

II.G.1 Photoelectrochemical Hydrogen Production: DOE PEC Working Group Overview

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Project End Date: various funded projects within the DOE PEC Working Group with different end dates within 2010/2011

Objectives

The DOE photoelectrochemical (PEC) Hydrogen Production Working Group's primary objective is to collaboratively develop practical solar hydrogen-production technology, using innovative semiconductor materials and devices research and development (R&D) to foster the needed scientific breakthroughs for meeting DOE Hydrogen Program goals.

Technical Barriers

The DOE PEC Working Group is working to address all of the technical barriers identified in the "Photoelectrochemical Hydrogen Production" section of the Fuel Cell 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
- (AD) Systems Design and Evaluation
- (AE) Diurnal Operation Limitations

Technical Targets

As recognized within the PEC hydrogen research community and the DOE PEC Hydrogen sub-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. This is reflected in Table 1, a reprint of the DOE Targets for PEC Hydrogen Production from the DOE's Multi-Year RD&D Plan [1].

The DOE PEC Working Group utilizes its collective expertise in theoretical materials modeling, synthesis, characterization and analysis to study a diverse portfolio of promising PEC thin-film materials classes with the potential for meeting the technical targets.

Accomplishments

Important milestones have been achieved this past year through the collaborative efforts of the DOE PEC Working Group, and the associated DOE-funded projects. Significant progress has continued in the development of the Working Group's "Tool Chest" of materials theory, synthesis, characterization and analysis techniques; and this enhanced "Tool Chest" has been

TABLE 1. DOE Targets for Photoelectrochemical Hydrogen Production

Characteristics	Units	2003 Status	2006 Status	2013 Target	2018 Target ^b
Usable semiconductor bandgap ^c	eV	2.8	2.8	2.3	2.0
Chemical conversion process efficiency (EC) ^d	%	4	4	10	12
Plant solar-to-hydrogen efficiency (STH) ^e	%	not available	not available	8	10
Plant durability ^f	hr	not available	not available	1000	5000

instrumental in the development and optimization of important PEC materials classes. In nano-structured molybdenum disulfide photocatalyst materials systems, for example, band-gaps up to 1.8 eV have been demonstrated for the first time, with important implications for efficient PEC production. Progress has also continued in other PEC materials classes falling within the DOE-defined “useable” band-gap range. Important new results have been achieved in tungsten-trioxide, iron-oxide, silicon-carbide, copper-chalcopyrites, and the III-V materials classes, among others. DOE PEC Working Group efforts are ongoing to render these potentially “useable” materials for high-efficiency PEC hydrogen production. General accomplishments of the PEC Working Group, detailed further in following sections, can be summarized broadly as follows:

- Successful development and application of new PEC “Tool Chest” capabilities.
- Advances in PEC Focus Materials Classes toward meeting DOE-PEC performance targets.
- Further expansion of collaborative research efforts.



Introduction

PEC hydrogen production, the splitting of water into hydrogen and oxygen using sunlight, is an important enabling technology for future energy economies which will rely, in part, on hydrogen as an energy currency [2]. The traditional semiconductor-based PEC material systems studied to date, however, have been unable to meet all the performance, durability and cost

requirements for practical hydrogen production. PEC semiconductors such as titanium-dioxide and other metal-oxides, for example, have proven to be stable in aqueous solutions, but suffer from low solar conversion performance due to their high band-gaps [3]. Based on these inherent limitations, it has become increasingly clear that new, more advanced materials need to be developed. Technology enabling breakthroughs in materials R&D are needed for the success of PEC hydrogen production.

Toward this end, the U.S. DOE currently funds a number of research institutions from the academic, industrial and national laboratory sectors with the objective of discovering, engineering and optimizing such advanced PEC materials systems for solar water-splitting. To facilitate progress, the project participants, have formed a national Working Group on PEC hydrogen production, bringing together experts in analysis, theory, synthesis and characterization from the academic, industry and national laboratory research sectors. The 2010 DOE Hydrogen Program Annual Merit Review held in Washington D.C. featured numerous presentations from participating PEC Working Group institutions, as illustrated in Figure 1. An overview of the collective approach and past-year’s progress is presented in the following sections.

Approach

The general approach of the collaborative effort among 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



FIGURE 1. PEC Working Group Members with current DOE financial support, including the 2010 DOE Hydrogen Program Annual Merit Review oral/poster presentation designations.

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 employing microstructural, electron spectroscopic, and electrochemical characterization techniques, a comprehensive picture of the materials properties and resulting performance is being developed. Within the DOE PEC Working Group, the approach has been applied to a number of “focus materials” deemed of particular interest for PEC applications.

PEC Hydrogen Production has already been successfully demonstrated on the laboratory scale. High solar-to-hydrogen (STH) efficiencies, between 12-16%, have been demonstrated for limited durations in devices based on expensive high-quality crystalline semiconductors, such as the III-V tandem GaAs/GaInP₂ cell [4]. In addition, lower STH efficiencies, in the 3-5% range have been demonstrated in devices based on lower priced thin-film semiconductor materials. Multi-junction devices, for example using WO₃ films as a PEC top-junction, have been reported in this performance category [5]. To achieve practical PEC hydrogen production, new semiconductor materials systems with both high performance and low cost are needed. One specific approach is the further development of the traditional PEC semiconductor thin-films and nano-structures for higher efficiencies. Examples include improvements to iron-oxide and tungsten trioxide. Another approach is the adaptation of efficient photovoltaic semiconductor thin-films and nano-structures for effective use in PEC. This includes, for example, copper chalcopyrites and amorphous silicon compounds. Other innovative approaches include the development of entirely new materials classes, such as quantum-confined WS₂ and MoS₂ nanoparticle systems, and the development of breakthrough synthesis technologies to reduce the cost of high-performance crystalline semiconductors, such as GaAs/GaInP₂. Future progress in all these approaches is integrally tied to the DOE PEC Working Group’s continued development and deployment of its tool-chest capabilities, and continual feedback among the theory, synthesis and characterization efforts

Results

To expedite technical progress, the DOE PEC Working Group has initiated Task Forces to coordinate important PEC research activities. While some of the

collaborative task forces center on the R&D of specific PEC materials classes, others focus on critical activities to advance the supporting science and technologies in the PEC tool chest. Important activities in the latter category have resulted in significant progress, including:

- Significant Progress in Establishing PEC Testing Standards [6,7]
 - First revision drafts of 16 protocol documents completed.
 - Summary paper published in Journal of Materials Science.
 - Web site set up to facilitate international review/revision process.
- Important Advances in PEC Characterizations [8,9]: Project PD051
 - Ultraviolet/soft X-ray/electron spectroscopic tools for evaluating optoelectronic and chemical properties of PEC materials’ surfaces, near-surfaces and bulk fully operational.
 - “Solid And Liquid Spectroscopic Analysis” characterization facility installed at the Lawrence Berkeley National Laboratory Beamline 8.0 Advanced Light Source for the in situ evaluation of PEC semiconductor/electrolyte interfaces (as illustrated in Figure 2).
- New Advances in PEC Materials Theory [10,11,12]: Projects PD052, PD058
 - First principle models of the PEC interface constructed based on III-V semiconductors, exploring effects of O, H and OH termination (as illustrated in Figure 3a).

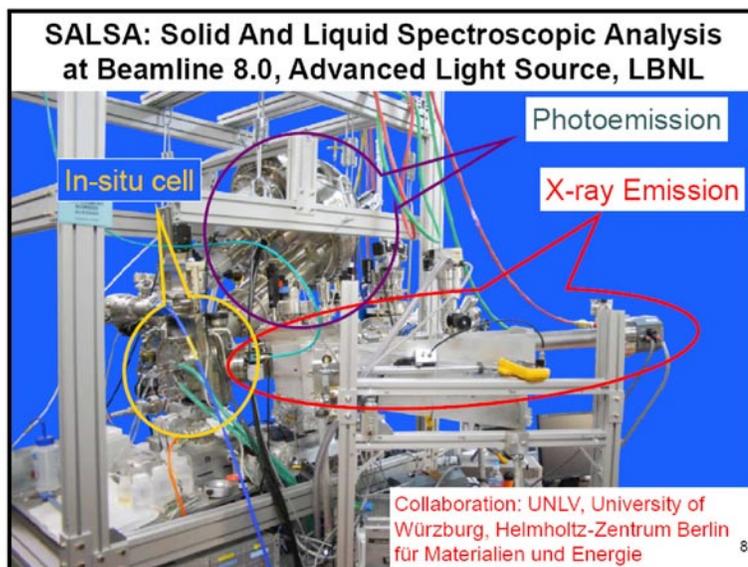


FIGURE 2. “Solid And Liquid Spectroscopic Analysis” characterization facility at the Lawrence Berkeley National Laboratory Beamline 8.0 Advanced Light Source for the in situ evaluation of PEC semiconductor/electrolyte interfaces [C. Heske, PD051].

- Important correlations between surface morphology and interaction with interfacial water molecules established.
- Theoretical band structures of new PEC materials classes investigated (as illustrated in Figure 3b).
- First Phase of PEC Hydrogen Production Techno-economic Analyses Completed [13]
 - Incorporating performance and processing cost feedback from the broader materials R&D efforts, coordinated through Directed Technologies, Incorporated.
 - Sensitivity analyses indicating hydrogen production costs as low as \$1.86/kg hydrogen for some PEC systems configurations based on available plant technologies, and

using projected high-performance PEC semiconductor materials.

Continued feedback between the theory, synthesis, characterization and analysis among PEC Working Group participants is providing fundamental insights needed to promote technical breakthroughs in a broad spectrum of promising PEC materials classes. The Working Group serves to organize, focus, and track scientific research progress in PEC R&D. This approach over the past year has resulted in important progress toward DOE PEC Materials & Device Targets. Examples include:

- Successful first-time demonstration of bandgap tailoring in photoactive MoS₂ nanoparticles at Stanford University [14,15]: Project PD033
 - Nanoparticle sizes ranging from 25 down to 5 nm have exhibited band-gaps ranging from 1.0–1.8 eV (as shown in Figure 4a).
 - Initial exploration of photocatalyst nanorods, in collaboration with University of Louisville (as shown in Figure 4b).
- Identification of thin-film device configurations based on current chalcopyrite and silicon compound materials at MVSystems Incorporated and the University of Hawaii with potential for meeting DOE Performance Targets [16,17]: Projects PD053, PD055
 - Identified complex multi-junction device having >5% STH using current copper gallium diselenide materials.
 - PEC interfacial barrier identified as limit to >10% STH tandem.
 - New theory and characterization tools to be used to address the interface barrier problem for meeting DOE performance targets.
- Identification of crystalline semiconductor device configurations based on current III-V materials with >15% STH conversion efficiency at the National Renewable Energy Laboratory [18]: Project PD035

In addition, notable progress also has continued over the range of PEC materials classes under investigation by the PEC Working Group, including progress in:

- Tungsten-oxide and related modified compounds [19-21]: Project PD054
- Iron-oxide and related modified compounds [22,23]: Project PD034
- Amorphous silicon-carbide based photoelectrodes [24,25]: Project PD053
- Copper indium gallium diselenide based photoelectrode systems [26,27]: Project PD055

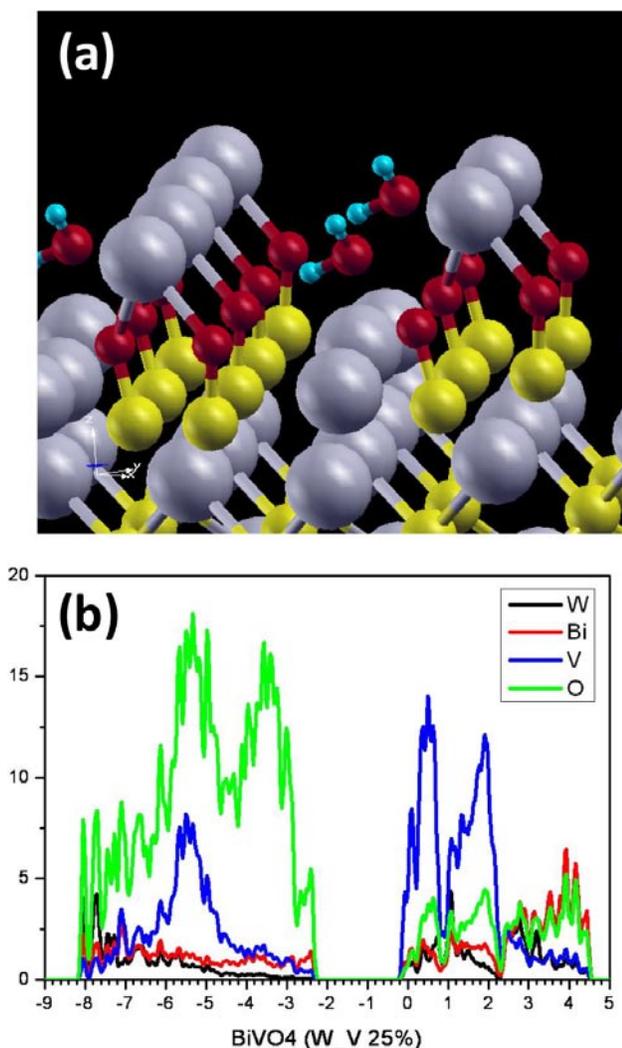


FIGURE 3. (a) Theoretical model of semiconductor/electrolyte PEC junctions based on III-V model systems [T. Ogitsu, PD034]; (b) Theoretical model of doped band structure and density-of-states in BiVO₄ with tungsten doping on vanadium sites [Y. Yan, PD052].

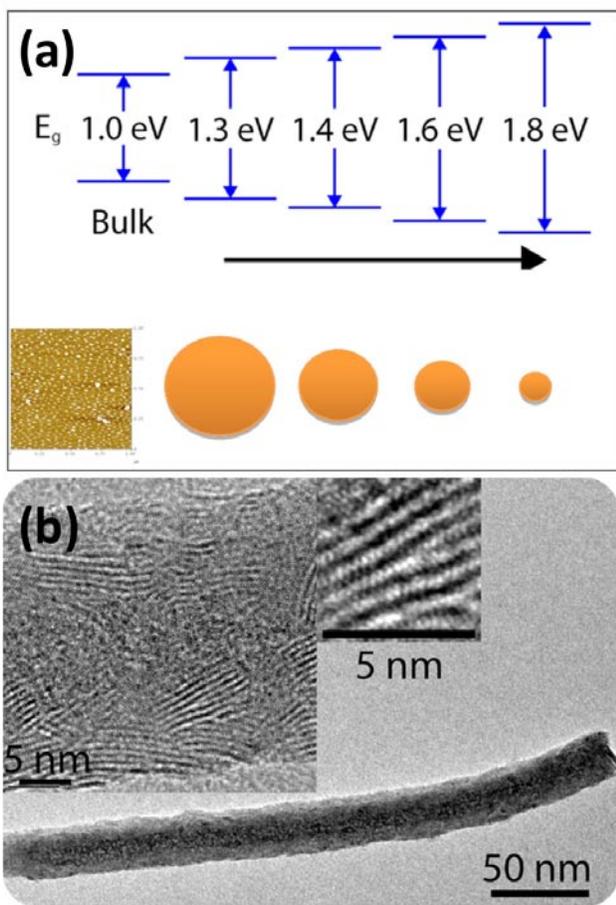


FIGURE 4. (a) first demonstration of band-gap engineering in molybdenum-disulfide nanoparticle photocatalysts; (b) initial exploration of molybdenum-disulfide photocatalyst nanorods [T. Jaramillo, PD033].

- Cadmium-sulfide and zinc-telluride compounds: Project PD061
- Integration schemes for thin-film PEC systems [28]: Project PD056

Although there is still work ahead for achieving high-performance low-cost PEC hydrogen production, research in promising candidate materials has seen significant progress this past year. The reader is referred to the cited references and to the progress reports for all of the DOE PEC Working Group 2010 AMR presentations (i.e., the presentations listed in Figure 1) for detailed progress in the individual materials categories.

Conclusions and Future Directions

The DOE's Working Group on PEC Hydrogen Production has taken a collaborative approach in the R&D of novel PEC material systems. This approach, incorporating a broad spectrum of state-of-the-art

techniques in theory, synthesis, characterization and analysis, is proving invaluable in the identification and development of the most promising materials for practical PEC hydrogen production. Continued Working Group efforts in conjunction with expanded international collaborations are expected to greatly facilitate the discovery and optimization of material systems and devices capable of meeting the DOE PEC hydrogen production targets. Specific future directions include:

- Continued Advancement of DOE PEC Working Group Efforts
 - Further PEC “Tool Chest” development efforts.
 - Standardization of materials and device testing protocols.
 - Further discovery and optimization of viable PEC semiconductor materials.
 - Integration of best available PEC materials into optimal device and system configurations.
- Continued Expansion of Collaboration Efforts: Nationally and Internationally
 - DOE PEC Working Group expansion.
 - United States-led “International Energy Agency PEC Annex-26”.

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

Special Recognitions & Awards/Patents Issued

1. Book Publication featuring contributions from numerous DOE PEC Working Group Participants: “Solar Hydrogen and Nanotechnology”, Lionel Vayssieres (ed.), Wiley and Sons, 2010.

Publications/Presentations

1. The publication list of the U.S. DOE PEC Working Group Members is extensive. The reader is referred to the progress reports of the 2010 DOE AMR presentations of the Working Group Participants (including presentations PD 033, 034, 035, 051, 052, 053, 054, 055, 056, 058, 061 and 062) for a comprehensive list of publications.

References

1. U.S. Department of Energy Efficiency and Renewable Energy. Hydrogen, Fuel Cells and Infrastructure Technologies Program – Multi-Year Research, Development and Demonstration Plan; 2007. <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/>.
2. J. Rifkin, *The Hydrogen Economy : The Creation of the Worldwide Energy Web and the Redistribution of Power on Earth*. JP Tarcher/Putnam: New York, 2002.

3. R. Rocheleau, E. Miller, Photoelectrochemical Production of Hydrogen: Engineering Loss Analysis. *International Journal Hydrogen Energy* 1997, **22**, 771-782.
4. O. Khaselev, A. Bansal, J.A. Turner, *Int. J. Hydrogen Energy*, **26**, 127-132 (2001).
5. E. Miller, B. Marsen, B. Cole, M. Lum, Low-Temperature Reactively Sputtered Tungsten Oxide Films for Solar-Powered Water Splitting Applications. *Electrochemical and Solid-State Letters* 2006; **9**(7), G248-G250.
6. Z. Chen, T.F. Jaramillo, T.G. Deutsch, A. Kleiman-Shwarsstein, A. Forman, N. Gaillard, R. Garland, K. Takanabe, C. Heske, M. Sunkara, E.W. McFarland, K. Domen, E.L. Miller, J.A. Turner, H.N. Dinh, "Accelerating materials development for photoelectrochemical (PEC) hydrogen production: Standards for methods, definitions, and reporting protocols", *Journal of Materials Research*, 2010, **25**, 3-16.
7. www2.eere.energy.gov/hydrogenandfuelcells/pec_standards_review.html#standards.
8. L. Weinhardt, M. Blum, M. Bär, 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.
9. Clemens Heske, "Using soft x-rays to look into (buried) interfaces of energy conversion devices", Chemistry and Geochemistry Department at the Colorado School of Mines, Golden, CO, September 25, 2009 (invited talk).
10. AronWalsh, Kwang-Soon Ahn, SudhakarShet, Muhammad N. Huda, Todd G. Deutsch, HeliWang, John A. Turner, Su-HuaiWei, YanfaYan, MowafakM. Al-Jassim, "Ternary cobalt spineloxides for solar driven hydrogen production: Theory and experiment", *Energy Environ. Sci.*, **2**, 2009, 774.
11. M. N. Huda, Y. Yanfa, C.-Y. Moon, S.-H. Wei, and M. M. Al-Jassim "Density-functional theory study of the effects of atomic impurity on the band edges of monoclinic WO₃" *Physical Review B* **77**, 2008, 195102.
12. S. Shet, K.S. Ahn, T.Deustch, H. Wang, N. Ravindra, Y. Yan, J. Turner, M. Al-Jassim, "Synthesis and characterization of band gap-reduced ZnO:Nand ZnO:(Al,N) films for photoelectrochemicalwater splitting" , *Journal of Materials Research*, 2010, **25**(1),69-75.
13. "Techno-Economics Analysis of Photoelectrochemical systems for Solar Hydrogen Production". DTI presentation, presented at the 2009 DOE Hydrogen Program AMR, Arlington VA (2009). http://www.hydrogen.energy.gov/pdfs/progress09/ii_h_2_james.pdf.
14. T.F. Jaramillo , 2009 American Institute of Chemical Engineers Annual Meeting, Nashville, TN. "Nanostructured MoS₂ for the Photoelectrochemical (PEC) Production of Hydrogen.", November 2009 (invited talk).
15. T.F. Jaramillo, K.P. Jørgensen, J. Bonde, J.H. Nielsen, S. Horch, and I. Chorkendorff, "Identifying the active site: Atomic-scale imaging and ambient reactivity of MoS₂ nanocatalysts", *Science*, 2007, **317**, 100 – 102.
16. J. Kaneshiro, E. Miller, N. Gaillard and R. Rocheleau, *Advances in Copper Chalcopyrite Thin Films for Solar Energy Conversion Sol. Energy Mater. and Sol. Cells*, 2010, **94**, 12-16.
17. Book chapter: "Solar Energy": Feng Zhu, Jian Hu, Ilvydas Matulionis, Todd Deutsch, Nicolas Gaillard, Eric Miller, andArun Madan, "Amorphous Silicon Carbide Photoelectrode for Hydrogen Production from Water using Sunlight" , edited by: Radu D. Rugescu, ISBN 978-953-307-052-0, pp. 432, February 2010, INTECH.
18. T.G. Deutsch, C.A. Koval, and J.A. Turner, "III-V Nitride Epilayers for Photoelectrochemical Water Splitting: GaPN and GaAsPN", *J. Phys. Chem. B*, 2006, **110**, 25297-25307.
19. N. Gaillard, B. Cole, B. Marsen, J. Kaneshiro, E.L. Miller, L. Weinhardt, M. Bär, C. Heske, K. -S. Ahn, Y. Yan, and M.M. Al-Jassim, "Improved current collection in WO₃:Mo/WO₃ bilayer photoelectrodes", *J. Mater. Res.*, 2010, **25**, 45.
20. B. Marsen, B. Cole, E.L. Miller, "Progress in sputtered tungsten trioxide for photoelectrode applications", *International Journal of Hydrogen Energy*, 2007, **32**, 3110-3115.
21. B. Cole, B. Marsen, E.L. Miller, Y. Yan, B. To, K. Jones, and M.M. Al-Jassim, "Evaluation of Nitrogen Doping of Tungsten Oxide for Photoelectrochemical Water Splitting", *J. Phys. Chem. C*, 2008, **112**, 5213-5220.
22. Y.-S. Hu, A. Kleiman-Shwarsstein, A. J. Forman., D. Hazen, J.-N. Park, and E. W. McFarland, "Pt-Doped α -Fe₂O₃ Thin Films Active for Photoelectrochemical Water Splitting", *Chem. Mater.*, 2008, **20** (12), 3803–3805.
23. A. Kleiman-Shwarsstein, Y.-S. Hu, A. J. Forman, G. D. Stucky, and E. W. McFarland, "Electrodeposition of α -Fe₂O₃ Doped with Mo or Cr as Photoanodes for Photocatalytic Water Splitting", *J. Phys. Chem. C* **112**, 2008, **40**, 15900–15907.
24. J. Hu, F. Zhu, I. Matulionis, A. Kunrath, T. Deutch, L. Kuritzky, E. Miller, and A. Madan, "Solar-to-Hydrogen Photovoltaic/Photoelectrochemical Devices Using Amorphous Silicon Carbide as the Photoelectrode", 23rd European Photovoltaic Solar Energy Conference, Valencia, Spain, 1–5 September, 2008.
25. I. Matulionis, F. Zhu, J. Hu, J. Gallon, A. Kunrath, E. Miller, B. Marsen, and A. Madan, "Development of a Corrosion-Resistant Amorphous Silicon Carbide Photoelectrode for Solar-to-Hydrogen Photovoltaic/Photoelectrochemical Devices", SPIE Solar Energy and Hydrogen 2008, San Diego, USA, 10–14 August 2008.
26. M. Bär, L. Weinhardt, S. Pookpanratana, C. Heske, S. Nishiwaki, W. Shafarman, O. Fuchs, M. Blum, W. Yang, and J.D. Denlinger, "Depth-dependent band gap energies in Cu(In,Ga)(S,Se)₂ thin films", *Appl. Phys. Lett.*, 2008, **93**, 244103.
27. B. Marsen, B. Cole, E. L. Miller, "Photoelectrolysis of water using thin copper gallium diselenide electrodes", *Solar Energy Materials & Solar Cells*, 2008. **92**, 1054– 1058.

28. W. Ingler Jr., A. Naseem “*RF Sputter Deposition of Indium Oxide / Indium Iron Oxide Thin Films for Photoelectrochemical Hydrogen Production*”, 2009 MRS Spring Meeting Symposium S Proceedings, Vol. 1171E, 2009.