
BES011 Joint Center for Artificial Photosynthesis: Corrosion Protection Schemes to Enable Durable Solar Water Splitting Devices

Principal Investigator: Carl Koval
California Institute of Technology, Pasadena, CA

Team Members:

- Ian Sharp (idsharp@lbl.gov, Team Lead), Jinhui Yang, Yongjing Lin, Ali Javey, Joel Ager (Project Lead)
Lawrence Berkeley National Laboratory
- Shu Hu, Michael Lichterman, Nate Lewis (Scientific Director and Project Lead)
California Institute of Technology

DOE Program Manager: Gail McLean

Phone: (301) 903-7807

Email: gail.mclean@science.doe.gov

enable the development of a new generation of robust integrated devices for efficient solar water splitting.

Abstract

Fabrication of overall water splitting devices requires the incorporation of all elements - catalysts, light absorbers, membranes, and interfacial layers - into an integrated system in which all materials are stable under identical conditions. Durability and compatibility of materials remain critical hurdles in the field. In addition to the discovery of new materials, a primary strategy for overcoming this limitation is aimed at utilizing thin film surface coatings for preventing corrosion of photoelectrodes, while also allowing efficient charge transfer between the semiconductor light absorber and catalysts. Here, we present a series of case examples highlighting approaches for thin film corrosion protection that enable sustained operation of both photocathodes and photoanodes. Each of these examples represents a significant technical advancement and provides complimentary insight into the important roles of interfacial energetics, physical and chemical structure, photon management, and defect engineering.

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. In pursuit of this mission, JCAP has initiated a focused activity devoted to the development of methods for stabilizing otherwise unstable semiconductor light absorbers under harsh acidic or alkaline conditions. This cross-cutting effort, involving multiple JCAP projects and investigators, aims to greatly expand the range of materials available for integrated solar water splitting devices by providing a broadly applicable portfolio of corrosion protection solutions.

Technical Barriers

A basic requirement for scalable solar fuel systems is safety; eliminating the possibility of forming explosive product mixtures necessitates incorporation of membranes in current integrated architectures and imposes a constraint for operation under extreme pH conditions, either acidic or alkaline, in order to eliminate pH gradients in the absence of recirculation.¹ At present, the central challenge of artificial photosynthesis is the availability of photoelectrodes that are capable of supporting high efficiency operation and possess long term durability under these harsh aqueous conditions. Indeed, many materials that are energetically well suited for driving water oxidation and reduction reactions rapidly degrade in aqueous environments. Stabilization of existing semiconductors against corrosion would have a significant impact on photoelectrochemical energy conversion and

Progress Report

Strategies for stabilizing photoanodes against corrosion and photocorrosion have been widely explored in recent years. [ENREF_21](#) General approaches involve introducing thin corrosion protection layers that allow interfacial charge transfer of photogenerated minority carriers while physically protecting the light-absorbers. In an alternative approach, recent advances in direct conformal deposition of catalytically active surface layers have been leveraged for providing corrosion protection without need for an interfacial layer. Case examples of advanced corrosion protection schemes developed within JCAP and their implications for development of integrated systems for photoelectrochemical energy conversion will be presented.

Photocathode protection using atomic layer deposited TiO₂

Favorable band alignment of chemically robust TiO₂ with a variety of photocathodes enables direct minority carrier injection into its conduction band with minimal interfacial resistance losses. Therefore, deposition of conformal TiO₂ layers onto photocathodes using processes that are substrate-compatible provides a powerful opportunity for facile corrosion protection. While initial literature demonstrations were performed on planar, single crystalline substrates, researchers at JCAP have extended this strategy

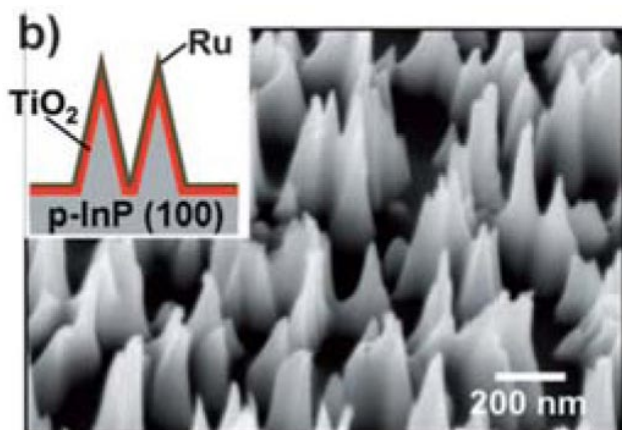


FIGURE 1. SEM image of p-InP nanopillar array formed by reactive ion etching. The inset shows a schematic of the protected structure, which incorporates a thin, conformal ALD TiO_2 layer.²

to encompass high surface area photocathodes. For example, p-InP nanopillared (NPL) arrays exhibit improved solar-driven hydrogen generation compared to planar controls due to a combination of reduced reflectivity and promoted H_2 bubble desorption. However, gradual loss of NPL fidelity, and corresponding hydrogen generation efficiency, over time was observed. Stable photocathodes were formed by introducing a thin interfacial layer of ALD TiO_2 (Fig. 1).² Given that mesostructured materials with high surface areas are desired for achieving reaction rates that take full advantage of the solar energy flux and reducing ionic transport lengths, the demonstration that ALD TiO_2 provides sufficient conformality for long-term corrosion protection of high surface area photoelectrodes represents an important advancement.

In complimentary work, JCAP researchers sought to extend photocathode protection to amorphous Si (a-Si) solar cells. In this study, the possibility of replacing ALD with reactively co-sputtered TiO_2 , which is an inherently scalable deposition process, was investigated.³ The resulting structure provided a stable onset potential of 930 mV vs. RHE, one of the highest reported to date. Furthermore, the integration of inexpensive NiMo hydrogen evolution catalysts to replace precious metal catalyst, such as Pt or Ru, was accomplished with minimal efficiency loss. The demonstration of high voltage photocathodes that are entirely formed using Earth-abundant elements and low-cost manufacturing processes represents an important advance in the drive towards scalable solar water splitting technologies.

Photoanode protection using atomic layer deposited TiO_2

Although many traditional semiconductors are energetically well-suited for efficient solar-driven water splitting, these materials are unstable when operated under photoanodic conditions in aqueous electrolytes. Recently, JCAP researchers demonstrated a stabilization method that enables the use of an entire class of existing, technologically important semiconductors with optimal band gaps for solar energy conversion as viable photoanodes in solar-driven water-splitting schemes.⁴ In this work, Si, GaAs and GaP photoanodes were stabilized against photocorrosion and photopassivation in aqueous alkaline media by ALD of thick, chemically stable, electronically defective TiO_2 overlayers, combined with a Ni catalyst for driving the oxygen evolution reaction. Unlike photocathodes, where electrons can be expected to inject into the conduction band of stoichiometric TiO_2 , the TiO_2 in this study should present a tunneling barrier for holes in the valence band. However, the key to enabling conduction of holes across the thick TiO_2 protective layers was the use of unannealed ALD- TiO_2 which combines

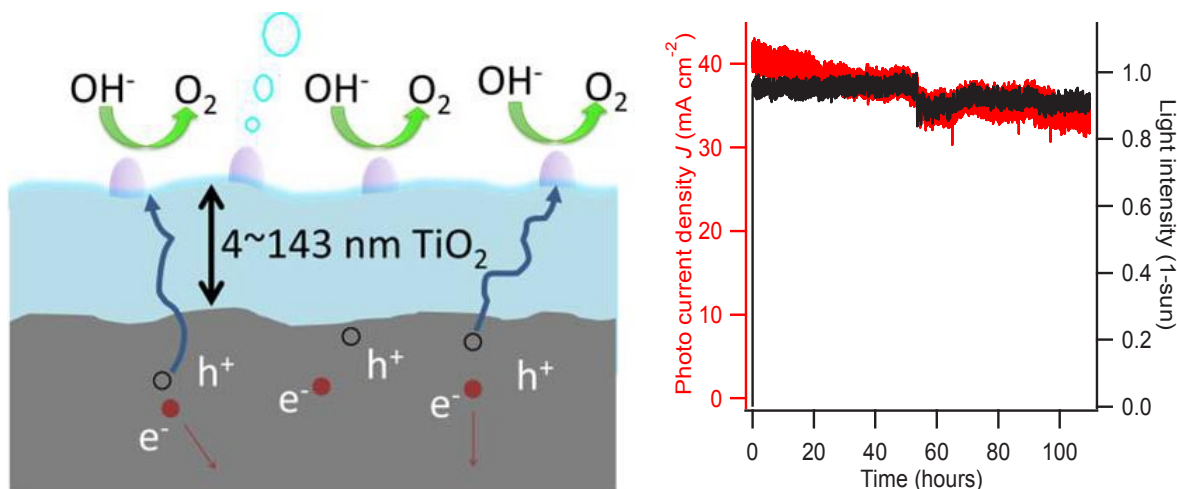


FIGURE 2. (left) Schematic representation of the corrosion protection scheme based on thick, defective TiO_2 layers, together with Ni catalyst, on photoanode surfaces. (right) Stability of Si in 1M KOH(aq) is demonstrated for over 100 h using this approach.⁴

optical transparency and high electrical conductivity to both electrons and holes. The resulting films were electronically defective and thus highly conductive with the exception of a thin insulating barrier layer at the surface of the as-grown film. Importantly, intermixing of the deposited Ni catalyst provided electrical contact through the insulating surface layer, thus allowing the thick ALD-TiO₂ films to act as a highly effective corrosion barrier while facilitating interfacial charge transport with minimal resistance loss. The thick ALD-TiO₂ films were formed without pinholes and can thus protect semiconductor material over macroscopic areas. In addition to enabling a wide range of existing materials to be further developed for incorporation in autonomous solar water splitting devices, these results demonstrate the power of film and defect engineering, as well as interfacial chemistry, on controlling interfacial charge transport.

Photoanode protection via direct catalyst deposition

As an alternate approach to photoanode protection, JCAP researchers have explored the possibility of photoelectrode stabilization via direct deposition of the catalyst onto the semiconductor light absorber. Although the precursors and processes for ALD of many catalytically active materials are available, the properties of atomic layer deposited materials can differ significantly from those of films fabricated with more traditional methods. Therefore, it is essential to understand the structures and morphologies of the deposited films, the effect of ALD on availability of catalytically active surface sites, and the physical and chemical properties of the interfaces between catalysts and underlying semiconductors. Here, two recent examples of cobalt oxide (CoO_x) ALD onto model photoanode materials, BiVO₄ and Si, are discussed.

BiVO₄ is a 2.4-eV band gap n-type semiconductor that is comprised of Earth-abundant elements but is kinetically sluggish for water oxidation, which leads to poor photoelectrical performance and photocorrosion in

alkaline media. Within JCAP, this material has been selected as a model metal oxide photoanode for detailed study; it exhibits many of the complexities associated with this class of material and can be used to guide understanding that is expected to be useful in the development of next generation oxide semiconductors for photocatalysis. Recently, JCAP researchers demonstrated that the use of ALD to form thin layers of cobalt oxide on n-type BiVO₄ produced photoanodes capable of water oxidation with essentially 100% faradaic efficiency in alkaline electrolytes.⁵ While improved performance was observed upon thin CoO_x deposition, decreased performance was found with slightly thicker layers. This finding highlights a critical consideration that is central to corrosion protection of photoanode materials: in the absence of a buried junction, the semiconductor/electrolyte junction provides the driving force for charge separation within the photoelectrode and conformal layers for corrosion protection and catalysis must be optimized to ensure that the interfacial electronic structure is not adversely affected.

In a separate study, plasma-enhanced ALD of cobalt oxide directly onto p+n-Si devices was investigated as a function of surface pre-treatment.⁶ As shown in Fig. 4, a combined nanotexturing and ALD process enabled efficient photoelectrochemical water oxidation and effective protection of Si from corrosion at high pH (pH 13.6). Physical sputtering of the Si surface prior to catalyst deposition led to nanometer scale texturing that was critical to defining the crystallinity of the deposited catalyst and its electronic registry with the light absorber. In particular, this process provided regions of reduced interfacial silica thickness that improved tunneling probability and dramatically reduced the interfacial charge transfer resistance. Furthermore, texturing the surface inhibited crystallization of CoO_x and enabled formation of a highly conformal amorphous catalyst layer with reduced pinhole densities in inter-grain regions compared to crystalline materials. This work revealed that

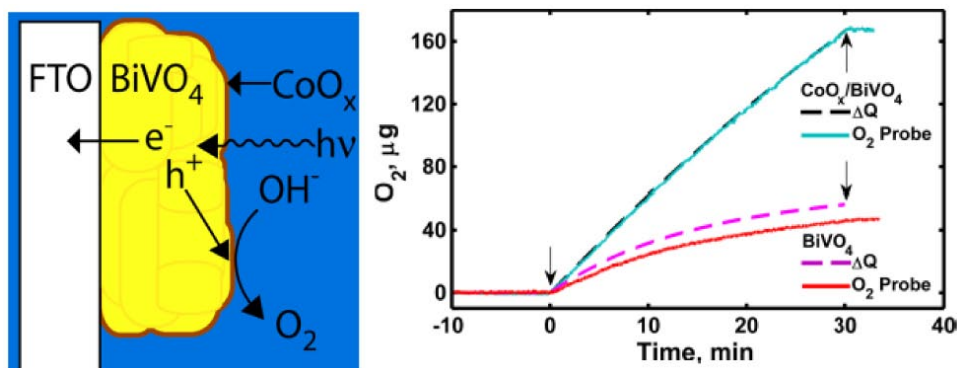


FIGURE 3. (left) Schematic illustration of conformal ALD CoO_x on BiVO₄ photoanode, which provides enhanced catalytic activity and stability to the material. (right) Oxygen production as detected by probe and coulometry at 0.97 V vs RHE in pH 13 KOH(aq), AM 1.5G illumination. Arrows mark the beginning and end of current flow from the potentiostat.⁵

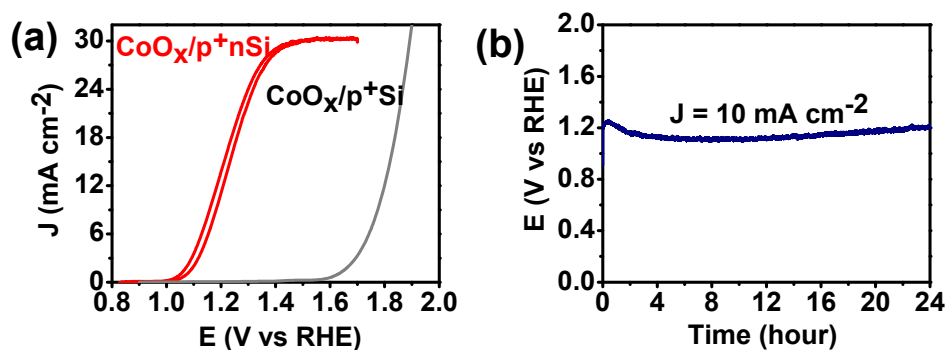


FIGURE 4. Photoelectrochemical behavior of nanotextured CoO_x/p+n-Si photoanode in aqueous 1.0 M NaOH under 100 mW/cm² of simulated solar illumination. **(a)** J - E response of CoO_x/p+n-Si (red) under illumination and CoO_x/p+Si (grey) in the dark. **(b)** Chronopotentiometry of nanotextured CoO_x/p+n-Si photoanode at a constant current density of 10 mA/cm².⁶

specific engineering of the interface is essential to improving catalytic activity and enhancing long term durability.

Future Directions

The results presented here highlight the significant potential for utilization of high efficiency semiconductors in systems for overall water splitting. Ongoing work is devoted to integrating materials and processes for assessment of these corrosion protection schemes in functional demonstration devices, to deep studies aimed at understanding the fundamental physical and chemical processes that govern interfacial charge transport, and to identification and elimination of deleterious failure mechanisms. Furthermore, with the demonstration of long-term stability, the need to develop general protocols for accelerated testing and failure analysis becomes more urgent. Mechanistic understanding of factors affecting efficiency and durability, as well as their sensitivities to processing and environment, will enable the fabrication of scaled prototypes. Ultimately, application of these concepts to monolithically integrated mesostructured materials systems will enable the next generation of high efficiency solar photoreactors.

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

1. 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 H₂ in a Stable, Self-regulating, and Continuously Operating Solar Fuel Generator, *Energy Environ. Sci.* **2014**, *7*, 297.

2. Lee, M.H.; Takei, K.; Zhang, J.; Kapadia, R.; Zheng, M.; Chen, Y.-Z.; Nah, J.; Matthews, T.S.; Chueh, Y.-L.; Ager, J.W.; Javey, A., p-Type InP Nanopillar Photocathodes for Efficient Solar-Driven Hydrogen Production, *Angewandte Chemie* **2012**, *124*, 10918.
3. Lin, Y.; Battaglia, C.; Boccard, M.; Hettick, M.; Yu, Z.; Ballif, C.; Ager, J.W.; Javey, A., Amorphous Si Thin Film Based Photocathodes with High Photovoltage for Efficient Hydrogen Production, *Nano Lett.* **2013**, *13*, 5615.
4. Hu, S.; Lichterman, M.; Lewis, N.S. *Science* **2014** *in press*.
5. Lichterman, M.F.; Shaner, M.R.; Handler, S.G.; Brunschwig, B.S.; Gray, H.B.; Lewis, N.S.; Spurgeon, J.M., Enhanced Stability and Activity for Water Oxidation in Alkaline Media with Bismuth Vanadate Photoelectrodes Modified with a Cobalt Oxide Catalytic Layer Produced by Atomic Layer Deposition, *J. Phys. Chem. Lett.* **2013**, *4*, 4188.
6. Yang, J.; Walczak, K.; Anzenberg, E.; Toma, F.M.; Yuan, G.; Beeman, J.; Schwartzberg, A.; Lin, Y.; Hettick, M.; Javey, A.; Ager, J.W.; Yano, J.; Frei, H.M.; Sharp, I.D., Efficient and sustained photoelectrochemical water oxidation by cobalt oxide/silicon photoanodes with nanotextured interfaces, *J. Am. Chem. Soc.* **2014**, *136*, 6191.