II.G.10 Joint Center for Artificial Photosynthesis: An Overview

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Objectives

The mission of the Joint Center for Artificial Photosynthesis (JCAP) is to produce fundamental scientific discoveries and major technological breakthroughs to enable the development of energy-efficient, cost-effective, and commercially viable processes for the large-scale conversion of sunlight directly to fuels. JCAP's 5-year goal is discovery of robust, Earth-abundant light absorbers, catalysts, linkers, membranes, and scale-up science required to assemble the components into a complete artificial photosynthetic system.

Technical Barriers

While a substantial advances in materials components and subassemblies that demonstrate water splitting have been reported in the literature, the work has been focused primarily on making scientific progress rather than creation of efficient, stable, durable, and scalable solar fuels generator systems. JCAP's work aims to bridge that gap.

Abstract

JCAP's technical program spans discovery science through early technology demonstration. In this talk an overview of the Center is presented, highlighting unique capabilities developed by JCAP, and briefly summarizing recent scientific advances.

Progress Report

A cartoon of JCAP's target, a fully integrated photoelectrochemical device architecture, is shown in Figure 1. The assembly is a tandem semiconductor microwire array embedded in a conductive gas-separation membrane and decorated with catalysts for water splitting and/or carbon dioxide reduction. The assembly is immersed in 1 Molar aqueous acid or base to support photoelectrochemical device efficiency. The diversity of science and engineering research challenges that must be met to achieve JCAP's mission of building and demonstrating such a device is extremely broad. In order to focus its portfolio, JCAP's approach is to start with development of robust concepts for complete solar-fuels generators containing the devices, then to break them down into essential assemblies of active components, and finally to adapt or discover the materials needed to fabricate those assemblies, as illustrated in Figure 2.

Prototypes

JCAP's prototyping strategy is to use robust engineering principles and processes to design, model, assemble, test and analyze prototypes of complete artificial photosynthetic systems. As a result, JCAP's prototyping team is able to (a) evaluate component-level performance within integrated systems under realistic operating conditions; (b) utilize

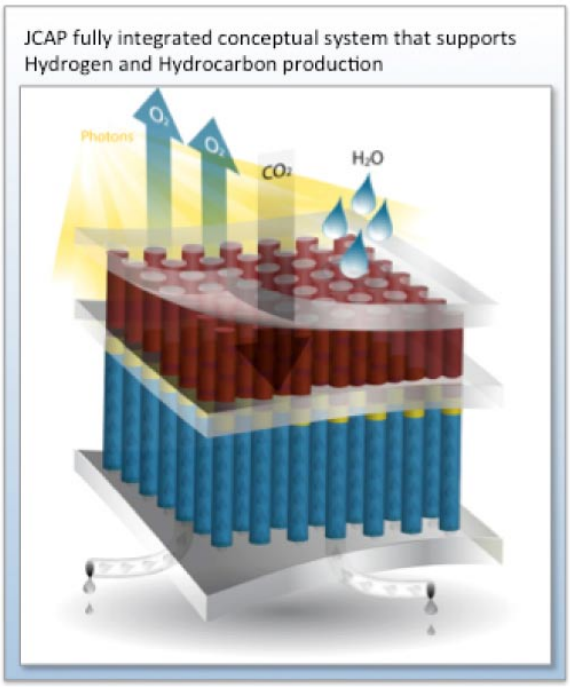

FIGURE 1. JCAP solar fuels device concept

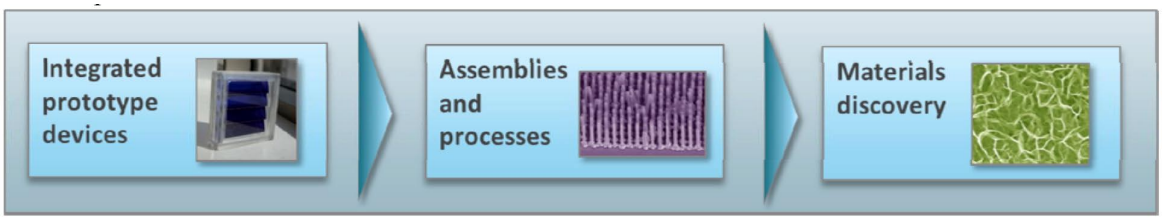

FIGURE 2. Schematic of JCAP's research and development flow.

3-D and 2-D modeling tools to develop and characterize prototype modules; (c) gain insight into which scientific and engineering approaches prove to be more robust and are therefore preferable; and (d) inform the R&D agenda on key bottlenecks associated with JCAP's technology. Specific focus areas are material selection, assembly and integration strategies, with evaluation of stability, performance, and ultimately cost. In the past year, JCAP has initiated analytical studies aimed at understanding requirements for solar-fuels generating facilities at the GW scale, and also manufacturing strategies for solar water-splitting modules.

Materials Integration and processing

In order to assemble solar-fuels generators, JCAP needs to develop and understand the integration of materials and processes over a wide range of length scales. One of JCAP's most important accomplishments has been the development of n-p+-Si/n-WO_3 and n-p+-Si/n-TiO_2 core-shell microwire devices for solar water splitting in acidic and basic electrolytes. These are embodiments of the concept in Figure 1. Preparation of these complex structures requires optimization and control of a series of processing techniques and instruments. Furthermore, even after the procedures for making highly integrated materials is accomplished at a laboratory scale (< 1 cm^2), there are many other additional challenges associated with scaleup and characterization of these processes to dimensions that are necessary for prototypes (10 cm^2 or larger). Another critical integration issue is the ability to protect materials from corrosion and other damaging processes during operation in extreme pH in a complete device. JCAP has made significant progress in the ability to use atomic layer deposition (ALD) and nanostructuring to protect both photocathodes and photoanodes for up to hundreds of hours under hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) conditions, respectively, in highly acidic and basic electrolytes. The performance and stability of individual material components also greatly depend on the integrity of their interfaces. JCAP is addressing the knowledge gaps in the field of heterogeneous catalyst-light absorber interfaces by systematically investigating the effect of catalyst deposition strategies on photoelectrochemical energy-conversion, product selectivity, and stability for different classes of photoanodes and photocathodes to determine how and why certain physical attachment techniques work. Advanced spectromicroscopy and surface mapping techniques are being utilized to investigate, at the nanoscale, the surface potential and conductivity of various catalyst and light capture systems to understand their properties and to identify why some materials form good contacts while others do not. The findings will increase understanding of the criteria necessary for effective device integration and allow for optimization of the catalyst-semiconductor assemblies. JCAP is also investigating the stable attachment of molecular catalysts on photocathodes and photoanodes in aqueous electrolytes without adversely influencing the performance of the semiconductor light absorber or catalyst.

Discovery, characterization and understanding of materials

Many of the materials required for integrated, efficient, and stable solar-fuels generators do not yet exist. Therefore the Hub is accelerating the needed discovery process by utilizing both traditional (i.e.,directed) and high-throughput synthesis and characterization methods, and by appropriate use of computational theory and DOE User Facilities. JCAP materials discovery and characterization efforts have resulted in the development of entirely new capabilities and techniques that benefit the entire solar-fuels community.

Objective performance characterization of the most promising catalyst and light absorbing materials is critical facilitating of comparisons of newly discovered materials to existing ones in a meaningful way. JCAP Benchmarking develops and implements uniform methods and protocols for characterizing the activities of OER, HER, and carbon dioxide reduction reaction (CO2RR) catalysts under solar-fuels generator operating conditions.

To complement JCAP's directed approach toward material development, the Hub is heavily invested in the accelerated, high throughput synthesis and analysis of promising materials by the High-Throughput Experimentation Project. The HTE project demonstrated significant breakthroughs in instrumentation innovation and has enabled discovery of new classes of water oxidation catalysts.

JCAP has a portfolio of research projects aimed at the directed discovery, characterization and understanding of light absorber, catalyst and membrane materials. JCAP's

computational theory effort elucidates how the composition and structure of molecular and heterogeneous catalysts affect their activity for the HER, OER and CO2RR. JCAP is focused on identifying either a single or a tandem combination of stable, scalable, and efficient light absorbers that provide the required photovoltage to produce fuels from sunlight. JCAP has developed suitable materials choices for photocathodes, including Si and WSe_2, that are relatively stable and have demonstrated high efficiency for the solar-driven production of H_2 from H_2O. However, a major technology gap is to obtain a stable earth-abundant light absorber having a band gap in the 1.7–2.3 eV range, to either complement these materials in a tandem structure as a photoanode, or to autonomously enable the direct production of fuel from sunlight. New photoanodes are identified through a variety of routes. JCAP has aimed a significant and fundamental theory effort at this gap, and is working to predict, using ab initio calculations, the synthesis conditions, performance, and stability of promising photoanode materials. Guided by a detailed understanding of optical interactions, researchers from JCAP and the Center for Energy Nanoscience, a DOE Energy Frontier Research Center, demonstrated that a sparse array of GaAs nanowires (<10% areal coverage) has nearly 100% photoelectrochemical charge conversion efficiency. JCAP has discovered and characterized a new class of light absorbers, $ZnSn_xGe_{1-x}N_2$, whose direct band gap can be tuned from 2 eV to 3.1 eV by simple control of the composition. Two new and scalable thin-film deposition methods for $BiVO_4$, a photoanode material composed of earth-abundant elements, were developed. Both methods provide control of stoichiometry, which is important for their use. It also enables understanding of the basic properties of the materials and maximizing OER performance through learning how to work with complex oxide film stacks.

Each half reaction in solar water-splitting requires discovery of stable catalysts that promote the oxidation of water and the reduction of protons at low overpotentials. The challenge is to identify earth-abundant elements for use as catalysts that are comparable or superior in activity to rare and precious metals. JCAP's Heterogeneous Catalysis project is addressing these technical gaps by performing characterization of the physical and chemical properties of catalytic materials using state-of-the-art in surface science and beamline capabilities, and participates in the work of the HTE project to discover completely new catalyst systems. JCAP is also investigating molecular catalysts for CO2RR, because no catalysts (molecular or heterogeneous) exist at present that can selectively reduce CO_2 at rates and efficiencies required by a JCAP solar-fuels device.

A fully integrated solar-fuels generator requires separation of gaseous products for both safety and efficiency, while maintaining sufficient ion-conduction between the reduction and oxidation chambers. JCAP is developing mechanically stable ion conducting and gas impermeable membranes that can be fully integrated with assemblies of photocatalytic units and enable their efficient function.

Future Directions

Work in progress in JCAP places strong focus on continuing the discovery of new photoanode materials, corrosion protection schemes, and acid-stable oxygen evolution reaction catalysts in order to demonstrate stable devices capable of 10% hydrogen generation efficiency from water splitting. Catalyst studies have also expanded to include heterogeneous CO_2 reduction catalysts with a specific focus on understanding the reaction mechanisms so that selective catalysts can be designed.

Publication list (including patents) acknowledging the DOE grant or contract

(please note – JCAP has over 100 papers published and submitted since October 2010. The following are a selection. Please see the other JCAP abstracts in this collection for additional key publications.)

1. Chen, S.Y.; Wang, L.W., Thermodynamic Oxidation and Reduction Potentials of Photocatalytic Semiconductors in Aqueous Solution. *Chemistry of Materials* **2012**, *24*, 3659-3666

2. Haussener, S.; Xiang, C.X.; Spurgeon, J.M.; Ardo, S.; Lewis, N.S.; Weber, A.Z., Modeling, simulation, and design criteria for photoelectrochemical water-splitting systems. *Energy & Environmental Science* **2012**, *5*, 9922-9935.

3. Casalongue, H.S.; Kaya, S.; Viswanathan, V.; Miller, D.J.; Friebel, D.; Hansen, H.A.; Norskov, J.K.; Nilsson, A.; Ogasawara, H., Direct observation of the oxygenated species during oxygen reduction on a platinum fuel cell cathode. *Nature Communications* **2013**, *4*, 6

4. Hu, S.; Chi, C.Y.; Fountaine, K.T.; Yao, M.Q.; Atwater, H.A.; Dapkus, P.D.; Lewis, N.S.; Zhou, C.W., Optical, electrical, and solar energy-conversion properties of gallium arsenide nanowire array photoanodes. *Energy & Environmental Science* **2013**, *6*, 1879-1890.

5. Hu, S.; Xiang, C.X.; Haussener, S.; Berger, A.D.; Lewis, N.S., An analysis of the optimal band gaps of light absorbers in integrated tandem photoelectrochemical water-splitting systems. *Energy & Environmental Science* **2013**, *6*, 2984-2993

6. Sampson, M.D.; Froehlich, J.D.; Smieja, J.M.; Benson, E.E.; Sharp, I.D.; Kubiak, C.P., Direct observation of the reduction of carbon dioxide by rhenium bipyridine catalysts. *Energy & Environmental Science* **2013**, *6*, 3748-3755

7. Schneider, Y.; Modestino, M.A.; McCulloch, B.L.; Hoarfrost, M.L.; Hess, R.W.; Segalman, R.A., Ionic Conduction in Nanostructured Membranes Based on Polymerized Protic Ionic Liquids. *Macromolecules* **2013**, *46*, 1543-1548

8. Zhai, P.; Haussener, S.; Ager, J.; Sathre, R.; Walczak, K.; Greenblatt, J.; McKone, T., Net primary energy balance of a solar driven photoelectrochemical water-splitting device. *Energy & Environmental Science* **2013**, *6*, 2380-2389

9. Modestino, M.A.; Walczak, K.A.; Berger, A.; Evans, C.M.; Haussener, S.; Koval, C.; Newman, J.S.; Ager, J.W.; Segalman, R.A., Robust production of purified H_2 in a stable, self regulating, and continuously operating solar fuel generator. *Energy & Environmental Science* **2014**, *7*, 297-301