

## II.G.3 Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials

Eric W. McFarland (Primary Contact),  
Peng Zhang, Arash Shahryari, and  
Nick Hight-Huf  
University of California, Santa Barbara  
Dept. of Chemical Engineering  
Santa Barbara, CA 93106-5080  
Phone: (805) 893-4343  
E-mail: mcfar@engineering.ucsb.edu

DOE Technology Development Manager:  
Eric Miller  
Phone: (202) 287-5829  
E-mail: Eric.Miller@hq.doe.gov

DOE Project Officer: David Peterson  
Phone: (303) 275-4956  
E-mail: David.Peterson@go.doe.gov

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Fuel Cell Technologies Program Multi-Year Research,  
Development and Demonstration Plan:

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AA) PEC Device and System Auxiliary Material
- (AB) Bulk Materials Synthesis

### Technical Targets

Characteristics	Units	2003 Target	2007 Target	Achieved 2008	2013 Target
Usable semiconductor bandgap	eV	2.8	2.1	2.1	2.3
Chemical conversion process efficiency (EC)	%	4	1	1	10
Plant solar-to-hydrogen efficiency (STH)	%	NA	NA	NA	8
Plant durability	hr	NA	<100	<100	1,000

NA - not applicable

### Objectives

- A focus on the use of abundant and non-toxic elements in the development of improved photoelectrocatalyst materials for the capture of solar radiation to catalyze chemical reactions of interest.
- Utilize high-throughput screening to identify candidate materials that, with optimization, might meet the DOE performance and stability targets.
- Explore the effects of morphology on the photoelectrochemical (PEC) material system efficiency making use of nanostructures to minimize charge carrier path lengths and maximize reactive surface area.
- Explore processing and synthesis parameters to optimize efficiency through increased conductivity and minimized charge trapping and surface recombination of selected materials.
- Continue synthesis of libraries of semiconductor heterostructures for improved charge separation efficiency and/or stability.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the

### Accomplishments

- Investigation of iron oxide electrodes with different levels of Ti doping by spray pyrolysis.
- Investigation of the PEC performance of Ti-doped hematite photoanode with oriented crystallography and different Ti%.
- Synthesis of bulk  $Ga_{1-x}Mo_xP$  ( $x \leq 0.1$ ) powders and deposition of cocatalyst.
- Exploration of the PEC activity of  $Ga_{1-x}Mo_xP$  ( $x \leq 0.1$ ) powders for hydrogen iodide (HI) and hydrogen bromide (HBr) splitting.
- Investigation of surface modification/passivation of InP wafer for increased corrosion resistance during HI and HBr splitting using simulated solar radiation.



### Introduction

The overall project objective is to discover and optimize an efficient, practical, and economically sustainable material for PEC production of bulk hydrogen from water – a clean, renewable route to

hydrogen energy. The properties of the semiconductors investigated for this application, which are similar to those in photovoltaic devices, must satisfy conditions in several areas if cost-effective hydrogen production is to be realized: (1) efficient solar absorption, (2) effective charge separation/transport, (3) appropriate conduction band/valence band energies relative to H<sub>2</sub> and O<sub>2</sub> redox potentials (“band matching”), (4) facile interfacial charge transfer, (5) long-term stability, and (6) low cost. A material which satisfies all the above conditions simultaneously could provide clean hydrogen in bulk and at low cost; unfortunately, no such material or system has been discovered or developed to date. The DOE has identified the following future targets for solar-to hydrogen efficiency and durability: 2006, 4%; 2013, 8% and 1,000 hrs; 2018, 10% and 5,000 hrs.

Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has many potential advantages for hydrogen photoproduction. It has a bandgap of 2-2.2 eV (absorbs approximately 40% of the solar spectrum), it is stable in electrolytes over a wide range of pHs and is abundant, inexpensive and non toxic [1-3]. However, several qualities have limited the use of this material as an efficient photocatalyst, including high electrical resistance and recombination rates of photogenerated electrons [4,5] and a lower conduction band-edge relative to the redox level of H<sup>+</sup>/H<sub>2</sub>. Our hypothesis is that by deliberately doping hematite with selected heteroatoms [6] (e.g. Ti) and controlling the growth dimensions, crystal orientation and facets exposed, these limitations may be overcome. Phosphides have a narrow bandgap (~1.3 eV), which can utilize most of the visible light radiation, and a higher conduction band potential relative to the redox level of H<sup>+</sup>/H<sub>2</sub>, which is preferable for hydrogen production using solar energy [7,8]. By surface modification and back contact engineering, a respectable incident photon conversion efficiency (IPCE) and chemical stability can be achieved in strong acid electrolyte.

## Approach

The approach of this project involves the application of spray pyrolysis and solid state reaction methods to synthesize and optimize PEC materials and systems for cost-effective hydrogen production. This represents a systematic exploration of new metal-oxide-based solid-state materials. Our approach focuses upon the investigation of semiconductor materials that are inherently inexpensive, such as iron oxide, InP, and GaP. Iron oxide thin films doped with various amount of titanium have been synthesized by rapid spray pyrolysis of Fe(CO)<sub>5</sub> and TiCl<sub>4</sub> and screened by investigation of their PEC performance using a high through-put screening system. Gallium molybdenum phosphide powders were prepared through solid state reaction involving alloying of a stoichiometric amount of Ga<sub>2</sub>O<sub>3</sub> and Mo metal through high temperature calcination.

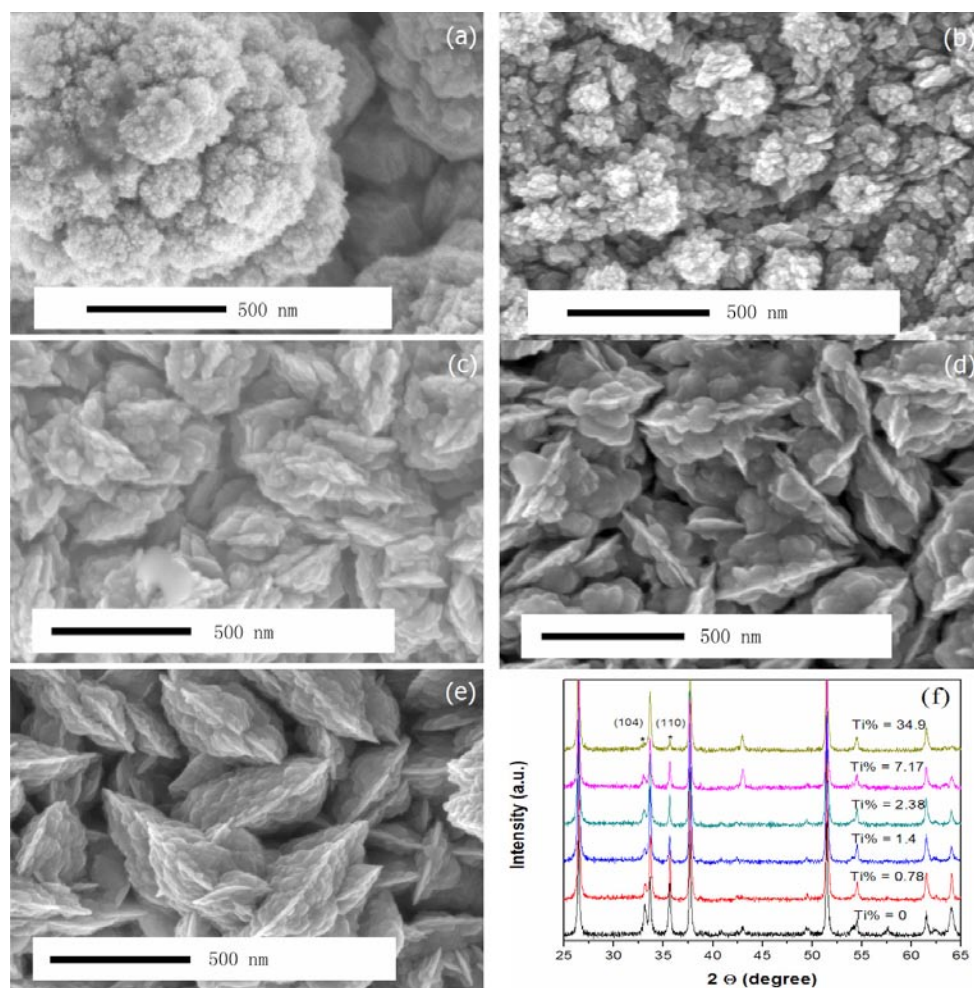
The resulting alloy was treated with H<sub>3</sub>PO<sub>4</sub> and calcined in air at 500°C for 24 h and further reduced in H<sub>2</sub> flow at 875°C for 20 h. Pt nanoparticles were deposited on the powder samples which were then dispersed in 0.5 M HI or HBr solution in sealed vials. The PEC performance of these slurry systems were then tested in a high-throughput PEC reactor.

In parallel to our research on particulate phosphide systems, the PEC performance of n- and p-type InP wafers with ohmic contacts in HI and HBr systems were also investigated. Various passivation treatments were implemented in order to minimize the dark (corrosion) current of InP in the acidic solutions. Moreover, using the planar electrodes of InP would allow for determination of IPCE and PEC properties of InP in any electrolyte of interest. The ultimate results from these experiments enable one to select the best working conditions for any particular synthesized transition metal phosphide in a PEC particle system. Sulfur passivation was achieved by treatment of InP wafer with 7% aqueous (NH<sub>4</sub>)<sub>2</sub>S with added elemental sulfur (saturated solution) [9].

## Results

Hematite photoanodes with various Ti doping densities were prepared by spray pyrolysis of Fe(CO)<sub>5</sub> and TiCl<sub>4</sub> and their PEC performance in water splitting was investigated. The feature size of the thin films increases from 10 nm to larger than 300 nm with an increase of Ti from 0-35% (Figure 1a-e). Orientated crystallography was observed in all the thin films as prepared with different Ti%, as shown in the X-ray diffraction (XRD) patterns (Figure 1f). The IPCE of the thin films at 0.4 and 0.6 V vs. Ag/AgCl was plotted as a function of Ti% in Figure 2a, which shows the highest IPCE of 27.5% at 400 nm from sample with Ti% of ~0.78%. With the increase of Ti%, the IPCE decreases. All samples show a low IPCE at 0.2 V vs. Ag/AgCl, which was ascribed to the high density of trap states and the presence of the magnetite crystal phase when titanium was used in higher concentrations (7.17% and 34.5). Calcination at 500°C diminished the amount of magnetite present in these two samples and improved the performance of the Ti-doped hematite thin films at 0.2 and 0.4 V vs Ag/AgCl, except the sample with 34.9% of Ti. The pure hematite sample shows almost no photoelectrocatalytic activity both before and after 500°C calcinations. This indicates that the poor performance of this thin film is not related to its crystallinity.

The PEC H<sub>2</sub> production from HI splitting on bulk Ga<sub>1-x</sub>Mo<sub>x</sub>P and Pt/Ga<sub>1-x</sub>Mo<sub>x</sub>P (x≤0.1) particles is shown in Figure 3a and b. The improvement of the performance by deposition of cocatalyst (Pt nanoparticles) is significant. The Ga<sub>0.95</sub>Mo<sub>0.05</sub>P sample with and without Pt cocatalyst in HI splitting showed



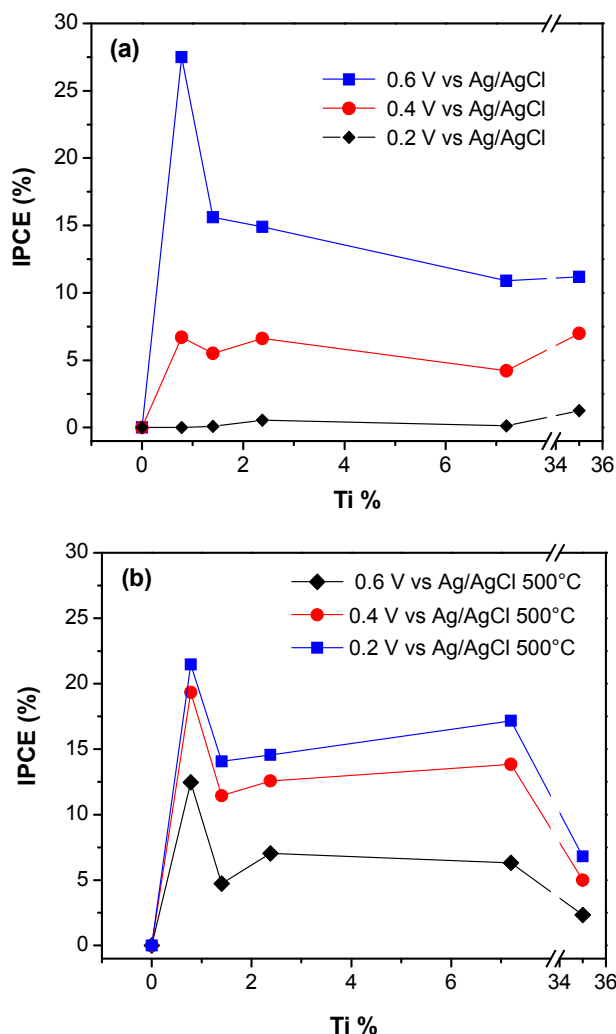
**FIGURE 1.** (a-e) Scanning electron microscope images of  $\text{Fe}_2\text{O}_3$  films grown by atmospheric pressure chemical vapor deposition on fluorine-doped tin oxide conducting glass with Ti% of 0, 0.78, 1.4, 7.17, and 34.9. (f) XRD pattern of the samples with Ti% ranged from 0 to 34.9; an oriented growth along (110) is observed in all the hematite samples.

the best performance. The  $\text{Ga}_{1-x}\text{Mo}_x\text{P}$  samples also showed a high activity in HBr splitting, a much more valuable reaction than pure hydrogen production. Figure 3c shows the performance of the  $\text{Ga}_{0.95}\text{Mo}_{0.05}\text{P}$  sample in both HBr and HI over the course of 50 hours continuously. The efficiency of HBr splitting is approximately half of HI splitting.

Intensive hydrogen evolution from p-InP wafer surface was observed in 0.5 M HI solution under  $100 \text{ mW/cm}^2$  white light illumination. The efficient hydrogen production was confirmed by the IPCE and photocurrent measurements in a two electrode configuration under no applied bias. The IPCE of this p-InP in 0.5 M HI yields an average value of ca. 35% in a wide range of visible light from 500-900 nm, Figure 4a. A short-circuit photocurrent of  $10 \text{ mA/cm}^2$  was also observed under 1 sun illumination, Figure 4b. The abrupt change of photocurrent as shown in Figure 4b is

attributed to the bubbling of hydrogen. In addition, our experimental data has shown that n-InP is a promising candidate for HBr splitting even in the absence of any cocatalyst. However, compared to our obtained results in HI, the photocurrent recorded in HBr electrolyte is in the range of  $0.5\text{--}1.0 \text{ mA/cm}^2$ .

One of the main flaws of n- and p-InP in HI and particularly HBr solutions is the relatively high dark (corrosion) current. Undoubtedly, one of the main requirements of any potential material to function as a sustainable and stable photocatalyst is to exhibit an acceptable corrosion rate. Thus, a great deal of effort in our laboratory has been devoted to the investigation of efficient chemical passivation to minimize the corrosion rate with no adverse impact on the photoactivity of the material. To date, sulfur passivation of n-InP has been the most effective passivation treatment, remarkably minimizing the corrosion rate of n-InP in

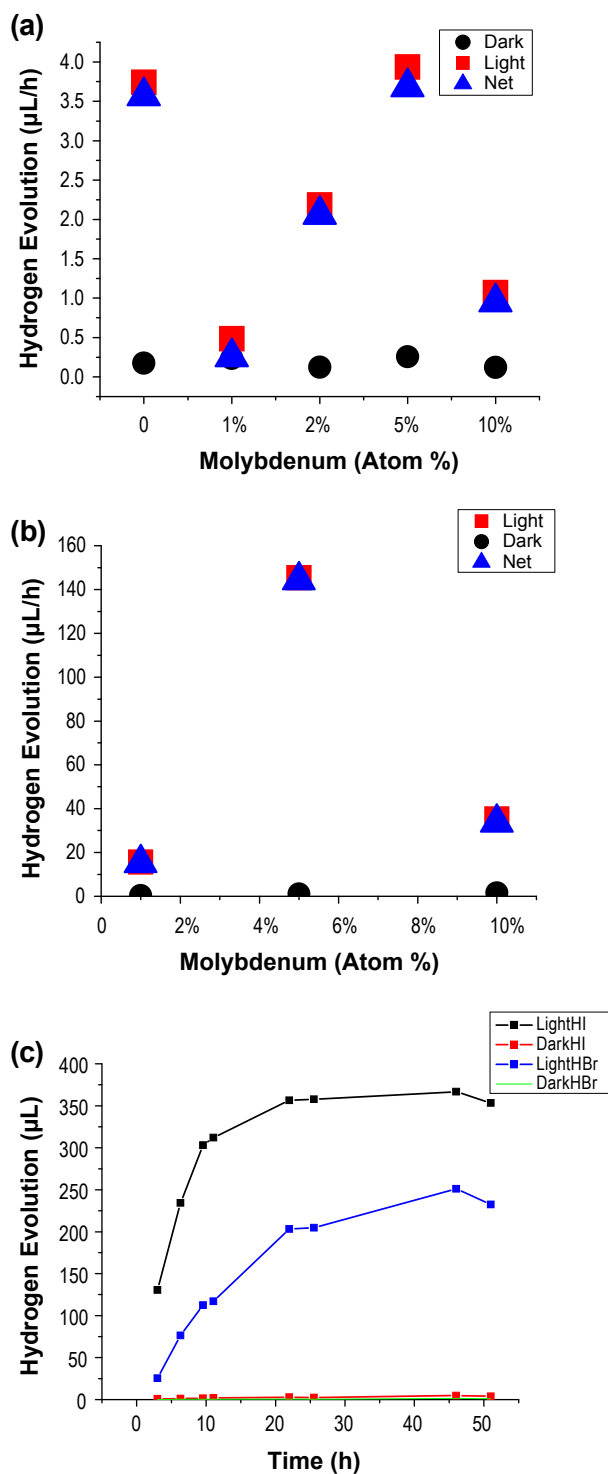


**FIGURE 2.** (a) IPCE of samples prepared with different  $\text{TiCl}_4$  flow rates with  $\text{Fe}(\text{CO})_5$  flow rate keeping as 40 sccm. (b) IPCE of the samples with different Ti% after calcination at 500°C. The black, red and blue curves represent IPCE of the samples measured under 0.2, 0.4 and 0.6 V vs. Ag/AgCl.

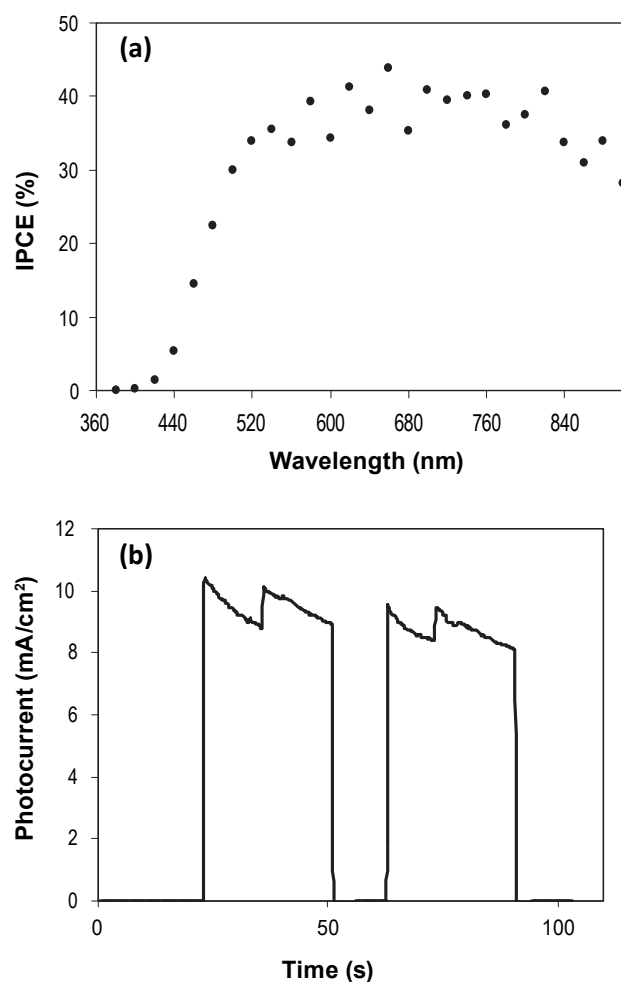
concentrated HBr solution. The dark current over the course of 1 week in solution and three 16 h light periods ( $100 \text{ mW}/\text{cm}^2$ ) remained constant at about  $0.1 \mu\text{A}/\text{cm}^2$ . Untreated samples display dark current on the order of  $200 \mu\text{A}/\text{cm}^2$  after a single light cycle. The main advantage of this treatment is the possibility of application of this treatment to our slurry phosphide systems such as  $\text{Ga}_{1-x}\text{Mo}_x\text{P}$  with no need to apply any external bias.

### Conclusions and Future Directions

- The methodology of combinatorial material science has been applied to expedite the discovery of improved photocatalytic materials for hydrogen production.



**FIGURE 3.** The hydrogen evolution from closed vials containing 20 mg samples of  $\text{Ga}_{1-x}\text{Mo}_x\text{P}$  without (a) and with (b) Pt cocatalyst in 0.1 M HI continuously illuminated over 24 h; (c) long-term  $\text{H}_2$  evolution of  $\text{Ga}_{0.95}\text{Mo}_{0.05}\text{P}$ , with platinum cocatalyst deposited on the surface, in 0.1 M HI and 0.5 M HBr.



**FIGURE 4.** (a) IPCE (a) and photocurrent (b) of  $3 \times 10^{16}$  p-InP wafer with ohmic contact and surface Pt deposition in 0.5 HI solution. The photocurrent in (b) was recorded under 1 sun illumination.

- A spray pyrolysis system has been used to synthesize Ti-doped iron oxide thin films with various Ti concentration and orientated cryptography.
- The Ti-doped iron oxide thin films show a remarkable improvement in efficiency for PEC water splitting compared to undoped samples.
- Surface modification by saturated aqueous ammonium sulfide solution has been successfully applied to passivate InP wafer for PEC use in strong acid electrolyte.

- $\text{Ga}_{1-x}\text{Mo}_x\text{P}$  ( $x \leq 0.1$ ) powders have been prepared and shown high activity in HI and HBr splitting under visible light illumination with Pt cocatalyst.
- Development of novel synthetic methods for nanoscale/nanostructured  $\text{Ga}_{1-x}\text{Mo}_x\text{P}$  ( $x \leq 0.1$ ) powders.
- Synthesis of  $\text{Ga}_{1-x}\text{M}_x\text{P}$  ( $\text{M} = \text{Ni}, \text{W}, \text{Fe}$ ) powders and PEC performance testing in HI and HBr splitting under visible light illumination with Pt cocatalyst.

### FY 2010 Publications/Presentations

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3. P. Zhang, A. Kleiman-Shwarscstein, Y.S. Hu, J. Lefton, S. Shama, A. Forman, and E. McFarland, "Nanostructured Ti-doped Hematite Thin Films as Photoanodes by APCVD" to be submitted *Adv. Func. Mats.* (2010)

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