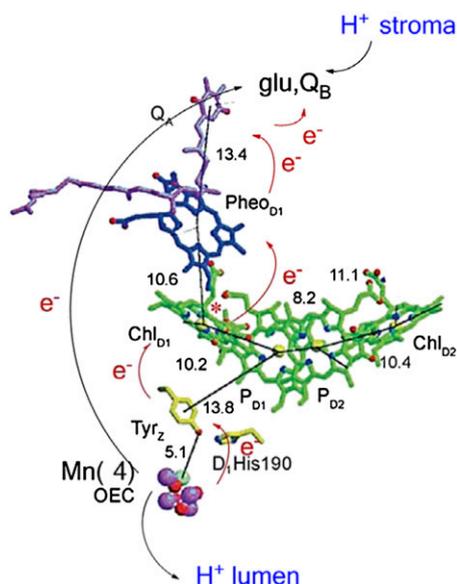
This goal takes us back to the famous Honda–Fujishima experiment showing water splitting with TiO<sub>2</sub>. The simplicity and promise of their result opened new research doors to using sunlight to make solar fuels. In 1974, another door was opened. It came with the experimental demonstration that the metal-to-ligand charge transfer excited state, Ru(2,2'-bipyridine)<sub>3</sub><sup>2+\*</sup> [Ru(bpy)<sub>3</sub><sup>2+\*</sup>], could undergo electron transfer quenching (scheme 1) (3, 4). The work by Rehm and Weller (5) had earlier shown electron transfer as a viable reaction for organic excited states, and the works by Vogler and Adamson (6), Zinato et al. (7), and Demas and Adamson (8) had suggested that Ru(bpy)<sub>3</sub><sup>2+\*</sup> could undergo electron transfer quenching by Co(III) ammine complexes (6–8); however, their results were equivocal and could also be explained by energy transfer quenching.

As shown by the reactions in scheme 1 and flash photolysis measurements, visible excitation of the dπ<sup>6</sup> Ru(bpy)<sub>3</sub><sup>2+</sup> ground state gives the corresponding <sup>3</sup>(dπ<sup>5</sup>π<sup>\*</sup><sub>bpy</sub>)<sup>1</sup> excited state. It was sufficiently long-lived, ~1 μs, to undergo diffusional electron transfer quenching with added methylviologen dication, MV<sup>2+</sup> (3). In the overall scheme, the energy of the incident light is captured and transiently stored in the excited state, and then, it is converted into the transient redox equivalents produced by excited state electron transfer.

Author contributions: J.J.C., R.L.H., J.M.P., and T.J.M. wrote the paper.

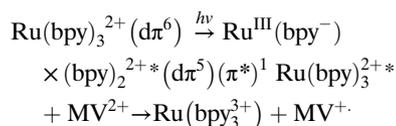
The authors declare no conflict of interest.

<sup>1</sup>To whom correspondence should be addressed. E-mail: tjmeyer@unc.edu.



**Fig. 1.** The sequence of events after antenna-sensitized formation of  $^1P_{680}$  (Chl<sub>D1</sub>) in the initial step in the Kok cycle. D<sub>1</sub>His190, Histidine190; glu, glutamate; OEC, 4 Mn containing oxygen evolving complex; Pheo<sub>D1</sub>, pheophytin D1; Q<sub>A</sub>, quinone A; Q<sub>B</sub>, quinone B; Tyr<sub>Z</sub>, tyrosine Z. Modified from refs. 12 and 13.

### Scheme 1



Excited state quenching results in conversion of 2.1 eV excited state free energy into 1.7 eV separated, transiently stored oxidative [ $\text{Ru}(\text{bpy})_3^{3+}$ ] and reductive ( $\text{MV}^+$ ) equivalents. Given their redox potentials, with  $E^{\circ} = 1.3$  V (vs. normal hydrogen electrode) for the  $\text{Ru}(\text{bpy})_3^{3+/2+}$  couple and  $E^{\circ} = -0.4$  V for the  $\text{MV}^{2+/+}$  couple, the quenching products are thermodynamically capable of water splitting over an extended pH range. The reaction in scheme 1 (3) gave birth to the concept of chemical approaches to artificial photosynthesis (9–11).

Without control of structure in an isotropic fluid, the transiently stored redox equivalents in scheme 1 (3) undergo diffusional back electron transfer, and the stored redox energy is lost as heat. To be useful, a light absorption–excited state quenching cycle must produce, separate, and store transient redox equivalents. It must be used at physically separated catalytic sites for driving the solar fuel half reactions, all before back electron transfer can occur.

To put this concept into perspective, at photosystem II (PSII) in natural photosynthesis, sunlight drives water oxidation by plastoquinone (PQ):  $2 \text{PQ} + 2\text{H}_2\text{O} + 4 h\nu \rightarrow 2 \text{PQH}_2 + \text{O}_2$ . A transmembrane pH gradient is also created for ATP production. The reductive equivalents in the reduced

form, the hydroquinone plastoquinol, are transferred to PSI, where light-driven  $\text{CO}_2$  reduction occurs in conjunction with the Calvin cycle.

Water oxidation and  $\text{O}_2$  evolution occur at the reaction center in PSII (1, 12–24). Oxygen is evolved after sequential absorption of four photons through the four stages of the Kok cycle from  $S_0$  to  $S_4$ . The Kok cycle is driven by antenna sensitization of the chlorophyll excited state  $^1P_{680}$ . In the  $S_0 \rightarrow S_1$  stage, absorption of the first photon and production of  $^1P_{680}$  trigger a cascade of five coupled electron–transfer events, with time scales ranging from picoseconds to microseconds (Fig. 1). The net result is transfer of an oxidative equivalent to the oxygen evolving complex separated by  $\sim 50$  Å from the re-

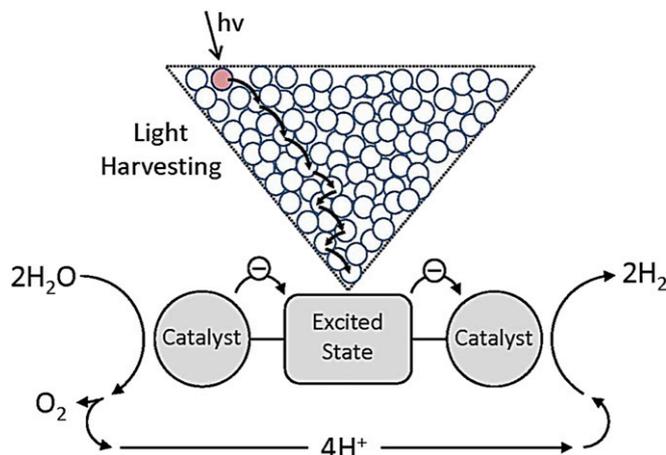
ductive equivalent at PQ as the semiquinone,  $\text{PQ}^-(\text{Q}_B^-)$  (Fig. 1). At this distance, back electron transfer is sufficiently slow to not interfere with the water oxidation cycle.

Photosynthesis in green plants is an inspiration but not an answer. It evolved slowly, and has remained the same for 2.4 billion years. It is amazingly complex, with five integrated, membrane-bound assemblies involving thousands of atoms bound in the thylakoid membrane of chloroplasts and is integrated with the Calvin cycle for  $\text{CO}_2$  reduction. However, its low efficiency for biomass production of  $\sim 1\%$  is inadequate for the high-density power production needed to power our increasingly urban societies.

There is a need for new, more efficient solar solutions. They need to be inexpensive, with their materials in sufficient supply for vast collection areas; also, they need to minimize environmental impact and overcome complications from longevity, production, and distribution.

The basic principles are understood: light absorption, excited state electron transfer, separation of electron transfer-generated oxidative and reductive equivalents by free energy gradients, electron transfer activation of catalysts for multi-electron, multiproton solar fuel half reactions, and separation and collection of the products. In semiconductors, band gap excitation gives electron–hole pairs directly, which are the delocalized versions of reductive and oxidative equivalents. Once formed, electron–hole pairs are separated by internal electric fields and directed to spatially separated catalytic sites on the semiconductor surface.

The direct band gap approach pioneered in the works by Fujishima and Honda (1) and Honda et al. (2) is remarkable for its simplicity, but the semiconductor is



**Fig. 2.** Molecular assembly for water splitting. In the absence of an antenna array, multilayer structures are required to achieve sufficient light absorption.

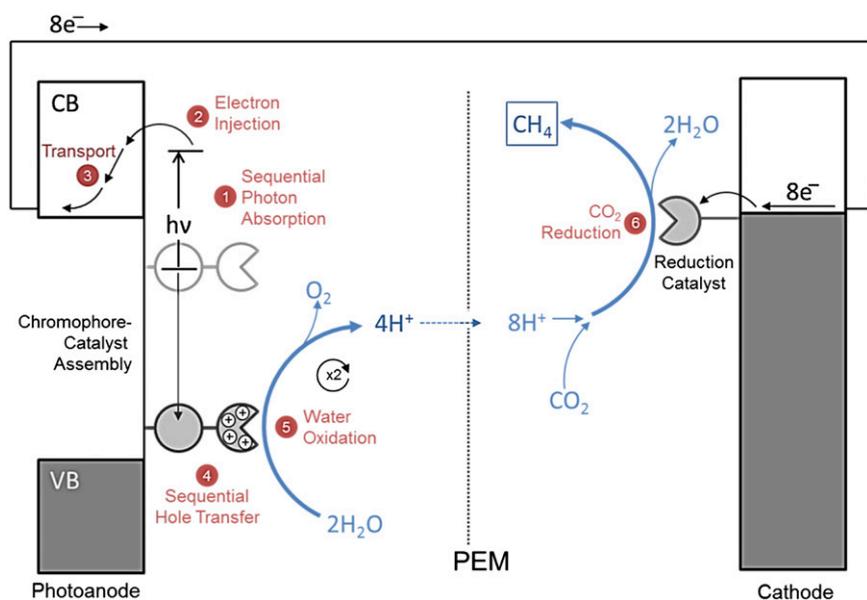


Fig. 3. Dye sensitized photoelectrosynthesis cell (DSPEC) for water reduction of  $\text{CO}_2$  to methane.

supposed to do it all—light absorption, charge separation, transport, and even catalysis—without degradation or decomposition. Pure chemical approaches have been proposed with the underlying theme of allowing the molecules to do the work. An example is shown in Fig. 2.

Chemical approaches offer the advantage of using a modular approach (6), with individual components for light absorption, etc. investigated separately, maximized in performance, and integrated in appropriate architectures. They offer the advantages of rapid iteration by chemical synthesis and the ability to study individual components separately.

Contemporary interest in chemical approaches to artificial photosynthesis is apparent by the large number of reviews that have appeared in recent years (25–38).

The most straightforward approach to solar fuels is combined photovoltaics–electrolysis, a proven technology with known long-term device efficiencies. Light is absorbed by a stand-alone PV device with electrical or wireless connections to the electrodes of the electrolyzer. The overall efficiency of the device is the product of efficiencies for the PV device and electrolyzer. An example of the wireless approach appears in recent results reported in the work by Reece et al. (39), which used a triple-junction, amorphous Si solar cell with electrodeposited catalysts for water reduction (NiMoZn) and oxidation (amorphous cobalt oxide). This configuration is similar to the one adopted earlier in the work by Khaselev et al. (40), which used Pt catalysts in a wired arrangement. The work by Walter et al. (41) at the Department of Energy-sponsored

Joint Center for Artificial Photosynthesis (JCAP) Solar Hub developed a wireless approach, in which at least one of the photoelectrodes incorporated semiconductor nanowires functionalized with catalysts.

The molecular assembly approach is elegant, but in the absence of a viable spontaneous assembly strategy, it requires multiple synthetic steps and is impractical. This result leads to a second guiding theme in solar fuels research—keep it simple—and the hybrid photoelectrochemical approach shown in Fig. 3. It illustrates a dye-sensitized photoelectrosynthesis cell (DSPEC) based on a photoanode for water oxidation. DSPECs are closely related to dye-sensitized solar cells in that light absorption occurs at a light absorber (dye or chromophore)—a molecule, cluster, or quantum dot—bound to the surface of a high band gap semiconductor, typically  $\text{TiO}_2$ . The first example appeared in 1999 for the dehydrogenation of isopropanol (42), and the works by Youngblood et al. (43, 44) developed a DSPEC for water splitting based on  $\text{IrO}_2$  as a water oxidation catalyst.

Light absorption and injection initiate a series of electron transfer events. For the example in Fig. 3, the injected electron is directed to a separate cathode for catalytic reduction of water or  $\text{CO}_2$ . A DSPEC device differs from a dye-sensitized solar cell device in using sunlight to drive spatially separated solar fuel half reactions rather than generate a photopotential and photocurrent.

In principle, multiple approaches and alternate architectures may contribute to a solar fuels future. The state of the art

at the moment is still very much on the basic research side. However, there is growing comprehension of the importance of anticipating the future and beginning the process of translation of basic science results to the marketplace. The key to future success will be a productive iteration among basic research, translation, engineering, and economics in a highly integrated environment. The goal is to shorten the timescale for evolving a technology or technologies that could help transform our energy future.

An overview of the state of the art in chemical approaches to artificial photosynthesis is the theme of this account. The focus is on basic research and progress made in key areas that have the ability to contribute to an ultimate solution. Enjoy the volume, because there is much to come.

### Architectures

Information on architectures is given in Grimm et al.: Step-by-step self-assembled hybrids that feature control over energy and charge transfer (45); Fukuzumi et al.: Formation of a long-lived electron-transfer state in mesoporous silica-alumina composites enhances photocatalytic oxygenation reactivity (46); and Megiatto et al.: Mimicking the electron transfer chain in photosystem II with a molecular triad thermodynamically capable of water oxidation (47).

### Catalysis

Information on catalysis is given in Duan et al.: Highly efficient and robust molecular ruthenium catalysts for water oxidation (48); Valdez et al.: Catalytic hydrogen evolution from a covalently linked dicobaloxime (49); McNamara et al.: Cobalt-dithiolene complexes for the photocatalytic and electrocatalytic reduction of protons in aqueous solutions (50); Tanaka et al.: Similarities of artificial photosystems by ruthenium oxo complexes and native water splitting systems (51); and Chen et al.: Splitting  $\text{CO}_2$  into CO and  $\text{O}_2$  by a single catalyst (52).

### Devices

Information on devices is given in Zhao et al.: Improving the efficiency of water splitting in dye-sensitized solar cells by using a biomimetic electron transfer mediator (53); Surendranath et al.: Interplay of oxygen-evolution kinetics and photovoltaic power curves on the construction of artificial leaves (54); and Xiang et al.: Evaluation and optimization of mass transport of redox species in silicon microwire-array photoelectrodes (55).

## Mechanism

Information on mechanism is given in Farnum et al.: Visible light generation of I–I bonds by Ru-tris(diimine) excited states (56); Pool et al.: Acidic ionic liquid/water solution as both a medium and proton source for electrocatalytic H<sub>2</sub> evolution by [Ni(P<sub>2</sub>N<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> complexes (57); Barroso et al.: Dynamics of photogenerated holes in surface modified α-Fe<sub>2</sub>O<sub>3</sub> photoanodes for solar water splitting (58); Smieja et al.: Kinetic and structural studies, origins of selectivity, and interfacial charge transfer in the artificial photosynthesis of CO (59); and Vagnini et al.: Ultrafast pho-

to-driven intramolecular electron transfer from an iridium-based water-oxidation catalyst to perylene diimide derivatives (60).

## Theory

Information on theory is given in Muckerman et al.: Calculation of thermodynamic hydricities and the design of hydride donors for CO<sub>2</sub> reduction (61); Horvath et al.: Insights into proton-coupled electron transfer mechanisms of electrocatalytic H<sub>2</sub> oxidation and production (62); and Lin et al.: Theoretical study of catalytic mechanism for single-site water oxidation process (63).

## Photocatalysis

Information on photocatalysis is given in Tamaki et al.: Photocatalytic CO<sub>2</sub> reduction with high turnover frequency and selectivity of formic acid formation using Ru(II) multinuclear complexes (64).

**ACKNOWLEDGMENTS.** We thank Will Thauer for his yeoman work in helping to pull together this special edition. It would have not been possible without his attention to detail and leadership. This material is based on research supported as part of the University of North Carolina Energy Frontier Research Center (EFRC), Center for Solar Fuels, an EFRC funded by US Department of Energy, Office of Science, Office of Basic Energy Sciences Award Number DE-SC0001011.

- Fujishima A, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238: 37–38.
- Honda K, Fujishima A, Kikuchi S (1969) Photosensitized electrolytic oxidation on semiconducting n-type TiO<sub>2</sub> electrode. *Kogyo Kagaku Zasshi* 72:108–113.
- Bock CR, Meyer TJ, Whitten DG (1974) Electron transfer quenching of the luminescent excited state of tris(2,2'-bipyridine)ruthenium(II). Flash photolysis relaxation technique for measuring the rates of very rapid electron transfer reactions. *J Am Chem Soc* 96:4710–4712.
- Young RC, Meyer TJ, Whitten DG (1975) Kinetic relaxation measurement of rapid electron transfer reactions by flash photolysis. Conversion of light energy into chemical energy using the Ru(bipy)<sub>3</sub><sup>3+</sup>-Ru(bipy)<sub>3</sub><sup>2+</sup> couple. *J Am Chem Soc* 97:4781–4782.
- Rehm D, Weller A (1969) Kinetik und Mechanismus der Elektrohumbertragung bei der Fluoreszenzloschung in Acetonitril. *Ber Bunsenges Phys Chem* 73:834–839.
- Vogler A, Adamson AW (1968) Photosensitized decomposition of some cobalt amines. *J Am Chem Soc* 90: 5943–5945.
- Zinato E, Lindholm RD, Adamson AW (1969) Photochemistry of complex ions. 6. Aqueous thiocyanatopentaamminechromium(3). *J Am Chem Soc* 91:1076–1085.
- Demas JN, Adamson AW (1973) Tris(2,2'-bipyridine) ruthenium(II) sensitized reactions of some oxalato complexes. *J Am Chem Soc* 95:5159–5168.
- Meyer TJ (1989) Chemical approaches to artificial photosynthesis. *Acc Chem Res* 22:163–170.
- Alstrum-Acevedo JH, Brennaman MK, Meyer TJ (2005) Chemical approaches to artificial photosynthesis. 2. *Inorg Chem* 44:6802–6827.
- Adeyemi SA, Doveltoğlu A, Guadalupe AR, Meyer TJ (1992) Redox and spectral properties of the four-electron oxidant trans-aquadioxo(terpyridine)ruthenium (2+) diperchlorate. *Inorg Chem* 31:1375–1383.
- Strouse GF, Worl LA, Younathan JN, Meyer TJ (1989) Long-range energy transfer in a soluble polymer by an energy-transfer cascade. *J Am Chem Soc* 111: 9101–9102.
- Ferreira KN, Iverson TM, Maghlaoui K, Barber J, Iwata S (2004) Architecture of the photosynthetic oxygen-evolving center. *Science* 303:1831–1838.
- Yachandra VK, Sauer K, Klein MP (1996) Manganese cluster in photosynthesis: Where plants oxidize water to dioxygen. *Chem Rev* 96:2927–2950.
- Renger G, Renger T (2008) Photosystem II: The machinery of photosynthetic water splitting. *Photosynth Res* 98: 53–80.
- Meyer TJ, Huynh MHV, Thorp HH (2007) The possible role of proton-coupled electron transfer (PCET) in water oxidation by photosystem II. *Angew Chem Int Ed Engl* 46:5284–5304.
- McEvoy JP, Brudvig GW (2006) Water-splitting chemistry of photosystem II. *Chem Rev* 106:4455–4483.
- Kern J, Renger G (2007) Photosystem II: Structure and mechanism of the water-plastoquinone oxidoreductase. *Photosynth Res* 94:183–202.
- Dau H, Zaharieva I (2009) Principles, efficiency, and blueprint character of solar-energy conversion in photosynthetic water oxidation. *Acc Chem Res* 42: 1861–1870.
- Brudvig GW (2008) Water oxidation chemistry of photosystem II. *Philos Trans R Soc Lond B Biol Sci* 363: 1211–1218.
- Barber J, Andersson B (1994) Revealing the blueprint of photosynthesis. *Nature* 370:31–34.
- Barber J (2006) Photosystem II: An enzyme of global significance. *Biochem Soc Trans* 34:619–631.
- Yano J, et al. (2006) Where water is oxidized to dioxygen: Structure of the photosynthetic Mn<sub>4</sub>Ca cluster. *Science* 314:821–825.
- Loll B, Kern J, Saenger W, Zouni A, Biesiadka J (2005) Towards complete cofactor arrangement in the 3.0 Å resolution structure of photosystem II. *Nature* 438: 1040–1044.
- Magnuson A, Styring S (2012) Molecular chemistry for solar fuels: From natural to artificial photosynthesis. *Aust J Chem* 65:564–572.
- Carraro M, et al. (2011) Artificial photosynthesis challenges: Water oxidation at nanostructured interfaces. *Top Curr Chem* 303:121–150.
- Andreadis ES, Chavarot-Kerlidou M, Fontecave M, Artero V (2011) Artificial photosynthesis: From molecular catalysts for light-driven water splitting to photoelectrochemical cells. *Photochem Photobiol* 87: 946–964.
- Hammarstrom L, Styring S (2011) Proton-coupled electron transfer of tyrosines in Photosystem II and model systems for artificial photosynthesis: The role of a redox-active link between catalyst and photosensitizer. *Energy Environ Sci* 4:2379–2388.
- Song WJ, et al. (2011) Making solar fuels by artificial photosynthesis. *Pure Appl Chem* 83:749–768.
- Michl J (2011) Photochemical CO<sub>2</sub> reduction: Towards an artificial leaf? *Nat Chem* 3:268–269.
- Gagliardi CJ, et al. (2010) Integrating proton coupled electron transfer (PCET) and excited states. *Coord Chem Rev* 254:2459–2471.
- Gust D, Moore TA, Moore AL (2009) Solar fuels via artificial photosynthesis. *Acc Chem Res* 42:1890–1898.
- Concepcion JJ, et al. (2009) Making oxygen with ruthenium complexes. *Acc Chem Res* 42:1954–1965.
- Hammes-Schiffer S (2009) Theory of proton-coupled electron transfer in energy conversion processes. *Acc Chem Res* 42:1881–1889.
- Wasielewski MR (2009) Self-assembly strategies for integrating light harvesting and charge separation in artificial photosynthetic systems. *Acc Chem Res* 42: 1910–1921.
- Hambourger M, et al. (2009) Biology and technology for photochemical fuel production. *Chem Soc Rev* 38:25–35.
- Turner J (2008) Oxygen catalysis: The other half of the equation. *Nat Mater* 7:770–771.
- Guldi DM (2008) Photochemistry: Let there be light—but not too much. *Nat Nanotechnol* 3:257–258.
- Reece SY, et al. (2011) Wireless solar water splitting using silicon-based semiconductors and earth-abundant catalysts. *Science* 334:645–648.
- Khaselev O, Bansal A, Turner JA (2001) High-efficiency integrated multijunction photovoltaic/electrolysis systems for hydrogen production. *Int J Hydrogen Energy* 26: 127–132.
- Walter MG, et al. (2010) Solar water splitting cells. *Chem Rev* 110:6446–6473.
- Treadway JA, Moss JA, Meyer TJ (1999) Visible region photooxidation on TiO<sub>2</sub> with a chromophore-catalyst molecular assembly. *Inorg Chem* 38:4386–4387.
- Youngblood WJ, Lee SH, Maeda K, Mallouk TE (2009) Visible light water splitting using dye-sensitized oxide semiconductors. *Acc Chem Res* 42:1966–1973.
- Youngblood WJ, et al. (2009) Photoassisted overall water splitting in a visible light-absorbing dye-sensitized photoelectrochemical cell. *J Am Chem Soc* 131:926–927.
- Grimm B, et al. (2012) Step-by-step self-assembled hybrids that feature control over energy and charge transfer. *Proc Natl Acad Sci USA* 109:15565–15571.
- Fukuzumi S, et al. (2012) Formation of a long-lived electron-transfer state in mesoporous silica-alumina composites enhances photocatalytic oxidation reactivity. *Proc Natl Acad Sci USA* 109:15572–15577.
- Megiatt JD, Jr, et al. (2012) Mimicking the electron transfer chain in photosystem II with a molecular triad thermodynamically capable of water oxidation. *Proc Natl Acad Sci USA* 109:15578–15583.
- Duan L, Araujo CM, Ahlquist MSG, Sun L (2012) Highly efficient and robust molecular ruthenium catalysts for water oxidation. *Proc Natl Acad Sci USA* 109: 15584–15588.
- Valdez CN, Dempsey JL, Brunschwig BS, Winkler JR, Gray HB (2012) Catalytic hydrogen evolution from a covalently linked dicobaloxime. *Proc Natl Acad Sci USA* 109:15589–15593.
- McNamara WR, et al. (2012) Cobalt-dithiolenene complexes for the photocatalytic and electrocatalytic reduction of protons in aqueous solutions. *Proc Natl Acad Sci USA* 109:15594–15599.
- Tanaka K, Isobe H, Yamanaka S, Yamaguchi K (2012) Similarities of artificial photosystems by ruthenium oxo complexes and native water splitting systems. *Proc Natl Acad Sci USA* 109:15600–15605.
- Chen Z, et al. (2012) Splitting CO<sub>2</sub> into CO and O<sub>2</sub> by a single catalyst. *Proc Natl Acad Sci USA* 109:15606–15611.
- Zhao Y, et al. (2012) Improving the efficiency of water splitting in dye-sensitized solar cells by using a biomimetic electron transfer mediator. *Proc Natl Acad Sci USA* 109: 15612–15616.
- Surendranath Y, Bediako DK, Nocera DG (2012) Interplay of oxygen-evolution kinetics and photovoltaic power curves on the construction of artificial leaves. *Proc Natl Acad Sci USA* 109:15617–15621.
- Xiang C, Meng AC, Lewis NS (2012) Evaluation and optimization of mass transport of redox species in silicon microwire-array photoelectrodes. *Proc Natl Acad Sci USA* 109:15622–15627.
- Farnum BH, Jou JJ, Meyer GJ (2012) Visible light generation of I–I bonds by Ru-tris(diimine) excited states. *Proc Natl Acad Sci USA* 109:15628–15633.
- Pool DH, et al. (2012) Acidic ionic liquid/water solution as both medium and proton source for electrocatalytic

- H<sub>2</sub> evolution by [Ni(P<sub>2</sub>N<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> complexes. *Proc Natl Acad Sci USA* 109:15634–15639.
58. Barroso M, et al. (2012) Dynamics of photogenerated holes in surface modified  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanodes for solar water splitting. *Proc Natl Acad Sci USA* 109:15640–15645.
59. Smieja JM, et al. (2012) Kinetic and structural studies, origins of selectivity, and interfacial charge transfer in the artificial photosynthesis of CO. *Proc Natl Acad Sci USA* 109:15646–15650.
60. Vagnini MT, et al. (2012) Ultrafast photodriven intramolecular electron transfer from an iridium-based water-oxidation catalyst to perylene diimide derivatives. *Proc Natl Acad Sci USA* 109:15651–15656.
61. Muckerman JT, Achord P, Creutz C, Polyansky DE, Fujita E (2012) Calculation of thermodynamic hydricities and the design of hydride donors for CO<sub>2</sub> reduction. *Proc Natl Acad Sci USA* 109:15657–15662.
62. Horvath S, Fernandez LE, Soudackov AV, Hammes-Schiffer S (2012) Insights into proton-coupled electron transfer mechanisms of electrocatalytic H<sub>2</sub> oxidation and production. *Proc Natl Acad Sci USA* 109:15663–15668.
63. Lin X, et al. (2012) Theoretical study of catalytic mechanism for single-site water oxidation process. *Proc Natl Acad Sci USA* 109:15669–15672.
64. Tamaki Y, Morimoto T, Koike K, Ishitani O (2012) Photocatalytic CO<sub>2</sub> reduction with high turnover frequency and selectivity of formic acid formation using Ru(II) multinuclear complexes. *Proc Natl Acad Sci USA* 109:15673–15678.