II.H.5 Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials

Eric W. McFarland (Primary Contact),
Peng Zhang, Alan Kleiman-Shwarscstein,
Yongsheng Hu, and Nick Hight-huf
University of California, Santa Barbara
Dept. of Chemical Engineering
Santa Barbara, CA 93106-5080
Phone: (805) 893-4343; Fax: (805)893-4731
E-mail: mcfar@engineering.ucsb.edu

DOE Technology Development Manager:
Roxanne Garland
Phone: (202) 586-7260; Fax: (202) 586-2373
E-mail: Roxanne.Garland@ee.doe.gov

DOE Project Officer: David Peterson
Phone: (303) 275-4956; Fax: (303) 275-4788
E-mail: David.Peterson@go.doe.gov

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Objectives

- A focus on the use of abundant and non-toxic elements in the development of improved photoelectrocatalyst (PEC) 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 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.
- Use of GHz and THz photoconductivity as a tool to understand the photoresponse and carrier dynamics of semiconducting PEC materials.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure 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 (STH) efficiency	%	NA	NA	NA	8
Plant durability	hr	NA	<100	<100	1,000

NA - not applicable

Accomplishments

- Exploration of iron oxide electrodes with different levels of dopants made by electrodeposition.
- Explored the effect of poly-alcohols as alternate organic electron donors.
- Investigated surface processing for band edge position shift and electrocatalysis.
- Developed a spray pyrolysis synthesis system for hematite thin films with controlled Ti and Si doping.
- Developed a photoelectrochemical reactor and hydrogen production measurement system for colloidal photocatalysts.
- Designed and explore the synthesis of mesoporous and nanostructured delafossite and chalcogenide semiconductors.

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Introduction

The overall project objective is to discover and optimize an efficient, practical, and economically sustainable material for photoelectrochemical 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_2 and O_2 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 STH efficiency and durability: 2006, 4%; 2013, 8% and 1,000 hrs; 2018, 10% and 5,000 hrs.

Hematite (α-Fe_2O_3) 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]. 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 conduction surface band-edge that is lower than the redox level of H^+/H_2. The undesirable electrical properties are partially due to the hopping mechanism of charge transfer via oxygen vacancies, grain boundaries, and surface traps, which results in relatively low quantum yields, while the low conduction band is due to the Fe 3d electrons. Efforts have been devoted to reducing the resistivity of thin films by nanostructured crystal engineering, that is; electron transport along the (001) planes of the hematite has four orders or magnitude lower resistance than transport perpendicular to this plane. Our hypothesis is that by deliberately doping hematite with selected heteroatoms [6] and being able to control the growth dimensions, crystal orientation and facets exposed, these limitations may be overcome. There is much diversity to explore in searching for the appropriate combination of dopant species to improve photocatalytic performance, [5,8-10] as well as to understand and engineer the crystal structure, orientation and size of the crystalline domains of hematite. Another approach is to modify the surface reaction of semiconductors, through band edge shift, surface electrocatalyst deposition, and alternate poly-alcohol as electron donors, to further improve the performance of photocatalysts.

Approach

The approach of this project involves the application of combinatorial chemistry methods to synthesize and optimize PEC materials and systems for cost-effective hydrogen production. This represents a systematic and high-speed 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. Iron oxide materials can be synthesized by rapid serial electrodeposition techniques or can be synthesized by sol-gel or spray pyrolysis, however, the limiting step in this case is still the high-throughput screening of materials, thus by utilizing the high-throughput screening system we can expedite the material discovery. By investigating large arrays of diverse doped hematite films, we are working to improve the understanding of the fundamental mechanisms and composition-structure-property relationships within these systems. Surface modification has been attempted to shift the flat band potential of doped hematite and to increase the zero bias photocurrent. New hydrogen producing photocatalysts were synthesized and characterized using the PEC reactor and hydrogen production measurement system.

Results

The automated electrochemical synthesis system has been designed and improved allowing using electrodeposition for a variety of new materials with program controls over electrochemical parameters like voltage, scan rate, cycle numbers, etc. We have focused mainly on Fe_2O_3 host, investigating libraries of variable composition and structure. α-Fe_2O_3 thin films with different dopants have been synthesized by co-electrodeposition techniques. Around 30 dopants such as Al, Zn, Cu, Ni, Co, Cr, Mo, Ti, Pt, etc. were investigated. Doping with Al, Ti, Pt, Cr, and Mo exhibits the most promising results. Here we show the results of Al, Cr, and Mo doping in Figure 1. Besides their PEC performances, the phases, morphologies, optical properties and elemental components of the doped iron oxide thin films have also been characterized by X-ray diffraction, scanning electron microscopy, ultraviolet-visual, and X-ray photoelectron spectroscopy. Upon doping, the microstructures of the films varied; however, no preferred crystallographic orientation or dopant phase segregation was observed. There was only a small difference in the absorption properties of doped and undoped samples, which is mainly due to the variations in the sample thickness and morphologically dependent scattering of the films. Figure 1a, b and c show the photocurrent and incident photon conversion efficiency (IPCE) of Cr and Mo doped hematite thin films. The best performing samples were 5% Cr and 15% Mo doped which had IPCEs at 400 nm of 6% and 12%, respectively, with an
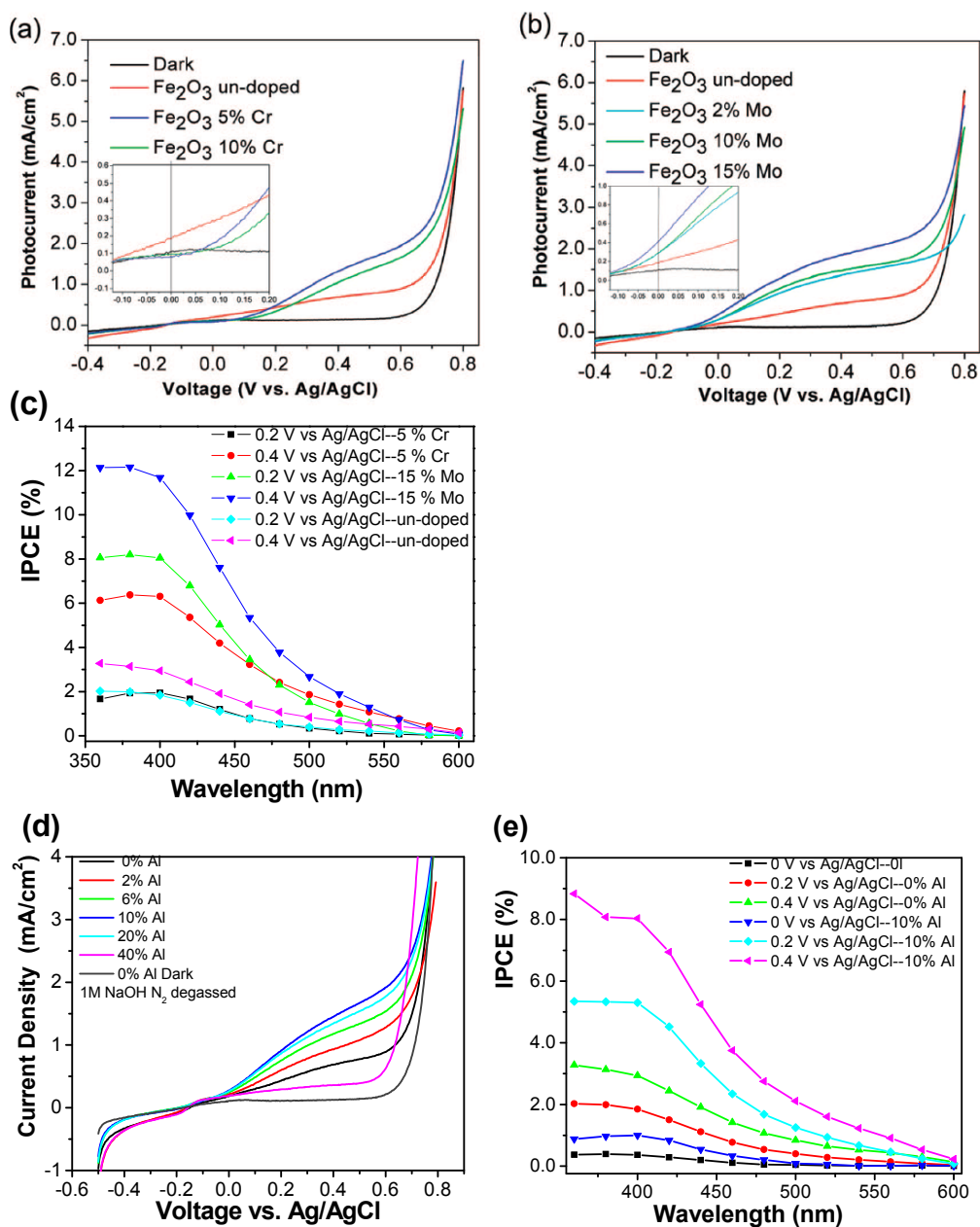
FIGURE 1. IV curves of (a) Cr doping and (b) Mo doping at 410 mW/cm^2 illumination. Inset shows magnification of origin. (c) IPCE of the electrodeposited films with and without doping at different applied potentials in N$_2$ degassed 1 M NaOH. (d) IV-Curves of control sample and Al doped samples (e) IPCE of selected samples at 0.2 and 0.4 V *vs.* Ag/AgCl.

applied potential of 0.4V vs. Ag/AgCl. These IPCE values were 2.2× and 4× higher than the undoped sample for the 5% Cr and 15% Mo samples, respectively. The chopped current-voltage (IV) curves for Al doped iron oxide thin films, Figure 1d, show the best performance with 10% of Al in the electrolyte bath. The 10% Al in the electrolyte bath, which corresponds to a 0.3-0.5% doping, gives the IPCE at 400 nm of 8%. The increase in performance is attributed to an improvement in the charge transport properties within the films and not due to significant

changes in the electrocatalytic rates due to dopants residing at the surface.

The doping of heteroatoms has been shown to increase the conductivity of hematite by orders of magnitude and thus the PEC performance on water splitting. However, the energy of the conduction band relative to the redox level of the H$_2$/H$^+$ couple is too low (~0.2 V vs. the normal hydrogen electrode) to efficiently drive the hydrogen evolution reaction. Therefore, all

publications with hematite require an external bias to shift the conduction band position above the hydrogen evolution potential. We have demonstrated an effective way to shift the band position of Ti doped hematite through surface modification using fluoride, which forms Ti-F bonds on surface. Figure 2 shows the improved PEC performance of Ti doped hematite thin films by CoF_3 (aqueous solution, pH~3.0) treatment. The CoF_3 treated samples show improvement in photocurrent at low bias (V <0.3 V *vs.* Ag/AgCl). The photocurrent onset potential for the treated sample is lower (~0.2 V) than the control sample. Furthermore, the untreated sample shows a negligible photocurrent at zero bias measured between the sample photoanode and the Pt mesh counter electrode without a reference electrode whereas a CoF_3 aqueous solution treated sample shows a photocurrent of approximately 150 mA/cm^2 under identical conditions and remains stable for more than 3,000 s (see Figure 2c). We propose that, the flat-band potential of the sample is more negatively shifted after CoF_3 treatment. This hypothesis is confirmed by the Mott-Schottky analysis, which shows a negative shift of ~0.15 V for the treated sample. When glucose was used as the electron donor, the photocurrent was further increased, as shown in Figures 2b, c and d, which is consistent with the slower rate for the oxygen evolution reaction of water oxidation than for the oxidation of glucose. The IPCE of the fluoride treated sample with the presence of glucose at zero bias (only 2-electrode) reaches 3.7% at 400 nm with respect to 1.5% in the absence of glucose and 0.1% for control sample, Figure 2d.

The effect of water and carbon on the photoactivity of Ti doped hematite thin films was investigated by the use of pyrolysis of anhydrous precursors, Figure 3a. Using iron carbonyl and $TiCl_4$ precursors, faceted nanoparticles with an average size of about 20 nm were obtained on the fluorine-doped tin oxide substrates (Figure 3b) and a photocurrent of 1.2 mA/cm^2 was observed at 0.2 V vs. Ag/AgCl under visible light illumination of 100 mW/cm^2 (Figure 3c). The IPCE of the sample approaches 11.4% and 15.5% at 400 nm with an applied bias of 0.2 V and 0.4 V vs. Ag/AgCl, respectively, Figure 3d. The onset potential for photocurrent is approximately -0.4 V vs. Ag/AgCl. A higher zero biased photocurrent (~400 μA) is also
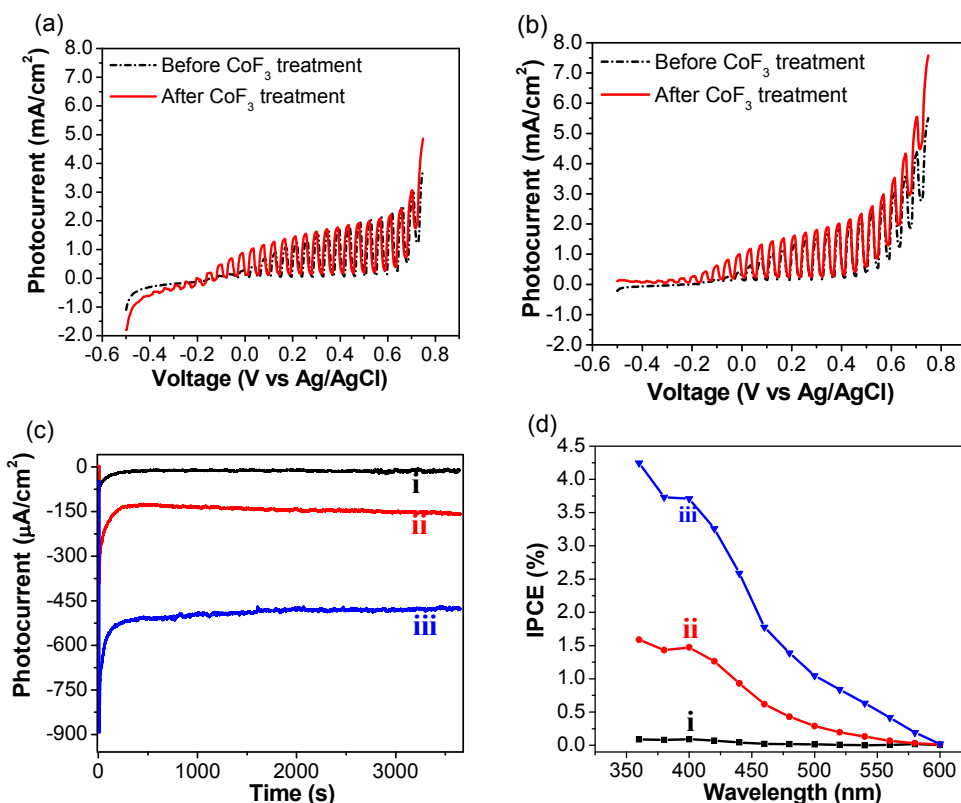

FIGURE 2. Chopped IV curves of 6% Ti-doped iron oxide thin films before and after CoF_3 aqueous solution treatment in N$_2$ degassed 1 M NaOH solution (a) without glucose and (b) with 10 mM glucose; (c) zero bias photocurrent under white light illumination for the same samples: (i) before and (ii) after CoF_3 aqueous solution treatment, (iii) after CoF_3 aqueous solution treatment in the presence of glucose in the electrolyte; and (d) IPCE performance at zero bias (i, ii, iii are the same as in (c)).
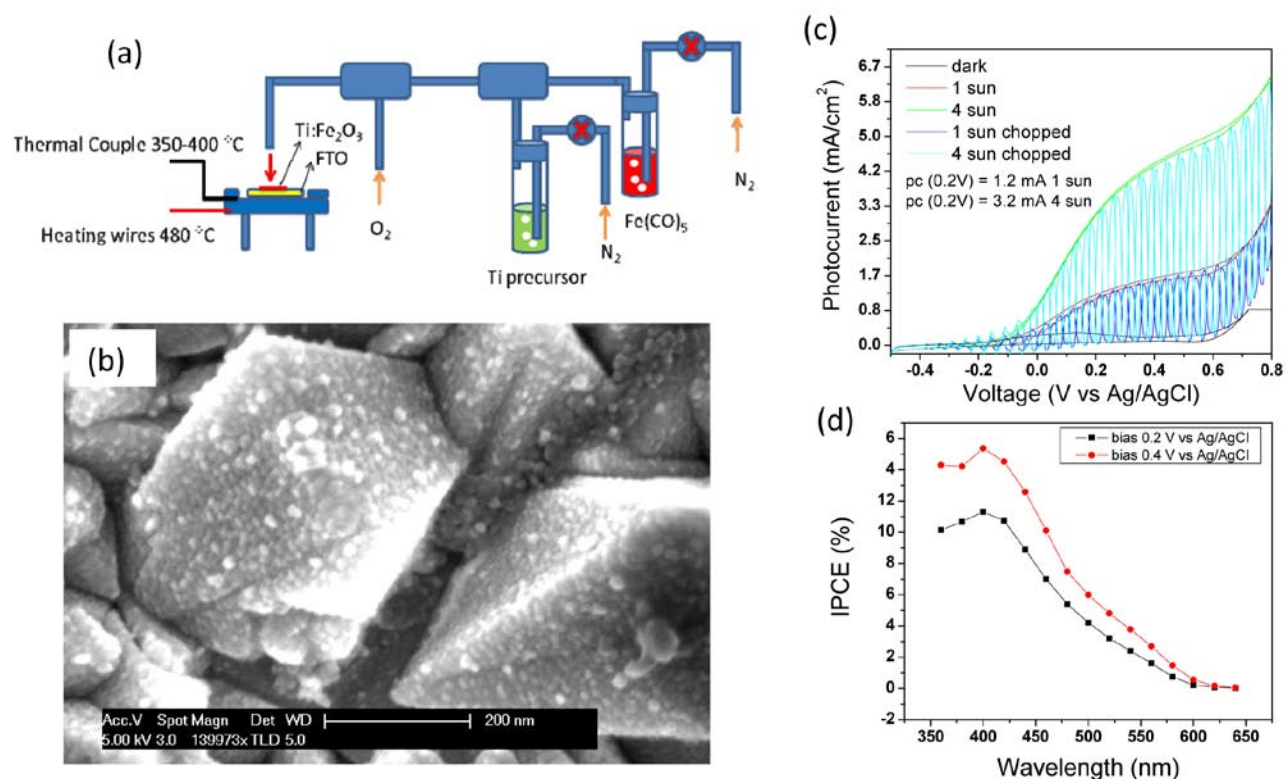
FIGURE 3. (a) Schematics of spray pyrolysis method for preparation of Ti doped hematite thin films; (b) scanning electron microsope image of Ti:Fe$_2$O$_3$ thin film sample prepared using TiCl$_4$ and Fe(CO)$_5$ precursors. (c) 3-electrode chopped IV curves showing the Ti:Fe$_2$O$_3$ sample under 100 and 403 mW/cm^2 visible light illumination and N$_2$ degassed 1 M NaOH; (d) IPCE for the Ti:Fe$_2$O$_3$ sample in N$_2$ degassed 1 M NaOH with 0.2 and 0.4 V applied bias *vs.* Ag/AgCl in 1 M NaOH solution.

observed for this sample. Different Ti precursors, e.g. aqueous TiCl$_3$ solution and Ti(butyloxide)$_4$, have been used for Ti doping, which results in a much lower efficiency. The control on dopant concentration, thickness, and crystalline growth orientation is under investigation. Surface modification using fluoride is in progress and a higher zero bias photocurrent (2-eletrode) is expected.

A photoelectrochemical reaction and characterization system for colloidal photocatalysts was designed and applied for screening of new potential photocatalysts, Figure 4. Photocatalyst powders (~10 mg) were dispersed in 15 mL electrolyte and sealed by a septum in a 20 mL glass vial. The vials were illuminated in a PEC reactor by two 1,000 W light bulbs with infrared filters. The PEC reactors can hold nine vials and do a screening for them by injecting gas samples from headspace of the vials into gas chromatograph. This system has been applied in screening a variety of semiconductors (Figure 4b) in terms of their photoelectrocatalytic hydrogen production rate under visible light illumination. Several semiconductors have been shown to be active in hydrogen production under visible light illumination in basic Na$_2$S solution, such as CuCrO$_2$, CuGaO$_2$, CuLaO$_2$, CuGaSe$_2$, InP, etc.

Quantitative analysis and screening of electrolytes for each semiconductor are in progress and the results will be reported in the next annual report.

Conclusions and Future Directions

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

- An automated electrochemical system has been used to reliably synthesize iron oxide thin films doped with various heteroatoms.

- The Al-, Ti-, Cr-, Mo-, and Pt-doped iron oxide thin films show a remarkable improvement in efficiency for photoelectrochemical water splitting compared to undoped samples.

- Surface modification by fluoride has been successfully applied to negatively shift the band-position of Ti doped hematite.

- Continue optimization of doped hematite; using theory to guide multi-atom substitutions in the α-Fe$_2$O$_3$ lattice, especially on both a donor and an acceptor co-doping.

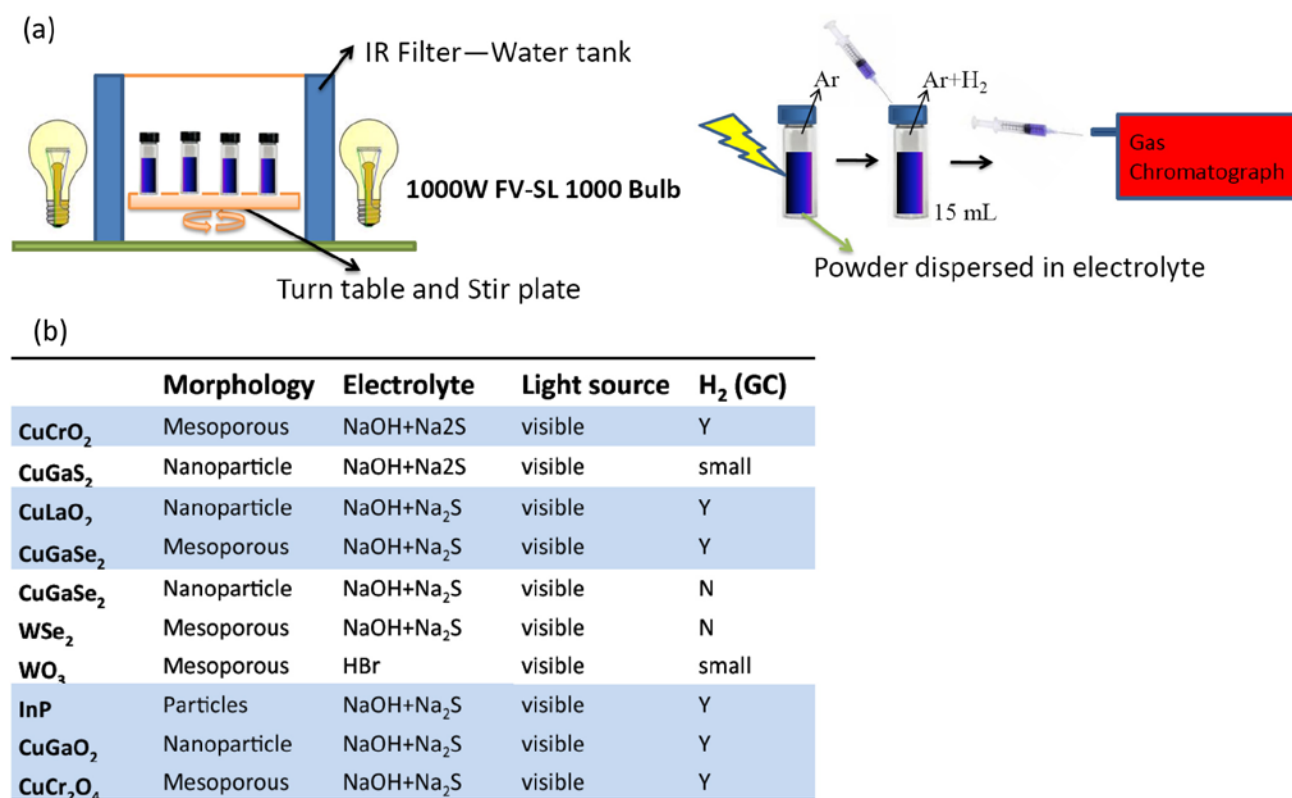|	Morphology	Electrolyte	Light source	H_2 (GC)
$CuCrO_2$	Mesoporous	NaOH+Na2S	visible	Y
$CuGaS_2$	Nanoparticle	NaOH+Na2S	visible	small
$CuLaO_2$	Nanoparticle	$NaOH+Na_2S$	visible	Y
$CuGaSe_2$	Mesoporous	$NaOH+Na_2S$	visible	Y
$CuGaSe_2$	Nanoparticle	$NaOH+Na_2S$	visible	N
WSe_2	Mesoporous	$NaOH+Na_2S$	visible	N
WO_3	Mesoporous	HBr	visible	small
InP	Particles	$NaOH+Na_2S$	visible	Y
$CuGaO_2$	Nanoparticle	$NaOH+Na_2S$	visible	Y
$CuCr_2O_4$	Mesoporous	$NaOH+Na_2S$	visible	Y

FIGURE 4. (a) Schematics of photoelectrochemical reactor and hydrogen production measurement system using gas chromatograph. The PEC reactor includes two 1,000 W bulbs and two water tanks as infrared filter. Nine sample vials can be held on the turn table in the metal box. Sample powders were dispersed in the vial and purged with Ar before illumination. After illumination, 500 μL gas sample were obtained from the headspace of the vial and injected into a gas chromatograph for hydrogen concentration analysis. (b) Screening results of semiconductors on hydrogen production under visible light illumination. The concentration of NaOH +Na_2S electrolyte is 1 M NaOH and 0.025 M Na_2S. The concentration of HBr electrolyte is 0.025 M.

- High-throughput synthesis of electrocatalysts on α-Fe_2O_3 substrates compatible with electrolyte, and reactant/product properties.
- Heterostructure design and synthesis with high efficiency of charge carrier separation.
- Ti doped iron oxide nano/mesoporous particles synthesis and control over growth structure, and surface modification for direct water splitting.
- Exploration of other narrow bandgap semiconductors, delafossite alloy, phosphide, and chalcogenides.
- Single-sample slurry reactor for IQE measurement and quantitative H_2 analysis.

FY 2009 Publications/Presentations

1. A. Kleiman-Shwarsctein, Y.-S. Hu, G.D. Stucky and E.W. McFarland, "NiFe-oxide Electrocatalyst for the Improvement of Oxygen Evolution Reaction on Ti-doped Hematite Photoelectrodes", Electrochemical Communication, doi:10.1016/j.elecom.2009.03.034.

2. A. Kleiman-Shwarsctein, P. Zhang, Y.-S. Hu, E.W. McFarland, "Solar Hydrogen and Nanotechnology", Chapter 13, Vayssieres, L., Ed.; John Wiley & Sons, (to be published 8/09).

3. Y.-S. Hu, A. Kleiman-Shwarsctein, G.D. Stucky and E.W. McFarland, "Improved Photoelectrochemical Performance of Ti-doped a-Fe2O3 Thin Films by Surface Modification with Fluoride", Chem. Comm. 2009, 2652 - 2654 (doi: 10.1039/b901135h).

4. A. Kleiman-Shwarsctein, Y.-S. Hu, A. Forman, G.D. Stucky and E.W. McFarland, "Electrodeposition of a-Fe2O3 of doped with Mo and Cr and its application towards water splitting", J. Phys Chem C., 2008; 20(12); 3803-3805.

5. A. Kleiman-Shwarsctein, "Solar Hydrogen Production by Photo-oxidation of Water from Doped Iron Oxide Photoanodes" Talk, presented at ACS Annual Meeting, March 2009.

6. P. Zhang, "Nanostructured Cu(X)O2 Delafossite Photoelectrocatalysts for Solar-to-Chemical Energy Conversion" Talk, presented at Materials Research Society, April 2009.

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