Final Scientific/Technical Report – BISfuel EFRC

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3. **Project Director:** **Devens Gust**
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6. Executive Summary

The vast majority of the country's energy needs are met with fossil fuels in the form of natural gas, coal and oil. The use of these fossil fuels contributes to climate change, the unequal distribution of fossil fuel deposits in the earth leads to geopolitical and economic problems, and eventually, fossil fuels will be exhausted. Thus, a renewable, widely distributed, environmentally benign, and inexpensive substitute large enough to meet the needs of society is required. Solar energy meets these criteria. Solar energy may be converted to electricity by photovoltaics, but the need for a continuous energy supply and high-density energy requirements for transportation necessitate technology for storage of energy from sunlight in a fuel. Cost-effective technologies for solar fuel production do not exist, prompting the need for new fundamental science.

Fuel production requires not only energy, but also a source of electrons and precursor materials suitable for reduction to useful fuels. Given the immense magnitude of the human energy requirement, the most reasonable source of electrons is water oxidation, and suitable precursor materials are hydrogen ions (for hydrogen gas production) and carbon dioxide (for production of reduced carbon fuels such as methane or methanol). Natural photosynthesis is the only proven "technology" for solar fuel production. It harvests solar energy on a magnitude much larger than that necessary to fill human needs, and has done so for billions of years, creating fossil fuels along the way. BISfuel has approached the design of a complete system for solar water oxidation and hydrogen production by applying the fundamental principles of photosynthesis to the construction of synthetic components and their incorporation into an operational unit. In this artificial photosynthetic approach, the functional blueprint of photosynthesis is followed using non-biological materials.

BISfuel brought together a group of investigators from the Department of Chemistry and Biochemistry at Arizona State University and integrated them into a cohesive, highly collaborative unit to attack the solar fuel problem. The investigators came from many disciplines, and worked together to apply their expertise in new areas in order to pursue Center goals. The primary goal, construction of a complete functional system for producing hydrogen fuel from water using sunlight, was realized, although much more work would be necessary to develop a practical device for doing so. The Center investigators discovered a great deal of important new chemistry, as is reported in 100 research publications and several patents and invention disclosures. A spin-off company was established based on some of the Center discoveries. Fundamental discoveries were made in the areas of molecular biotechnology, organic chemistry, inorganic chemistry, photochemistry, catalysis, materials science, physical chemistry and chemical physics. New instrumental techniques were developed, including femtosecond X-ray crystallography, which is an exciting approach to determination of the structures of both biological and synthetic molecules. The fundamental discoveries made by the Center will contribute to the development of not only solar fuel technologies, but also biomedical applications; technological uses of DNA; new materials for (opto)electronic, electrochemical, computational and display applications; fuel cells; industrial catalytic processes and related areas. In addition, Center studies of synthetic systems are leading to a better understanding of important natural biological systems, including natural photosynthesis.

7. Comparison of Accomplishments with Goals and Objectives

Center Goal. The mission of the ASU Center for Bio-Inspired Solar Fuel Production (BISfuel) was to develop fundamental knowledge necessary to construct a complete solar-powered system for production of fuels such as hydrogen via water splitting. Design principles were drawn from the basic concepts that underlie photosynthetic energy conversion. The premise is that because photosynthesis is a viable "technology" for producing fuels using sunlight and has been operating on a gigantic scale for billions of years, it is a good model for synthetic solar energy conversion systems. Although photosynthesis did not evolve to make fuel for humans and is relatively inefficient at fuel production, the initial steps can operate at very high efficiencies. Artificial photosynthesis seeks to embody the basic scientific principles underlying the natural process in synthetic systems that use sunlight to produce fuels such as hydrogen from water efficiently and inexpensively.

Accomplishments. The scientific accomplishments of the Center are summarized in over 100 peer-reviewed research papers, about 300 invited lectures, and 11 patent disclosures. Some of the highlights of the Center research that illustrate the significant progress made toward our goal include:

- We constructed a tandem photoelectrochemical cell for solar hydrogen production that uses a broad spectrum of visible light.
- We developed one of the best artificial hydrogenase catalysts for hydrogen production.
- We developed new transparent, nanoporous semiconducting electrode materials, including nanoporous antimony tin oxide and a *p*-type semiconducting material that may enable a simpler approach to a tandem photoelectrochemical cell for solar fuel production.
- We discovered how to interface various synthetic and natural photosynthetic components to the nanoporous electrodes and studied the optical and electrical properties of the resulting assemblies.
- We made significant progress in the use of DNA nanocages as hosts for biomimetic water oxidation and other catalysts.
- We reported the construction of synthetic "enzymes" for hydrogen production based on construction of metal complexes within synthetic peptides.
- We designed, synthesized and studied a variety of new chromophores, artificial photosynthetic reaction centers, artificial antennas and catalysts for potential use in solar energy conversion systems.
- Collaboratively, BISfuel contributed to the development of the new technique of femtosecond X-ray crystal structure elucidation, which provides an important new pathway for discovering the structures of complex proteins and the mechanisms of their action.

8. Summary of Project Activities

Basic research approach: The BISfuel concept for solar fuel production has been a complete, modular system consisting of artificial reaction centers that absorb sunlight and convert it to electrochemical potential energy, catalysts that use the oxidation potential to oxidize water to H^+

(protons) and oxygen, and catalysts that use the electrons from water oxidation to reduce protons to hydrogen (H_2). These components are organized by functionally nanostructured electrodes connected by conductors. Here, progress on construction of prototype cells is summarized, followed by results for development of components.

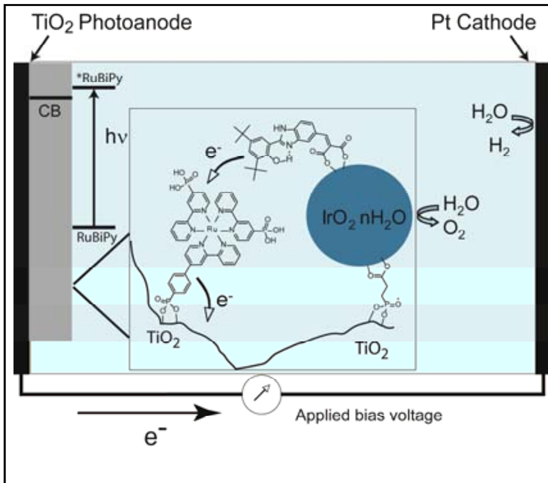

Fig. 1. Example of the BISfuel single photosystem water splitting cell.

Single photosystem photoelectrochemical cell for solar hydrogen production: In 2009, the Gust, Moore, Moore groups of BISfuel reported, in collaboration with Prof. T. Mallouk and coworkers (Penn State Univ.), the first example of a molecule-based complete photoelectrochemical cell for water splitting.[1] A more recent, improved version of this cell[2] (Fig. 1) operates by illumination of a nanoparticulate TiO_2 photoanode sensitized with a ruthenium or porphyrin dye.[3] Following injection from the dye excited dye into the TiO_2, electrons move through a wire to a platinum cathode that reduces solvated H^+ to hydrogen gas. The oxidized dye in turn oxidizes catalytic IrO_2 nanoparticles (NP), which accumulate holes in order to oxidize water to produce oxygen gas and H^+. Although the original cell had a quantum efficiency of only ~1% and required a small external bias, the efficiency was improved to 3% by use of a phenol-benzimidazole electron transfer mediator inspired by the tyrosine-histidine electron relay found in natural PSII (Fig. 1).[2,4-7] The performance increase was achieved even without chemical linkage of the mediator to the sensitizer.

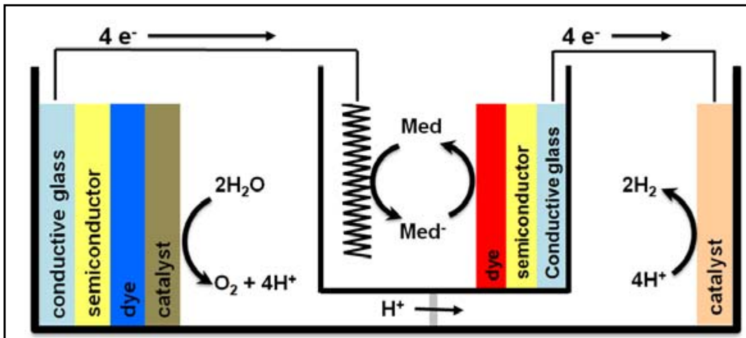

Fig. 2. Schematic of BISfuel tandem photoelectrochemical cell.

Tandem photoelectrochemical cell for water splitting: After development of the single-photosystem cell, research focused on a tandem approach to overcome the problems of low efficiency and requirement of an external bias. Working with other investigators, the thermodynamic limitations of natural and artificial photosynthesis were evaluated.[8] This work found that efficient use of the solar spectrum in an artificial photosynthetic system requires a series, or tandem, architecture with at least two light absorbers operating in different spectral regions.[9] In a two-photosystem tandem cell, two photons must be collected for each electron driven through the circuit. However, twice as much of the solar spectrum can be utilized, and ample electrochemical potential to overcome catalytic overpotentials, recombination

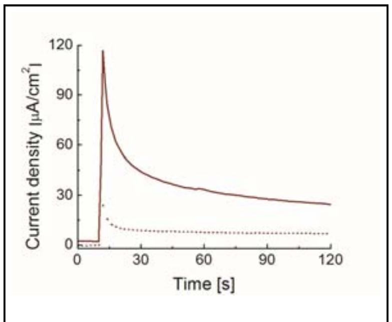

Fig. 3. Current density from tandem cell (solid) and single cell (dots).

reactions, and other losses is available. A prototype tandem cell is shown schematically in Fig. 2. The tandem design employs a water splitting cell similar to that shown in Fig. 1, but inserted electrically between the photoanode for water oxidation and the cathode for proton reduction is a dye-sensitized solar cell (DSSC). Electrically, the DSSC boosts the potential of the system so that water oxidation and proton reduction can be carried out without external bias and with ample overpotential. The sensitizers at the photoanodes of the two cells are spectrally complementary. Ideally, the water oxidation electrode absorbs higher energy photons (up to ~700 nm), while the sensitizer in the DSSC absorbs photons in the 700 - 1000 nm range. A first generation system using ruthenium and phthalocyanine sensitizers produces O_2 and H_2; with an AM 1.5 light intensity of 100 mW/cm^2, the system yields an initial current of ~120 $\mu A/cm^2$, which decays over a period of some seconds to ~30 $\mu A/cm^2$ by a polarization effect (not decomposition) (Fig. 3).

New dyes and artificial reaction centers suitable for sensitizing the tandem cells,[10-19] new water-stable methods for attaching sensitizers and catalysts to electrodes,[20-22] and new nanoparticles for electrodes[23-25] were studied, and time-resolved and theoretical studies of electron transfer between dyes and semiconductor nanoparticles were performed.[23,26-28]

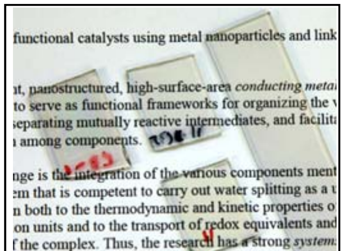

Fig. 4. Transparent nanoporous ATO.

Electrode materials: The electrodes must exhibit optical transparency, electrical conductivity, high surface area, controlled pore size, chemical and physical robustness, and electrical characteristics that favor injection of electrons or holes from sensitizers, coupled with slow recombination of the resulting carriers. Metal oxide nanoparticulate semiconductors have proven very suitable for these purposes. BISfuel developed novel, inexpensive methods for preparation of such materials. An important milestone was development of a synthetic route to highly transparent nanoporous antimony-doped tin oxide (ATO) coatings with controlled pore size (Fig. 4).[29,30] Related synthetic methods have since been developed for hierarchically porous ATO, nanoporous $MgAl_2O_4$,[31] nanoporous *p*-type semiconductor $CuAlO_2$,[32] nanoporous zirconium-doped TiO_2, and bioconjugatable reduced graphene oxysulfide.[33] These works have led to several patents, invention disclosures and a spin-off company (Nanovoltaics). BISfuel groups have successfully incorporated DNA nanostructures and redox proteins (e.g. cytochrome *c* and azurin) into pores of the ATO and related materials and demonstrated electrochemical activities.[21,34,35]

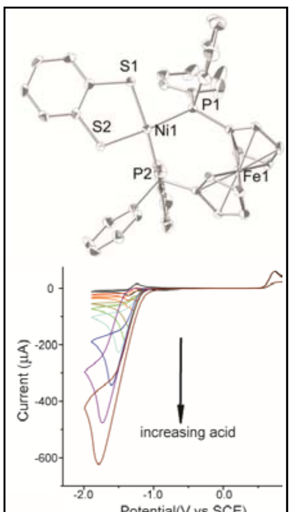

Fig. 5. Structure and H_2 production for an artificial hydrogenase.

Bioinspired H_2 production catalysts: The current BISfuel cells use Pt as the proton reduction catalyst. In nature, hydrogenase enzymes catalyze the same reaction using iron or nickel, demonstrating the feasibility of replacing Pt.

Proton reduction catalysts with redox non-innocent metal ligands: Based on previous ASU studies of electron flow in novel natural hydrogenases, BISfuel researchers synthesized an asymmetric proton reduction catalyst (μ-$S(CH_2)_3S)Fe_2(CO)_4(\kappa^2$-bpy)) that features a redox non-innocent bipyridine ligand[36] that displayed a modest catalytic activity. This work led to synthesis of a penta-coordinate mononuclear iron carbonyl complex (bdt)Fe(CO)(dppf) (bdt=benzene-1,2-dithiolate; dppf=1,1'-diphenyl-phosphinoferrocene), which showed proton reduction activity with low overpotential.[37] Here a combination of geometric strain/asymmetry and the redox non-innocent ligand contribute to the low overpotential. A mononuclear nickel complex [Ni(bdt)(dppf)] (X-ray crystal structure in Fig. 5) was then designed that shows H_2 production in 0-50 mM acetic acid in tetrahydrofuran at a rate of 1240 s^{-1} and an overpotential of only 265 mV. This is one of the most active artificial hydrogenases produced thus far.[38] Carbon dioxide promoted proton reduction using a manganese based catalyst was also reported.[39]

Artificial hydrogenases and redox centers associated with peptide frameworks: The low turnover rate and high overpotential for most artificial hydrogenases with structures mimicking active sites of the natural enzymes are likely due to the fact that in proteins, the second coordination sphere provided by the peptide plays an important role in the catalytic function. BISfuel researchers synthesized several artificial amino acids that can be incorporated into synthetic peptides and coordinate various organometallic complexes.[40] Incorporation of one of these[41] into a simple helical peptide resulted in hydrogen production when sensitized by a Ru complex.[42] The researchers also found that incorporation of a biotin-linked catalyst into streptavidin results in ~10 fold higher proton reduction activity and obtained a high-resolution crystal structure of the hybrid protein. BISfuel researchers also prepared Ni-Fe hydrogenase models in small peptide scaffolds.[43] A synthetic protein in which a ferredoxin mimic mediates electron transfer was reported,[44] as well as enhanced photoinduced hydrogen production by a cobalt porphyrin.[45]

CO_2 reduction catalysts: BISfuel began investigating promising metal complexes, including Ni-based hydrosilylation catalysts,[46] new Rh-based complexes,[47] and a new Mn-based hydrosilylation catalyst as steps toward catalysts for carbon dioxide reduction. The Mn complex exhibits ketone reduction turnover rates up to 21 s^{-1} (i.e. ~50 times higher than those of any reported)[48] and can cleave C-O bonds in esters.[49]

Water oxidation catalysts: Water oxidation is one of the most challenging aspects of the BISfuel solar fuel system. Accordingly, several approaches were taken.

Nanoparticulate metal oxide catalysts. The initial BISfuel water oxidation photoanode uses nanoparticulate IrO_2 as the catalyst (developed mainly by our collaborator, T. Mallouk). IrO_2 is an active, stable catalyst, and the only metal oxide catalysts that works well under acidic conditions. We investigated two approaches for preparing the photoanode: the catalyst is attached directly to the photosensitizer, or the dye and catalyst are separately bound to the electrode. Both methods give comparable performance. The Mallouk group has recently developed a method to sinter the Ir nanoparticles directly to the electrode to give an effective, robust, and reusable electrode. However, Ir is a rare metal, which will eventually limit the usefulness of Ir-based water splitting systems. We therefore also began investigation of a Co nanoparticle-based catalyst.[50]

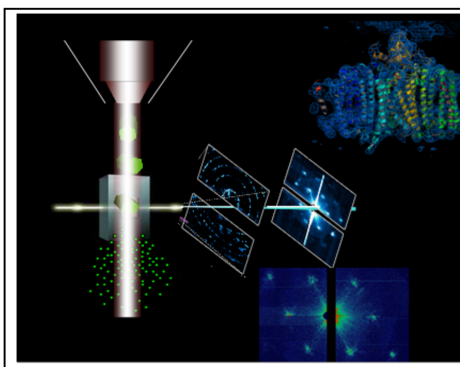

Fig. 6. Schematic of the fs X-ray crystallography experiment.

Structure and mechanism of the PSII water oxidation complex. Detailed knowledge of the structure and mechanism of the natural water oxidation complex will help in the design of efficient artificial catalysts. Fromme and her colleagues have developed a revolutionary technique, femtosecond X-ray nanocrystallography (Fig. 6), for determining the structures of very small crystals of molecules without X-ray damage[51-56] When coupled with excitation by a laser pulse, this technology also allows *time-resolved* crystal structure determination in the water oxidation complex. Conversion of the normal resting state to the triply-oxidized S3 state has now been observed by BISfuel researchers.[57,58]

Water oxidation complexes enclosed in DNA nanostructures. One approach to a PSII water oxidation complex mimic involved site-specific incorporation of peptides responsible for coordinating the Mn_4 cluster in the natural PSII into a DNA-based framework (see Fig. 7) followed by assembly of a Mn_4 cluster. In the resulting structure the DNA would replace the large protein framework of PSII. This bold approach has not yet resulted in a complete functional construct, but the attempt produced very interesting fundamental science that will pay off in a variety of disciplines. New methods have been developed for preparation of DNA nanostructures of controlled size and shape,[59-66] for attachment of materials (e.g. dyes, metal nanoparticles) to these DNA nanostructures,[67-71] and for crystallization of the nanostructures.[72] DNA tetrahedra containing redox-active molecules (e.g. ferrocene, cyt *c*) have been attached to electrodes, and the electron transfer properties have been examined.[73] We have created a general method for peptide incorporation into DNA nanostructures by attaching them to peptide nucleic acids (PNA) designed to anneal to a specific place in the DNA structure (Fig. 7).[74] This technique was used to position two different PNA-peptide-dye molecules within a single nanocage, and energy transfer experiments showed that the dye-dye distance was as predicted from molecular modeling.[75]

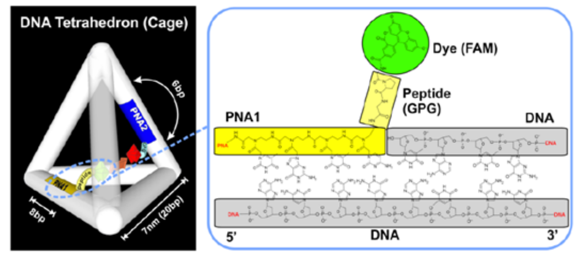

Fig. 7. DNA tetrahedron with 2 PNA strands linked to dye-binding peptides.

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9. Products Developed Under the Award

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b. Web site

The following web site was developed to showcase BISfuel and serve as a mechanism for communication among BISfuel researchers: http://solarfuel.clas.asu.edu/.

c. Networks or collaborations fostered

Collaborating PI's include: M. Adams (Univ. of Georgia), J. Appel (Universitaet Kiel), R. Blankenship (Washington Univ. St. Louis), E. Boekema (University of Leiden), D. Britt (Univ. of California, Davis), H. N. Chapman (Lawrence Livermore National Laboratory), A. Damjanovic (Univ. of California), J. Durrant (Imperial College London), G. R. Fleming (Univ. of California, Berkeley), M. Gidekel (University of La Frontera, Chile), J. Golbeck (Penn. State Univ.), M. Hanna (NREL), A. Holzwarth (MPI fuer Bioanorganische Chemie, Muehlheim), R.

Jankowiak (Univ. of Toronto), V. Karapetyan (MPI fuer Bioanorganische Chemie, Muehlheim), D. Lu (Beckmann Institute, Urbana), T. Mallouk (Penn. State Univ.), E. Marinõ (Instituto Tecnológico y de Estudios Superiores de Monterrey), N. Nelson (Tel Aviv Univ.), A. Nozik (NREL), J. Peters (Montana State University), O. G. Poluektov and T. Rajh, (Argonne National Laboratory), W. Rutherford (CEA Saclay, France), J. C. Scaiano (Univ. of Ottowa), A. Scherz, (Weizmann Institute), E. Schlodder, (T.U.-Berlin), K. J. Schulten (Beckmann Institute, Urbana), M. K. Sener (Beckmann Institute, Urbana), P. Setif (CEA, Saclay, France), D. Shapiro (Advanced Light Source, Lawrence Berkeley National Laboratory), J. Soll (Univ. of Munich), R. van Grondelle and J. Kennis, (Free Univ. of Amsterdam), A. Van der Est (Brock Univ. Ontario), I. Visoly-Fischer (Ben-Gurion University of the Negev, Beer Sheva), P. J. Walla (Technische Universität Braunschweig, and Max-Planck-Institute for Biophysical Chemistry, Göttingen), J. Weiss (Institute de Chimie, Université de Strasbourg), J. Whitelegge (Univ. of Califorfnia, Los Angeles), Z. Wu (Oak Ridge National Laboratory).

d. Technologies

BISfuel researcher Petra Fromme and her coworkers have major responsibility for development of the femtosecond X-ray crystallography technique, as discussed above. The technique uses the DOE free electron laser at SLAC.

e. Inventions/Patent Applications and Licensing Agreements

ASU Inv. Rept. #	Title	Inventor 1	Date	Licensed	Patent App.
M8-090P	Porous Metal Oxide Particles	Seo, D. K.	03/13/08	Nanovoltaics	WO/2009/140030
M9-149P	Fabricating Porous Materials using Thixotropic Gels	Seo, D. K.	06/04/09	Nanovoltaics	WO/2011/046910
M10-036P	Porous Geopolymer Materials	Seo, D. K.	09/03/09	Nanovoltaics	WO/2011/068830
M10-151P	Fabricating Porous Materials Using Interpenetrating Inorganic-Organic Composite Gels	Seo, D. K.	04/26/10	Nanovoltaics	WO/2012/018890
M11-094P	Treatment of Geopolymer Resin	Seo, D. K.	01/11/11	Nanovoltaics	
M11-094P1	Treatment of Geopolymer Resin and Materials Produced Thereby	Seo, D. K.	02/05/11	Nanovoltaics	WO/2013/044016, PCT/US2012/056552
M11-112P	Multifunctional Materials And Composites	Seo, D. K.	02/03/11	No	(22193-0078WO1
M13-201P	Nanostructured Metal Oxides From Acidic Solutions	Seo, D. K.	04/11/13	No	
M13-208P	Late First-Row Transition Metal Hydrogenation and Hydrosilylation Catalysts	Trovitch, R. J.	5/4/2013	No	61/834,220
M14-036P	Hydride-Containing and Hydride Derived First Row Transition Metal Hydrogenation and Hydrosilylation Catalysts	Trovitch, R. J.	8/26/2013	No	61/916,448

0488301-13-0103	Enhanced photosynthetic productivity through external electron injection.	Flory, J.	10/11/2013	No	0488301-13-0103