Artificial Photosynthesis

Walter Weare and Heinz Frei*

Physical Biosciences Division, Lawrence Berkeley National Laboratory

University of California, Berkeley, CA 94720

Abstract

The direct conversion of sunlight to high energy chemicals by a synthetic device made of inorganic, organic or hybrid materials is an attractive approach for harnessing sunlight in the form of a fuel. While proof of concept for the efficient conversion of solar energy to hydrogen and oxygen by water splitting has been demonstrated, such systems are not yet durable, made of materials that are not sufficiently abundant, or with synthetic processes that are not scalable. Exciting research developments over the past year in laboratories around the world are pointing the way toward robust artificial photosynthetic systems made of abundant elemental components by breaking down long-standing scientific barriers. This article describes research highlights on important improvements on the efficiency and durability of critical components of artificial systems, in particular catalysts. Catalytic systems are emerging that convert carbon dioxide directly to liquid alcohol molecules, desirable as transportation fuels. Moreover, substantial advances have been made on how to efficiently couple the captured solar photons to fuel-forming reactions.

Introduction

The direct conversion of visible photons to chemical energy by a synthetic device made of inorganic, organic or hybrid materials is an attractive method for harnessing sunlight in the form of a fuel. Such artificial photosynthetic devices, in contrast to the synthesis of biofuels via plants, are not restricted by the availability of arable land. Moreover, many efficiency limitations of biological photosynthesis, such as the ten-fold attenuation of the photon conversion yield at high solar light intensity (at noon) by light regulation mechanisms acting to prevent photooxidative damage of plant cell material, are absent in technological systems. Proof of concept for the efficient conversion of sunlight to hydrogen and oxygen by water splitting was demonstrated in a single integrated device by John Turner of the National Renewable Energy Laboratory ten years ago. The device is a monolithic, multilayer semiconductor material capable of splitting water with a conversion efficiency in excess of 10 percent for sunlight to chemical energy of H_2. However, the material degrades under use within days, is made of elements that are not sufficiently abundant, and employs fabrication processes akin to making a computer microchip - all of which make the device unsuitable for manufacturing on the scale needed for global fuel generation. Therefore, the most pressing need for making practical artificial solar fuel generators a reality is to develop robust systems that are made from abundant elemental components using scalable processes.

The essential components of an artificial photosynthetic system are light harvesting at a chromophore, charge separation, and catalytic conversion of water or carbon dioxide (CO_2) to fuel molecules (Figure 1). Major scientific breakthroughs are needed to make each of these components robust, efficient, and composed of abundant

materials. The most daunting scientific gaps persist for the fuel forming catalysts, namely for proton reduction to hydrogen ($H^+ \rightarrow H_2$) and for the reduction of CO_2 to liquid fuels like methanol or a higher order alcohols ($CO_2 \rightarrow CH_3OH \rightarrow C_nH_{2n+1}OH$). Moreover, the reducing electrons needed for making hydrogen, or a liquid fuel from CO_2, have to be taken from water. Using water as the electron source both creates oxygen as a byproduct and closes the formation and use cycle of such fuels as water and CO_2 are the result of utilizing the newly formed fuels. Yet, reaching the goal of efficient and robust catalysts for the complex, multi-step chemistries of water oxidation and proton/CO_2 reduction awaits major breakthroughs in the field of catalysis. Furthermore, the coupling of catalysts to solar photons, and integrating components into artificial photosynthetic systems that generate fuels under minimal loss of energy or charge, requires major progress in chemistry and the science of nanomaterials. The highlights discussed here show that substantial advances in these areas were achieved in the past year.

Development of robust oxidation catalysts

Well defined molecular catalysts capable of evolving oxygen from water feature one or several transition metal atoms surrounded by organic ligands that stabilize the catalytic core. While a definitive mechanistic role has been attributed to the typically heteroaromatic ligands in some cases, it is desirable to replace the organic ligands with an all inorganic environment. Since carbon-free ligands are substantially less oxidizable, the resulting complexes are expected to be much more stable to the high oxidation potentials needed to form oxygen from water.

Two teams, Y.V. Geletii et al. and A. Sartorel et al., have independently reported nearly identical molecules for water oxidation based on the all inorganic ligand [γ-$SiW_{10}O_{36}]^{8-}$. Two of these polyoxotungstenate ligands were used to stabilize a tetra ruthenium core (Ru_4O_6, adamantane-like structure) in which the four Ru centers span a distorted tetrahedron (Figure 2). When exposed to oxidizing equivalents (either $Ce(NO_3)_4$ or $Ru(bpy)_3^{3+}$), the complexes catalytically oxidize water to form oxygen. These catalysts appear to be stable during catalysis, maintaining their spectroscopic features after oxygen evolution over extended periods of time.

The rate-limiting step in these systems is thought to be charge transfer to the oxidant rather than an intrinsic limit of water oxidation catalysis itself. This implies that rates can be improved by coupling the catalyst more efficiently to an electron or photon source, which is very encouraging. While theses systems need further study in order to optimize charge transfer and unravel the underlying catalytic mechanism, the stability of these compounds, engendered by the all-inorganic nature, makes them an important step toward viable water oxidation catalysts for artificial photosynthesis.

Direct reduction of carbon dioxide to liquid fuel

A liquid solar fuel is attractive in terms of ease of distribution and transportation. Yet, less than a handful of catalytic processes are known to directly convert carbon dioxide and water to methanol or higher alcohol molecules. Now, E.E. Barton et al. have developed a method for the direct reduction of CO_2 to methanol with high selectivity. The reaction runs with a mild underpotential (220 mV) and high current efficiency at a semiconductor electrode in aqueous solution using pyridinium ion as a mediator.

While the step-by-step process by which pyridinium accomplishes the six electron reduction of carbon dioxide to methanol remains to be established, the work points to as yet undiscovered paths which lead directly to a liquid fuel. In particular, insertion of CC bond-forming steps into the mechanism would open up the possibility of developing practical methods for producing fuels approaching the high energy density of petroleum, while by-passing the need for other higher energy intermediates as utilized by nature (NADPH), or hydrogen. Moreover, the reaction can use visible light as the sole energy source. The semiconductor electrode used is made of GaP, which is an indirect bandgap semiconductor material (2.24 eV). While the researchers achieved the highest quantum efficiency for methanol production ever reported, exploration of more efficient direct-bandgap semiconductor electrodes is likely to afford substantial improvement over the current performance of the system.

Integrated photocatalytic unit for hydrogen generation by visible light

Coupling of the light harvesting components with fuel generating catalysts with minimal energy or charge loss, while transferring electrons at rates that keep up with the solar light flux, is a formidable task. Meeting the challenge requires tight control of spatial arrangement and electronic interaction of the chromophore and catalytic site. A. Fihri et al. have prepared a unit that features an organometallic ruthenium complex covalently linked via an electron-rich bridge to a cobalt complex that acts as efficient catalyst for the reduction of water to hydrogen (Scheme 1).

While turnover number (a measure of stability) and frequency (a measure of reaction rate) are still modest, they are much higher than in systems where the Ru

sensitizer and Co catalyst are not positioned relative to one another through a covalent linkage. In light of tremendous progress in recent years in the understanding of photo-induced electron transfer across organic linkers, knowledge is now available for structurally modifying the bridge between light harvesting and catalytic component for optimal coupling and efficient use of sunlight for hydrogen generation. This photocatalytic system features a first row transition metal, cobalt, for the catalytic site, another important step towards engaging cheap abundant elements for artificial photosynthesis.

Coupling all-inorganic chromophore and catalyst in nanoporous oxide scaffold

A complete artificial photosynthetic system requires the arrangement and coupling of light absorption, charge separation and catalytic units in nanostructured membranes. The high surface area of such supports are necessary to reach a sufficient density of photocatalytic sites so that the fuel forming chemistry can keep up with the photon flux at high solar intensities. Membranes also offer nanostructural physical barriers that separate the reduced fuel products from evolving oxygen, minimizing inefficient back reactions.

With the goal of combining the advantages of molecular components with the robustness of inorganic materials, H. Han et al. developed selective synthetic methods for the assembly of inorganic polynuclear photocatalytic units in inert nanoporous silica scaffolds. The chromophore is an all-inorganic oxo-bridged binuclear unit, $Ti^{IV}OCr^{III}$, covalently anchored on the nanopore silica surface. This can then act as a visible light powered electron pump. When coupled to oxygen evolving multi-electron catalysts, such as iridium oxide nanoclusters inside the nanopores, oxidation of water was observed

when the material is suspended in aqueous solution and illuminated with visible light (Figure 3). The molecular nature of the chromophore allows for precise tuning of the redox properties of the donor and acceptor by selecting appropriate metals and oxidation states. Such control is key for the optimization of light absorption, thermodynamic efficiency, and directional charge flow in photocatalytic devices.

To investigate electron transfer inside silica nanopores, W.W. Weare et. al used a structural model of molecular water oxidation catalysts, namely the di-μ-oxo bridged dinuclear Mn complex $(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2$. This system takes advantage of the spectroscopic precision of differing chemical and electronic states in discrete molecules at levels not readily attainable with heterogeneous metal oxide nanocluster catalysts. When loaded inside silica nanopores, the Mn_2O_2 unit is electronically coupled to a Cr based visible light excited chromophore. The initial and final redox states of the Mn_2O_2 core and Cr chromophore could be definitively observed upon light induced electron transfer, laying the foundation for detailed evaluation of the kinetics and energetics of light-induced electron flow between catalysts and molecular charge-transfer chromophores inside high-surface area nanostructured supports. Such advances will allow for the design and control of artificial photosynthetic systems.

Acknowledgements

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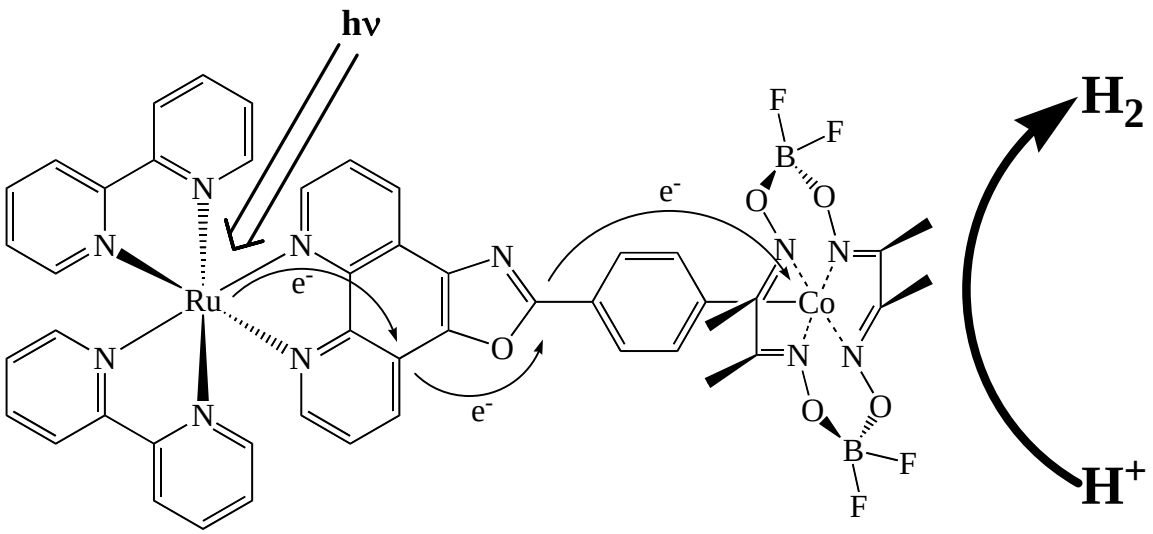

Scheme 1

Figure 1) An idealized diagram showing important aspects of artificial photosynthesis. The acceptor, chromophore, donor are imbedded across a membrane, and electronically connected to multi-electron reductive or oxidative catalysts (represented by FeNi and Mn_4 respectively). When light excites the chromophore, charge is separated and utilized at the catalysts to form H_2 and O_2. The membrane further serves to instantaneously separate H_2 and O_2 as they are made.

Figure 2) Structure of $[\gamma\text{-}SiW_{10}O_{36}][Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4][\gamma\text{-}SiW_{10}O_{36}]$ (ball and stick representation, Ru blue, μ-O red, $O(H_2)$ orange, hydrogen atoms omitted for clarity). This all-inorganic molecule catalytically oxidizes water to oxygen when treated with strong oxidants such as Ce(IV) or Ru(III).

Figure 3) This is a diagram of a light driven oxidative half-reaction on the surface of the nanoporous silicate MCM-41. The metal-to-metal charge transfer (MMCT) chromophore ($Ti\text{-}O\text{-}Cr^{III}$) serves to drive an iridium oxide multi-electron oxidation catalyst, forming oxygen from water.

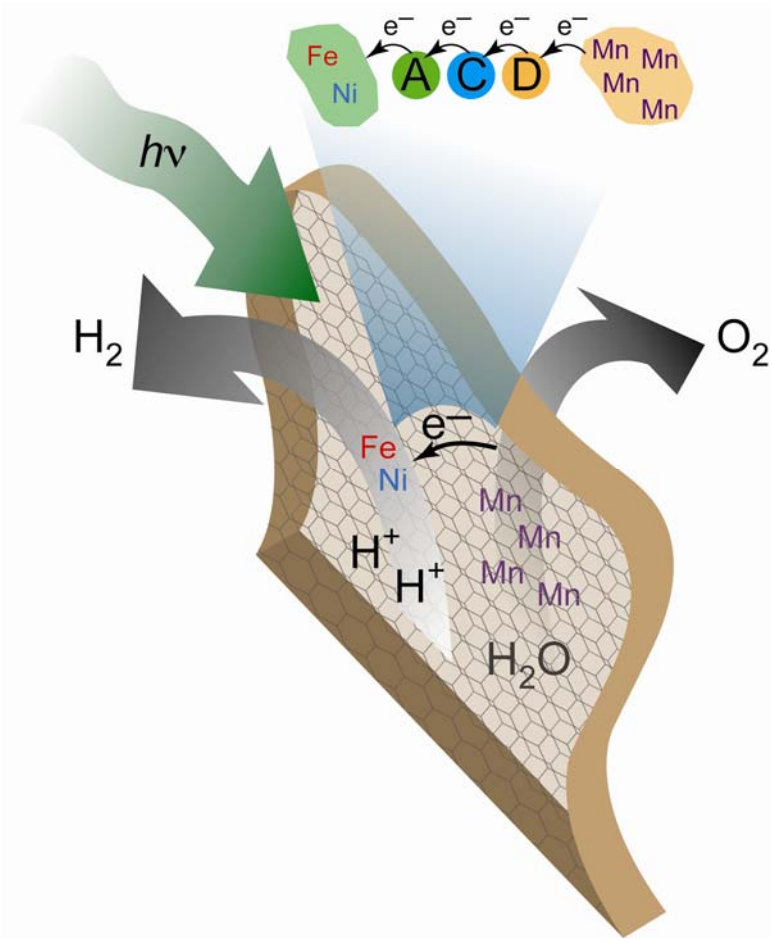

Figure 1

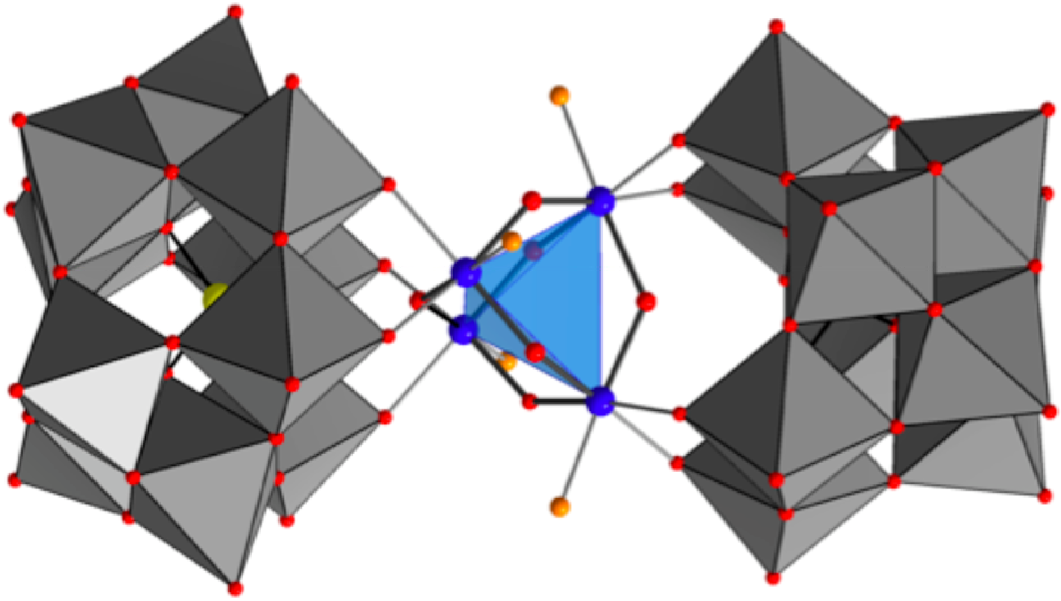

Figure 2

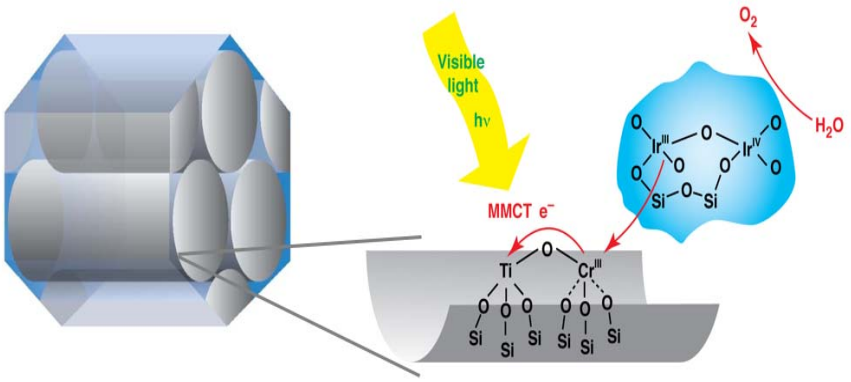

Figure 3