II.E.1 Photoelectrochemical Hydrogen Production: UNLV-SHGR at UH Project Subtask*

Robert Perret
The University of Nevada, Las Vegas (UNLV) Research Foundation
4550 Maryland Parkway, Box 452036
Las Vegas, NV 89154-2036
Phone: (702) 630-1542; Fax: (702) 413-0094
E-mail: ntsllc@rperret.com

Eric L. Miller (Primary Contact)
University of Hawaii at Manoa (UH)
1680 East-West Road, Post 109
Honolulu, HI 96822
Phone: (808) 956-5337; Fax: (808) 956-2336
E-mail: ericm@hawaii.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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Subcontractors:
- University of Hawaii at Manoa, Honolulu, HI (UH)
- MVSystems Inc., Golden, CO
- Intematix Corp., Fremont, CA
- National Renewable Energy Laboratory (NREL, integrated through cooperative agreement)

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Project End Date: December 31, 2007
(no-cost extension through August 31, 2008)

*Congressionally directed project

Objectives

- Identify and develop new photoelectrochemical (PEC) film materials compatible with high-efficiency, low-cost hydrogen production devices; Target: 1.6 mA/cm^2–6.5 mA/cm^2 AM 1.5 photocurrent.
- Demonstrate functional multi-junction device incorporating best-available PEC film materials; Target: 2-8 % solar-to-hydrogen (STH) efficiency under AM 1.5 illumination.
- Develop avenues, integrating new theoretical, synthesis and analytical techniques, for optimizing future PEC materials and devices.
- Explore avenues toward manufacture scaled devices and systems.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

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

Technical Targets

As recognized within the PEC hydrogen research community and the DOE PEC Hydrogen program, the technology is still far from maturity, and the most critical technical issues relate to the development of suitable photoactive semiconductors for water-splitting. Of the four DOE technical characteristics outlined in the Multi-Year RD&D Plan for PEC hydrogen production (see Table 1), targets in the first category ("useable semiconductor band gap") are the primary focus of this program's research, with secondary emphasis on the second category targets ("chemical conversion process efficiency"). To address the technical barriers for meeting the DOE targets, the project team has utilized its collective expertise in theoretical materials modeling, materials synthesis, and characterization to study a diverse portfolio of promising PEC thin-film materials classes.

TABLE 1. DOE Targets for Photoelectrochemical Hydrogen Production

Characteristic	Units	2006 Status	2013 Target	2018 Target
Useable semiconductor band gap	eV	2.8	2.3	2.0
Chemical conversion process efficiency (EC)	%	4	10	12
Plant STH efficiency	%	N/A	8	10
Plant durability	hrs	N/A	1,000	5,000

N/A - not applicable

As described in following sections, an important milestone achieved through this project has been the demonstration of 2.6 eV useable band gap in tungsten-based films compatible with integration into multi-junction devices with 3-4% chemical

conversion efficiency. Even lower band gaps have been demonstrated in silicon-carbide (2.1 eV) and copper-chalcopyrite (1.6 eV) materials, but work is ongoing to render these band gaps "useable" for PEC hydrogen production.

Accomplishments

- Successful Development and Application of New PEC "Tool-Chest" Capabilities
  - Successfully worked with an integrated DOE-PEC Working Group in advancing the use of materials theory, synthesis and characterizations to facilitate the materials discovery and development process for improved PEC devices.
  - Versatile modeling, synthesis and characterization tools developed with the DOE-PEC Working Group.
  - Comprehensive testing protocols being established by the DOE-PEC Working Group.
- Significant Advances in Focus Materials Classes Using the New PEC "Tool-Chest"
  - Further optimization of WO_3 films using Wo:Mo-Ox bi-layer approach.
  - Demonstration of high levels of stable PEC photocurrents through the modification and optimization of copper-chalcopyrite alloy film.
  - Demonstration of enhanced stability in highly-photoactive amorphous silicon carbide films.
- Key Milestones Met in Focus Materials Experiments
  - Photocurrents in excess of 3.5 mA/cm^2 in tungsten-based bi-layer films.
  - Photocurrents in excess of 8 mA/cm^2 and 18 mA/cm^2 in Si- and chalcopyrite-based films, respectively (with additional bias constraints to be corrected in band edge alignment modifications).
  - STH device efficiencies in excess of 3% in WO_3-based multi-junction structures under 1 sun.
- Further Expansion of Collaborative Research Efforts
  - Continued expansion work with the DOE-PEC Working Group.
  - Development of a new International-Energy-Agency (Hydrogen-Implementing-Agreement) Annex on PEC Materials for Hydrogen Production to expand the DOE Working Group efforts on an international scale.
- Avenues Developed for Continued Research Funding
  - DOE-funded PEC project at MVSystems Incorporated initiated to continue research and development (R&D) work on tungsten-oxide, copper-chalcopyrite, and amorphous silicon-carbide based thin-film compounds for PEC hydrogen production.

Introduction

The primary objective of this project has been the research and development of semiconductor materials for stable and efficient PEC hydrogen-production systems. The candidate materials have to be functional (1) as a photoactive layer, absorbing a significant fraction of the incident light; (2) as PEC junction with the electrolyte; and (3) as a facilitator of the gas evolution reaction (either hydrogen or oxygen, depending on the n- or p-type nature of the semiconductor, in conjunction with the specific integrated device configuration). The requirements on the material include adequate light absorption over the solar spectrum, high carrier collection efficiency, stability in suitable aqueous electrolytes, and favorable kinetics for the electrode reaction. As candidate materials with suitable properties emerge, additional requirements for the photoelectrode semiconductor device integration become increasingly important, such as process compatibility of the complete multi-junctions devices, as well as long durability and low material cost. This past year, the project has continued to make important progress in the discovery and development of promising PEC thin-film materials classes through the expanded collaborative efforts with the DOE-PEC Working Group, a group offering a broad palate of state-of-the-art theoretical and experimental tools and techniques.

Approach

The general approach of this collaborative effort between the UNLV-Solar Hydrogen Generation Research (SHGR) and the DOE PEC Working Group researchers is to integrate state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising materials classes to meet the PEC challenges in efficiency, stability and cost. From the application of density-functional theory to calculate band-structures and effects of co-incorporants on valence and conduction band positions; through the use of diverse synthesis techniques, including combinatorial methods, to create tailored materials; and by employment of microstructural, electron spectroscopic, and electrochemical characterization techniques, a comprehensive picture of the materials properties and resulting performance is being developed. Within the UH part of the UNLV-SHGR project, the approach has been applied to three classes of "focus materials" deemed of particular interest for PEC applications. These "focus materials" classes under current investigation include tungsten-based films, copper chalcopyrite-based films, and silicon-carbide-based films.

Results

Extensive studies of the three materials classes under investigation have focused on understanding and improving PEC behavior, specifically by applying our theoretical, synthesis and analytical techniques in identifying relevant aspects of structural, optoelectronic and electrochemical properties. Specific progress in developing each of the focus materials is detailed in the following subsections.

Tungsten-Based Films

Several experiments have been performed this past year on incorporation of new impurities into tungsten-based films in order to reduce the bandgap and enhance PEC electrode performances. The first series of experiments have been performed using molybdenum as an impurity. This incorporation was achieved using a co-sputtering process with W and Mo targets under oxygen ambient. Despite a net reduction from 2.6 eV (WO_3) to 2.3 eV (Mo:WO_3), linear sweep voltammetry (LSV) measurements performed on PEC electrodes in a 0.33 M H_3PO_4 solution under simulated AM 1.5_{global} light evidenced a saturated photocurrent density decrease from ~3.0 mA.cm^{-2} (WO_3) to ~1.5 mA.cm^{-2} (Mo:WO_3). Structural characterizations pointed out that molybdenum incorporation drastically changes WO_3 grain features, as shown in scanning electron microscopy (SEM) top views (Figures 1a and 1b). It is important to note that similar results concerning band gap decrease, poor PEC electrode performances and drastic morphological changes were obtained when nitrogen was incorporated into WO_3 films (as published in last year's DOE report). In both nitrogen and molybdenum incorporation experiments, it is observed that the modification of bulk features and surface morphology significantly affect both bulk and surface electronic properties. Consequently, high performance PEC electrode development requires progress on both absorber and surface properties.

One solution may reside in the use of bi-layer PEC electrodes, where a relatively thick bottom layer and a thin top film are selected for their absorption properties and band edge positions, respectively. Detailed characterizations of the band-structures of WO_3 versus Mo:WO_3 films (performed at UNLV) are shown in Figure 2a, illustrating the favorable band-edge shift needed for this bi-layer solution. Initial attempts have been performed using a 200 nm thick Mo:WO_3 film deposited on top of a WO_3 layer (1.8 μm). Light chopped LSV characteristics measured in a 0.33 M H_3PO_4 solution under simulated AM 1.5_{global} light on bi-layer (Mo:WO_3/WO_3), bulk Mo:WO_3 (2 μm) and bulk WO_3 (2 μm)-based PEC electrodes are presented in Figure 2b. Results show the benefits of bi-layers compared to bulk Mo:WO_3 and bulk WO_3-based PEC electrodes. In fact, a saturated photocurrent density

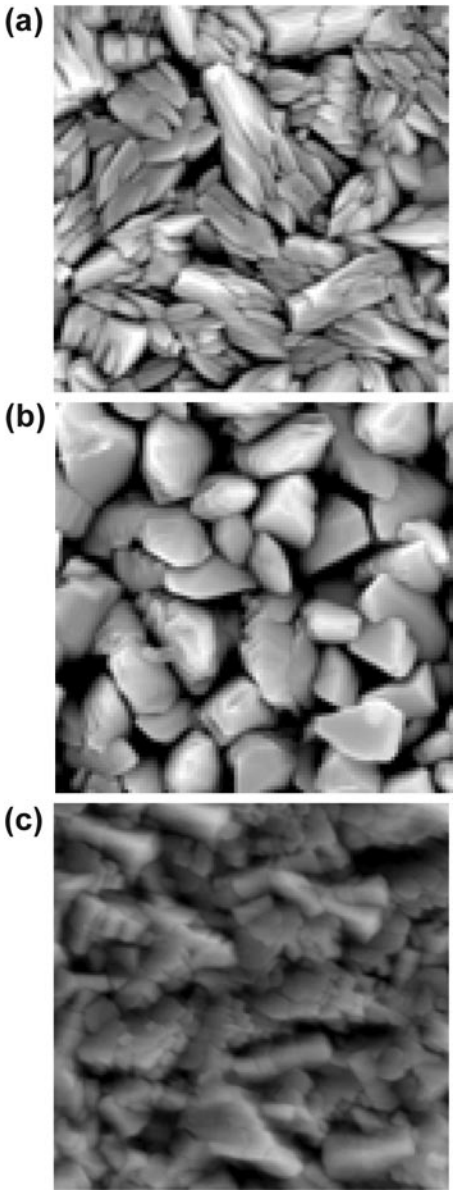

FIGURE 1. SEM top views (1×1 μm^2) of (a) WO_3 (2 μm thick), (b) Mo:WO_3 (2 μm thick), and (c) bi-layer (Mo:WO_3/WO_3 - 200 nm/1.8μm).

increase of 15% (from 3.17 to 3.63 mA.cm^{-2}) and an onset potential decrease of 160 mV has been achieved when a thin high-quality Mo:WO_3 layer is added on top of a thick WO_3 film. It is believed that the synthesis of an effective bi-layer relies on the beneficial effect of the bulk WO_3 bottom layer on the thin Mo:WO_3 film grain growth, as shown in Figure 1c. Additional analyses will be performed to validate this hypothesis. It is important to note that comparable optical absorption characteristics have been experimentally observed in both bi-layer and WO_3 electrodes. Therefore, to explain the saturated photocurrent enhancements, bi-layer charge collection must be higher compared to WO_3 film. A more optimal band-edge alignment

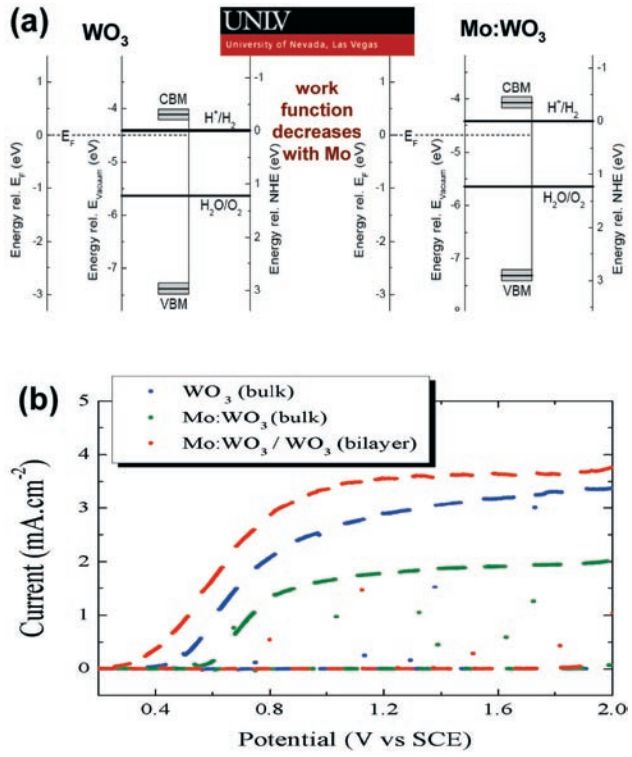

FIGURE 2. (a) Band diagrams of WO_3 and Mo:WO_3, obtained from ultraviolet photoelectron spectroscopy and inverse photoemission spectroscopy analyses showing work-function and band-edge shift; (b) Linear sweep voltammetry characteristics of Mo:WO_3, WO_3, and bi-layer showing enhanced PEC photocurrents in the bi-layer.

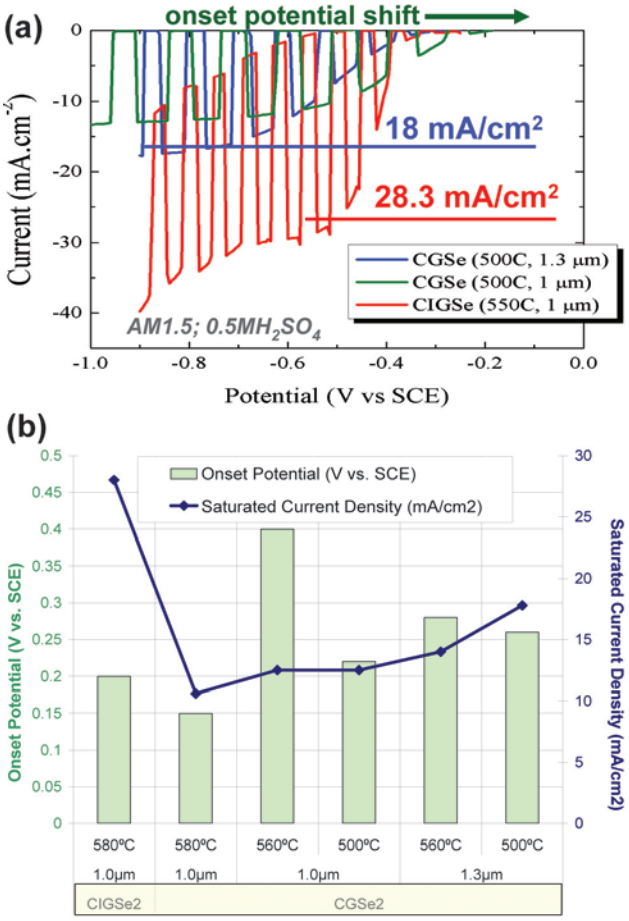

FIGURE 3. (a) Light chopped LSV curves showing performance of $CIGSe_2$ (red curve) vs. two $CGSe_2$ samples (blue and green curves) deposited under different conditions. PEC photocurrent levels and onset potential shifts are noted; (b) Absolute onset potential and saturated photocurrent density values measured on $CGSe_2$-based PEC electrodes fabricated with varying deposition temperature and thickness.

at the semiconductor-electrolyte interface has been experimentally verified as a plausible cause.

Copper Chalcopyrite Films

Previous work at UH has proven the viability of copper chalcopyrite thin films (copper alloyed with combinations of indium, gallium and selenium) as candidates for solar-powered water splitting for use in the sustainable production of hydrogen gas. While copper indium gallium diselenide ($CIGSe_2$) provides very efficient water cleavage with an external bias, the as-produced film has such a low optical band gap (~1.1-1.3 eV) that transmitted light is insufficient to drive a photovoltaic cell bottom layer, making incorporation of a $CIGSe_2$ PEC cell into a monolithic stack device difficult. Copper gallium diselenide ($CGSe_2$) films, however, have a higher optical band gap (~1.65 eV), resulting in higher photon transmission, thus offering the possibility of a multi-layer standalone solar-powered water cleavage device. However, as expected, allowing light transmission is done at the expense of diminished photocurrent as compared to $CIGSe_2$. Figure 3a shows how with similar fabrication parameters, $CIGSe_2$ photoelectrodes under simulated AM 1.5_{global} light produce ~28 mA/cm^2 saturated photocurrent while $CGSe_2$ photoelectrodes produce only ~18 mA/cm^2. This reduced photocurrent level is still sufficient for high-efficiency STH hydrogen conversion, but only if the biasing levels are reduced and if an appropriate multi-junction device can be designed. Recent experiments with fabrication parameters have shown improved PEC electrode performance over devices utilizing the standard parameters from literature, producing increased current densities, decreased required voltage bias, or both as shown in the comparison of different $CGSe_2$ samples in Figure 3b. As evident in the figure, it is possible that the lower deposition temperatures may be beneficial to PEC performance, while also bringing down manufacturing costs. A lower temperature limit determination is currently under investigation.

The current research direction is to further optimize the fabrication parameters for optimal photocurrent, onset potential, and "fill factor". Optical considerations necessitate that thinner films than previously synthesized

are required to transmit sufficient light to the PV bottom cell in a monolithic stack device. At the same time, high opto-electronic quality needs to be maintained in the thinner films. A balance must be established between electronic and optical tradeoffs in order to incorporate copper chalcopyrites into a standalone solar-powered water cleavage device meeting DOE performance targets.

Amorphous Silicon Carbide-Based Films

Amorphous silicon carbide is a promising tunable photoactive material, which would enable the fabrication of "all-silicon" multi-junction water-splitting devices. Research and development is currently performed by MVSystem to optimize a-SiC photo-response and stability in acidic media. A series of films deposited on different substrates, including stainless steel, molybdenum, tin oxide and zinc oxide have been characterized at NREL to evaluate material performances as PEC electrodes. Examples of these experiments are shown in Figure 4 for (a) stainless steel and (b) tin oxide, showing enhanced stability in the latter. All samples have been characterized in various electrolytes such as pH 2 buffer solutions, phosphoric acid and sulfuric acid. The LSV characterizations have shown that low photocurrent (~5 $mA.cm^{-2}$) is observed for all samples when tested in pH 2 buffer solutions. On the other hand, phosphoric acid leads to a high photocurrent generation, up to ~9 $mA.cm^{-2}$ when a stainless steel substrate is used, with low dark current observed. Finally, a high dark current was observed when sulfuric acid is used as electrolyte and observation of film features after tests in this media evidenced the presence of surface degradation indicative of film corrosion. As a consequence, it has been determined that sulfuric acid should be avoided in a-SiC-based PEC electrode characterization. Further optimization of film stability and band-edge positioning to lower observed potential shifts is planned in future work on this material.

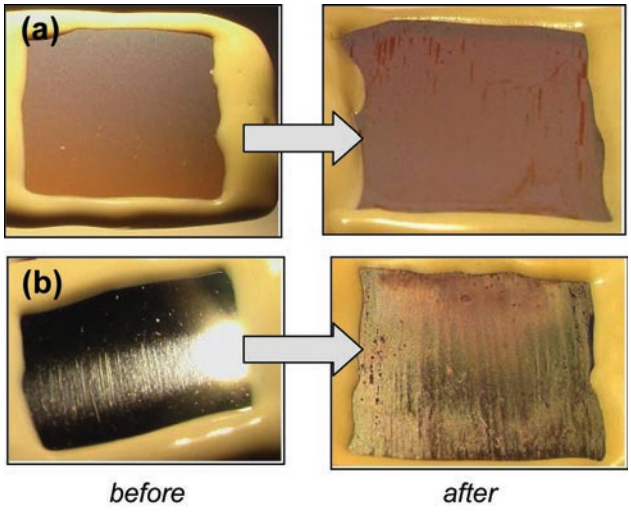

FIGURE 4. Stability experiments of a-PEC photoelectrodes deposited on (a) stainless steel and (b) tin oxide substrates, shown before and after PEC hydrogen production testing.

Conclusions and Future Directions

This project's approach of integrating state-of-the-art theoretical, synthesis and analytical techniques is proving to be invaluable in the identification and development of the most promising materials for practical PEC hydrogen production. Significant progress has been made this past year on several fronts.

- Collaborative Approach has been Successful:
  - The SHGR team, working closely with the DOE PEC Working Group, has developed an extensive "Tool Chest" of theoretical, synthesis and characterization techniques and successfully applied it in the R&D of important focus PEC materials systems.
- Major Technical Targets Met in Focus Materials Research:
  - Photocurrent target (>1.6 mA/cm^2) met in several films:
    - 3.5 mA/cm^2 demonstrated in low temperature WO_3 films.
    - >9.0 mA/cm^2 demonstrated in amorphous silicon carbide.
    - >18 mA/cm^2 demonstrated in copper chalcopyrite films.
  - Conversion efficiency target (2-8% STH) met in multi-junction devices:
    - 3.1% STH efficiency demonstrated using 2006 WO_3.
    - 4% STH efficiency expected using recent bi-layer WO_3.
  - Stability target (100 hour durability) met:
    - >100-hour stable operation demonstrated using WO_3.

Continued development along this pathway is expected to greatly facilitate the discovery and optimization of material systems and device configurations capable of meeting the DOE PEC production targets.

Specific future directions for the work initiated in this project include:

- Continue Current PEC R&D and Optimization Efforts Under New Funding Umbrellas:
  - Focus material R&D: tungsten-, silicon-, and chalcopyrite- compounds.

  - Accelerate interface, device and system development work.
- Continue DOE PEC Working Group Efforts:
  - Further PEC "Tool-Chest" development efforts.
  - Standardization of materials and device testing protocols.
  - Refinement of materials selection and prioritization criteria.
- Expansion of Collaboration Efforts: Nationally and Internationally:
  - DOE PEC Working Group Expansion.
  - USA-led "International Energy Agency PEC Annex-26" offshoot of SHGR work.
  - "International Partnership for a Hydrogen Economy" program proposal.

The ultimate aim is to make the materials and device breakthroughs necessary for high-efficiency, low-cost PEC hydrogen production.

Special Recognitions & Awards/Patents Issued

1. US Patents # 6887728 and 7122873, E. Miller, R. Rocheleau, "Hybrid Solid State/Electrochemical Photoelectrode for Hydrogen Production".

2. 2008 DOE Hydrogen Program R&D Award: E. Miller.

3. IEA-HIA PEC Annex-26 Operating Agent Appointment: E. Miller.

FY 2008 Publications/Presentations

1. B. Marsen, B. Cole, and E. Miller, "Photoelectrolysis of water using thin copper gallium diselenide electrodes", Solar Energy Materials & Solar Cells, 2008, 92, 1054–1058.

2. L. Weinhardt, M. Blum, M. Baer, C. Heske, B. Cole, B. Marsen, and E. L. Miller, "Electronic Surface Level Positions of WO3 Thin Films for Photoelectrochemical Hydrogen Production", J. Phys. Chem. C, 2008, 112, 3078-3082.

3. B. Marsen, B. Cole, E. Miller, "Influence of Sputter Oxygen Partial Pressure on Photoelectrochemical Performance of Tungsten Oxide Films", Solar Energy Materials and Solar Cells, 2007, 91, 1954-1958.

4. A. Walsh, S.-H Wei, Y. Yan, M. Al-Jassim, J Turner, M. Woodhouse and B. Parkinson, "Structural, Magnetic and Electronic Properties of Co-Fe-Al Spinel System" Phys. Rev. B, 2007, 76, 165119.

5. B. Marsen, E. Miller, D. Paluselli, R. Rocheleau, "Progress in Sputtered Tungsten Trioxide for Photoelectrode Applications", International Journal of Hydrogen Energy, 2007.

6. E. L. Miller, "Photoelectrochemical Hydrogen Production", presented at 2007 IMRC (Cancun, Mexico, August 2007).

7. E. L. Miller, "The Hydrogen Economy and Solar Hydrogen Generation", presented at 2007 POSTECH Symposium (Pohang South Korea, November 2007).

8. M.N. Huda , Y. Yan , S.-Hi Wei , M.M. Al-Jassim, "Density-functional theory study of the effects of atomic doping on the band edges of monoclinic WO3", presented at 2008 APS March Meeting, H37.00001, (New Orleans, March 2008).

9. M.N. Huda, Y. Yan and M.M. Al-Jassim, "A Density Functional Theory Study of the Tuning by Atomic Doping in ZnO", presented at the 2007 MRS Fall Meeting, L7.8 (Boston, November 2007).

10. B. Marsen, S. Dorn, B. Cole, R. E. Rocheleau, E.L. Miller, "Copper Chalcopyrite Film Photocathodes for Direct Solar-Powered Water Splitting, in Solar Energy Conversion, edited by Matt Beard (Mater. Res. Soc. Symp. Proc. 974E, Warrendale, PA, 2007), 0974-CC09-05.

11. B. Cole, B. Marsen, E.L. Miller, "Role of Nitrogen Doping on the Optical and Structural Properties of WO3 for Photoelectrochemical Applications, in Solar Energy Conversion, edited by Matt Beard (Mater. Res. Soc. Symp. Proc. 974E, Warrendale, PA, 2007), 0974-CC09-04.

12. A. Stavrides, A. Kunrath, J. Hu, R. Treglio, A. Feldman, B. Marsen, B. Cole, E. Miller, and A. Madan, "Novel Materials for use as Photoelectrodes for Hydrogen Production in Photoelectrochemical Cells", presented at TMS 2007 Annual Meeting (Orlando, 2007).