

II.F.1 Directed Nano-Scale and Macro-Scale Architectures for Semiconductor Absorbers and Transparent Conducting Substrates for Photoelectrochemical Water Splitting

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Fiscal Year (FY) 2012 Objectives

The main objective of this project is to develop third-generation materials and structures with new properties that can potentially meet DOE targets (2013 and 2018) for usable semiconductor bandgap, chemical conversion process efficiency, and durability.

- Develop a transparent conducting high surface area electrode (HSE) as a broadly applicable substrate for photoelectrochemical (PEC) devices utilizing scalable fabrication methods.
- Improve efficiency of charge transport limited PEC materials (e.g., α -Fe₂O₃) by integrating them into the HSE substrate and demonstrate efficacy.
- Develop efficient PEC materials consisting of nanostructured MoS₂ with a wider bandgap, improved band alignment with respect to H₂ and O₂ evolution potentials and improved surface catalysis for the hydrogen evolution reaction.
- Develop durable MoS₂ photo-cathodes.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

The focus of this project is the development of a broadly applicable substrate platform that enables the ability to integrate novel third-generation solar absorbers as well as charge transport limited solar absorbers into a complete PEC device. If successful, this project will address the following DOE technical targets as outlined in the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan.

TABLE 1. Progress towards Meeting Technical Targets for PEC Hydrogen Production

Characteristics	Units	2013 Target	2018 Target	2012 Status
Usable semiconductor bandgap	eV	2.3	2.0	1.8
Chemical conversion process efficiency	%	10	12	TBD
Plant solar-to-hydrogen efficiency	%	8	10	TBD
Plant durability	hr	1,000	5,000	TBD

TBD – to be determined

FY 2012 Accomplishments

- Developed and optimized a facile, scalable spray deposition route (patent pending) to fabricate HSEs of transparent conducting oxide (TCO) materials.
- Demonstrated a robust synthetic methodology that enables tunable control of surface area from ~1 to over 100x relative to a planar substrate as determined using extensive electrochemical characterization.
- Use of the HSE substrate as a support for α -Fe₂O₃ (a minority carrier charge transport limited PEC material)

yields performance enhancement over planar $\alpha\text{-Fe}_2\text{O}_3$ devices.

- Engineered nanoscale mesoporous architectures of MoS_2 to overcome thermodynamic structural limitations in bulk form to achieve a higher density of catalytically active sites for electrochemical hydrogen evolution.
- Determined band structures for quantum confined MoS_2 nanoparticles to show better conduction and valence band alignment for H_2 and O_2 evolution potentials



Introduction

The production of hydrogen (H_2) currently represents 2-3% of worldwide energy consumption due to the critical role of H_2 in large scale industrial processes such as ammonia synthesis and petroleum refining [1,2]. PEC water splitting is a promising route towards producing H_2 using only renewable resources (sunlight and water) [3]. Producing H_2 by this approach can reach costs as low as \$2-\$3/gasoline gallon equivalent [4] and represents a way to store solar energy to better match the intermittent solar collection profile with variable point-of-use energy demand profiles. To realize these competitive economics with PEC water splitting, it is necessary to create higher efficiency and lower cost devices than what is currently available today.

Successful development of an economical system to split water from solar irradiation requires optimizing multiple components that make up a complete PEC device, including discovery of efficient, earth-abundant, and stable photoelectrode materials and electrocatalysts, as well as appropriate architectural supports, followed by integration of these components into a complete system

Approach

One of the major limitations to efficient PEC device development is achieving high solar absorption while maintaining short charge transport distances in a typical planar electrode geometry. Thick samples improve light absorption at the expense of charge transport, while thin samples improve charge transport at the expense of light absorption. This challenge is general to thin-film solar technologies [5]. One method to decouple the two phenomena is to utilize transparent, HSE supports coated with ultra-thin layers of light absorbing material. HSEs enable the fabrication of high optical density devices without using thick absorber layers, thereby mitigating efficiency losses due to transport of both minority and majority charge carriers. This approach has been successfully demonstrated in dye-sensitized solar cells which often employ high surface area TiO_2 [6]. Furthermore, HSE architectures reduce local current densities by increasing interfacial surface area, decreasing

the kinetic overpotential required to turn over a reaction and further enhancing the efficiency of electrodes used in both solar applications as well as non-solar applications such as electrocatalysis. Development of these HSEs is therefore an enabling technology at both the fundamental and applied research levels. To further address the broad range of materials currently being studied for PEC water splitting, it is necessary to develop HSEs with tunable physical and electronic properties in order to optimize the light absorption, charge transport, and mass transport properties of a complete device.

While many materials have previously been studied for PEC water splitting, no one material currently meets the requirements of high efficiency and low cost. To develop novel solar absorber materials, we engineer nanostructures of MoS_2 , [7] a material which demonstrates promising photoactivity in bulk form, [8] but is otherwise hampered by a bandgap that is too small, misaligned conduction and valence bands with respect to the H_2 and O_2 evolution potentials, and poor catalysis. By nanostructuring MoS_2 , the electronic properties can be modified through quantum confinement, [9,10] and the catalytic activity for H_2 evolution can be dramatically enhanced by exposing a greater number of active edge sites [11,12].

Results

Previously, we successfully developed a synthetic route towards fabricating high surface area TCO substrates with hierarchical (nanometer-scale and micron-scale) porosity utilizing a scalable spray deposition technique. The design is applicable to a broad range of compositions, such as indium tin oxide, fluorine-doped tin oxide, aluminum zinc oxide. Figure 1a illustrates a schematic representation of the resulting film morphology from this scalable fabrication process. The amount of mixture sprayed onto the appropriate conductive substrate controls the final surface area of the HSE. These TCO HSEs are capable of enabling PEC materials to simultaneously address three of the DOE technical barriers for Production (Y, AA, AB). Compared to more classical HSE fabrication techniques such as lithographic patterning, spray deposition offers significant cost savings and scalability – absolute necessities for an emerging solar energy technology seeking to generate copious domestic fuel.

We have made significant progress in the development of HSE supports, including synthetic methods, characterization and most notably, in the utilization of the HSE as a PEC support. Spray fabrication conditions for the HSE have been optimized to yield high reproducibility and large area coverage (10's to 100 cm^2) in the laboratory setting. Electrochemical characterization of the HSEs yielded limitations when the active area was defined and sealed with an o-ring in a compression cell configuration, resulting in

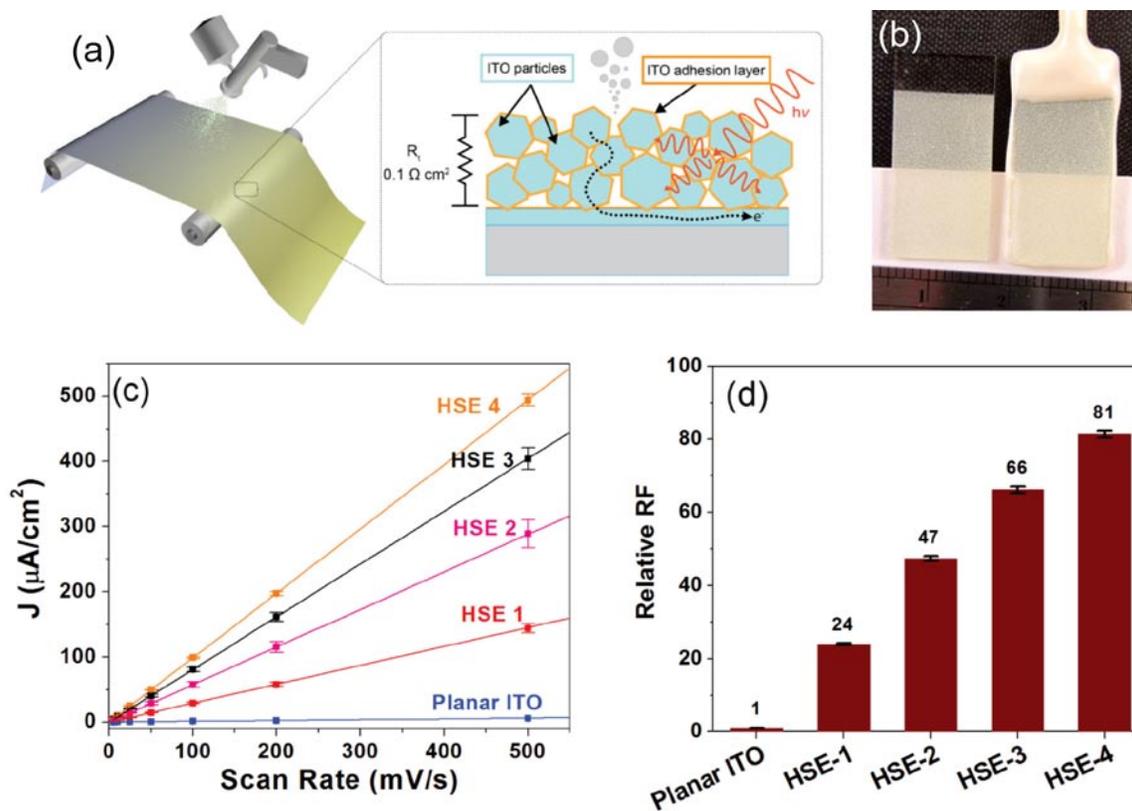


FIGURE 1. Transparent conductive HSEs are fabricated via spray deposition to yield substrates with tunable surface areas (a). Improved electrode mounting methods include conductive paint and insulating epoxy (b) resulting in non-diffusion limited performance (c) and high precision, high accuracy synthetic tunability of the roughness factor (d).

electrolyte leaking and erroneous diffusion limited signals. These problems have been eliminated by contacting the HSEs with conductive paint and defining and sealing the active area with insulating epoxy (Figure 1b). The result of this improved methodology is that the data interpretation for electrochemical surface area characterization is more straightforward – there are no diffusion limitations observed, as evidenced by the linear relationship between current density and scan rate (Figure 1c). The absence of diffusion limitations through the HSE bodes well for subsequent (photo)catalytic applications. The end result of the refined synthesis and electrode mounting procedures is that discrete roughness factors ranging from ~ 1 to >100 can be targeted with great accuracy and precision (Figure 1d) depending on the needs of the final application.

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) was chosen as a proof-of-concept material to test the enhancement afforded by the HSE scaffold for charge transport limited PEC materials. Hematite films were fabricated by dropcasting an ethanolic solution containing FeCl_3 and Ti-butoxide (1:10, Ti:Fe) followed by annealing at 550°C in air following the work of Li *et al.* [13]. For comparison, three samples were fabricated (Figure 2a): 1) HSE substrate with hematite layer. This resulted in a conformal, well adhered film with a high

optical density. 2) Planar substrate with identical hematite loading ($\mu\text{g}/\text{cm}^2_{\text{device}}$) to sample 1. This resulted in a thick, cracked film which delaminated from the substrate. 3) Planar substrate with hematite film thickness (nm) identical to sample 1. This resulted in a thin, low optical density film. The PEC performance of these three samples is presented in Figure 2b. Sample 1 on the HSE substrate shows the best performance, maintaining the expected photocurrent onset of $\sim 1 \text{ V}$ vs. reversible hydrogen electrode with a superior photocurrent due to high light absorption and charge extraction within the HSE. Samples 1 and 2 have an identical hematite loading, absorb the same number of incoming photons and should therefore be capable of generating the same photocurrent. However, because this high loading is placed on a planar substrate, the actual hematite film thickness is very large, resulting in physical instability and delamination from the substrate. The result is that sample 2 is unstable and gives no PEC signal. The take home message here is that it is desirable to have high loadings of material (per geometric device area) to achieve high optical densities and correspondingly high photocurrents. However, there is an upper stability limit when loading thicker films onto planar substrates which does not allow the desired loadings to be achieved. Yet, our HSE scaffolds do not encounter this same

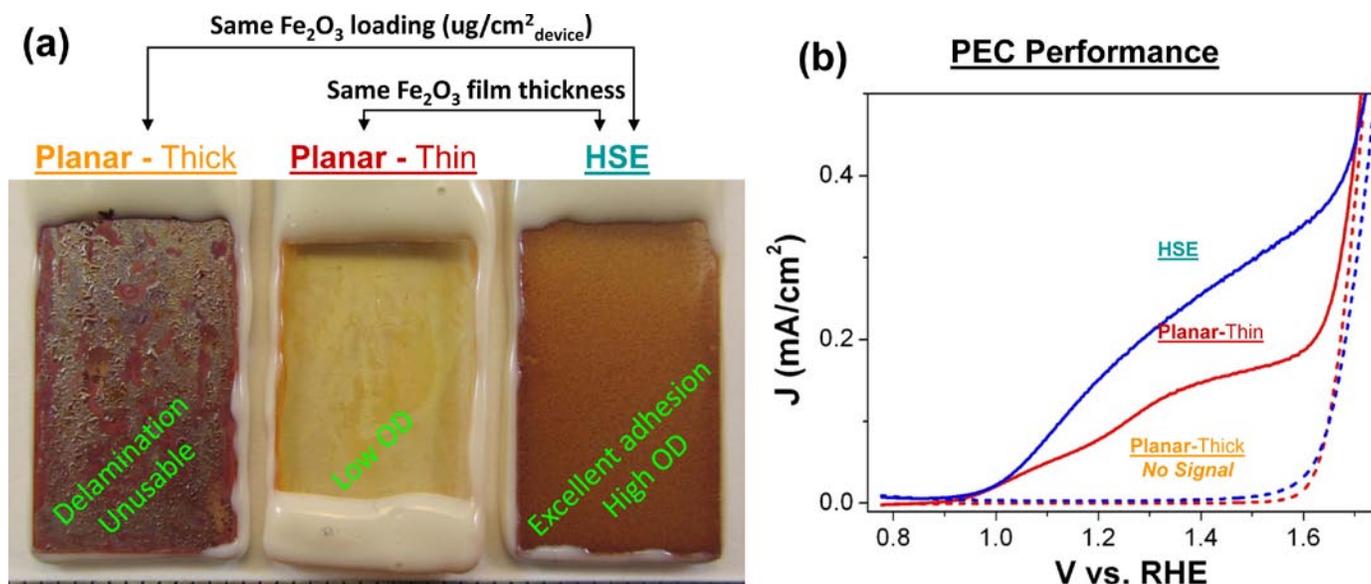


FIGURE 2. Optical photograph of hematite films on planar and HSE substrates (a), see text for synthetic details. (b) Current-voltage curves in the dark (dotted lines) and under 1 sun of illumination (solid lines) for the samples presented in (a).

loading limitation and can offer high optical densities of stable, delamination-free active layers.

Comparison of samples with an identical thickness of hematite, samples 1 and 3, indicates that the HSE substrate offers practical performance enhancement through increased light absorption (Figure 2b). It is clear, however, that there is room for further improvement of the HSE device as the current is only $\sim 2\times$ that of sample 3, while the loading is $\sim 12\times$ higher. Proposed routes to improvement include further optimization of the dropcasting procedure and introduction of an interfacial layer between the HSE and hematite layers [5,14-16]. Initial work in our labs using interfacial layers of SiO_2 and TiO_2 has shown promising results and must be further optimized to achieve full conformal coverage on the HSE.

Although hematite is an excellent material to study whose performance can be enhanced by the HSE, it is ultimately limited by a mismatched conduction band with respect to the hydrogen evolution potential. In order to engineer materials with more appropriate band structures that sufficiently straddle the water splitting potentials, we leverage the effects of quantum confinement to tune the electronic properties of MoS_2 [17]. We have previously demonstrated the synthesis of MoS_2 nanoparticles using a micelle encapsulation approach that exhibit a blueshift in the absorption onset with smaller size. This corresponds to an enlargement in the bandgap up to ~ 1.8 eV for MoS_2 nanoparticles of only a few nm in diameter. In order to further assess the flatband potential (E_{fb}) of the nanoparticles, we fabricated thin film electrodes. A number of fabrication techniques were explored such as dip coating, drop

casting, and spin coating, but spray coating yielded the most homogeneous films on a variety of substrates. Spray deposited films of nanoparticles on fluorine-doped tin oxide enabled PEC characterization and assessment of E_{fb} by photocurrent onset. When coupled to the optical absorption measurements, we were able to approximate the band structure (Figure 3), showing that the smallest nanoparticles appear to possess conduction and valence bands that adequately straddle the water splitting potentials.

We further enhanced the catalytic properties of MoS_2 for H_2 evolution (Figure 4a) by engineering its surface structure to display an increased density of active edge sites. In order to achieve this result, it is necessary to overcome a limitation in which the formation of these edge sites are thermodynamically unfavored compared to the formation of extended non-active basal planes at bulk length scales greater than a few tens of nanometers. To address this challenge, we synthesized highly ordered and extended films of a mesoporous double-gyroid MoS_2 architecture with features on the order of just $\sim 3\text{-}4$ nm. This highly interconnected porous morphology (Figure 4b) not only provided a high surface area for catalysis, but its high curvature limited the formation of extended basal planes and increased the density of catalytically active edge sites (Figure 4c), enabling excellent H_2 evolution.

Conclusions and Future Directions

In order to reach our goal of developing a fully operational PEC water splitting device, we have produced a high surface area transparent conducting electrode and demonstrated its ability to enhance efficiency for PEC. We

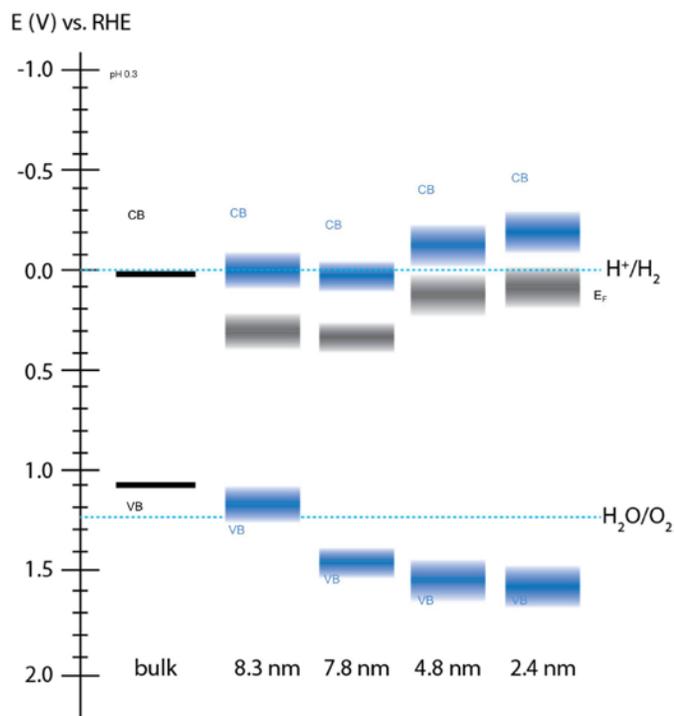


FIGURE 3. Band diagram comparing the position of the conduction and valence bands of several films of MoS₂ nanoparticles (nanoparticle size denoted in the figure) compared to bulk MoS₂ [17].

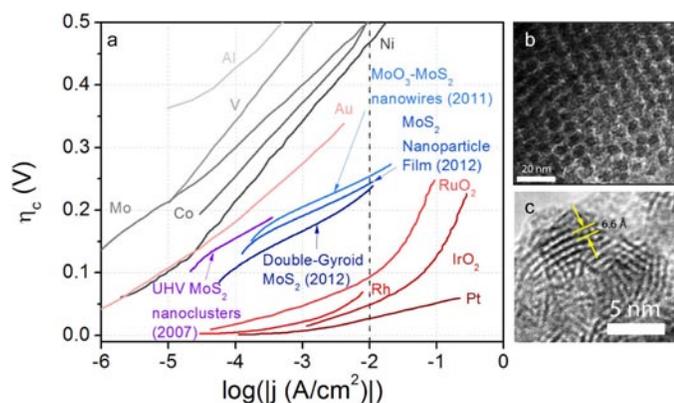


FIGURE 4. Tafel plot of numerous materials for electrochemical H₂ evolution (a). Transmission electron microscopy image of mesoporous double-gyroid architecture (b) and layered MoS₂ domains within the structure (c).

have also developed a third-generation light absorber material (MoS₂) and further enhanced its electrocatalysis. Specifically, we have achieved the following:

- A low-cost, scalable, facile route to fabrication of high surface area transparent conducting electrodes has been developed, a manuscript submitted and a patent application is pending.

- Physical and electronic characterization of these electrodes indicates tunable roughness factors from ~1 to >100 over large substrate areas.
- HSE scaffolds have been used to demonstrate enhanced PEC performance for Hematite thin films. Further improvements are underway.
- Developed quantum confined nanoparticles of MoS₂ with band structures that adequately straddle the redox potentials for water splitting.
- Engineered the surface structure of MoS₂ for enhanced electrocatalytic H₂ evolution.

The next step in our work is to tune the solid-solid interface by addition of hetero-layers. We will accomplish this task through various objectives:

- Identify appropriate methods and materials for deposition of thin, conformal interfacial layers onto HSEs.
- Evaluate and iteratively improve PEC devices which incorporate both interfacial layers and thin semiconductor films.
- Continue to identify and evaluate charge-transport limited PEC materials which benefit from the HSE architecture.
- Incorporate MoS₂ nanoparticles into the HSE and characterize their water splitting properties with respect to light absorption, charge transport, and stability.

Special Recognitions & Awards/Patents Issued

1. DOE Hydrogen and Fuel Cells Program R&D Award to Prof. Thomas F. Jaramillo (PI)
2. Arnold J. Forman, Zhebo Chen, and Thomas F. Jaramillo, "Synthesis of High Roughness Factor Transparent Conducting Oxide Thin Films" (patent application pending).

FY 2012 Publications/Presentations

1. A.J. Forman, Zhebo Chen, and Thomas F. Jaramillo, "Development of a High Surface Area Transparent Conducting Oxide Electrode" (submitted).
2. Jakob Kibsgaard, Zhebo Chen, Benjamin N. Reinecke, and Thomas F. Jaramillo, "Engineering the surface structure of MoS₂ to preferentially expose active edge sites for electrocatalysis" (submitted).
3. I.S. Cho, Z. Chen, A.J. Forman, D.R. Kip, P.M. Rao, T.F. Jaramillo, X. Zheng, "Branched TiO₂ Nanorods for Photoelectrochemical Hydrogen Production," *Nano Letters*, Vol. 11, No. 11, pp. 4978-4984, 2011.
4. Zhebo Chen, Dustin Cummins, Benjamin N. Reinecke, Ezra Clark, Mahendra K. Sunkara, and Thomas F. Jaramillo, "Core-shell MoO₃-MoS₂ Nanowires for Hydrogen Evolution: A functional Design for Electrocatalytic Materials" *Nano Letters*, Vol. 11, pp. 4168-4175, 2011.

5. T.F. Jaramillo, A.J. Forman, Z. Chen, I. Thomann, B.A. Pinaud, I.S. Cho, D.R. Kim, P.M. Rao, B.M. Clemens, X. Zheng, M. Brongersma, "Bridging the gap between optical absorption and charge transport in metal oxide materials for the synthesis of solar fuels," Spring Meeting of the Materials Research Society (MRS), San Francisco, CA, April 13, 2012.

6. T.F. Jaramillo, "Tailoring Electrocatalyst Materials at the Nano-Scale: Controlling Activity, Selectivity, and Stability for Energy Conversion Reactions,"

- University of California, Santa Barbara, Dept. of Chemistry and Chemical Engineering, Santa Barbara, CA, March 7, 2012.
- Massachusetts Institute of Technology (MIT), Energy Initiative Seminar Series, Cambridge, MA, December 2011.
- California Institute of Technology, Chemical Engineering Department Seminar, Pasadena, CA, October 2011.
- University of New Mexico, Chemical and Nuclear Engineering Department Seminar, Albuquerque, NM, October 2011.
- Catalysis for Sustainable Energy (CASE) Seminar Series, Technical University of Denmark, Lyngby, DK, August 2011.

7. T.F. Jaramillo, A.J. Forman, Z. Chen, B.A. Pinaud, J.D. Benck, S.-H. Baeck, Y. Gorlin, E. Cave, K.P. Kuhl, "Advanced electrode and photo-electrode structures for the synthesis of fuels from sunlight," Fall Meeting of the Materials Research Society (MRS), Boston, MA, November 2011.

8. Zhebo Chen, Dustin Cummins, Benjamin N. Reinecke, Ezra L. Clark, Mahendra K. Sunkara, and Thomas F. Jaramillo, "MoS₂ Nanostructures as Efficient, Stable, and Earth-Abundant Catalysts for Hydrogen Evolution in Acid," 2011 Annual Meeting of the American Institute of Chemical Engineers, Minneapolis, MN, October 19, 2011.

9. Zhebo Chen and Thomas F. Jaramillo, "Quantum Confined MoS₂ Nanoparticles for Band Gap Engineered Photoelectrochemical Water Splitting," 220th meeting of the Electrochemical Society, Boston, MA, October 13, 2011.

10. T.F. Jaramillo, "Semiconductors and catalysts for the production of solar fuels," Haldor Topsøe Catalysis Forum: Catalysis & Future Energy, Munkerupgaard, DK, Aug. 2011.

11. T.F. Jaramillo, "Tailoring electrocatalyst materials at the nano-scale: Controlling activity and selectivity for energy conversion reactions," Lawrence Livermore National Laboratory, Livermore, CA., July 2011.

12. Zhebo Chen, Jakob Kibsgaard, and Thomas F. Jaramillo, "Nanostructured MoS₂ for Solar Hydrogen Production," 2011 Materials Research Society Spring Meeting, San Francisco, CA, April 29, 2011.

References

1. A. Midilli and I. Dincer: Key strategies of hydrogen energy systems for sustainability. *Int. J. Hydrog. Energy* **32**, (2007).
2. M. Balat: Potential importance of hydrogen as a future solution to environmental and transportation problems. *Int. J. Hydrog. Energy* **33**, (2008).
3. M.G. Walter, E.L. Warren, J.R. McKone, S.W. Boettcher, Q. Mi, E.A. Santori and N.S. Lewis: Solar Water Splitting Cells. *Chem. Rev.* **110**, (2010).

4. B.D. James, G.N. Baum, J. Perez and K.N. Baum: *Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production* (2009).

5. F. Le Formal, M. Grätzel and K. Sivula: Controlling Photoactivity in Ultrathin Hematite Films for Solar Water-Splitting. *Advanced Functional Materials* **20**, (2010).

6. A. Yella, H.-W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W.-G. Diau, C.-Y. Yeh, S.M. Zakeeruddin and M. Graetzel: Porphyrin-Sensitized Solar Cells with Cobalt (II/III)-Based Redox Electrolyte Exceed 12 Percent Efficiency. *Science* **334**, (2011).

7. Our applied research on the photoelectrochemistry of MoS₂ is funded through this program; our more fundamental research on MoS₂ is currently supported by Center on Nanostructuring for Efficient Energy Conversion (CNEEC) at Stanford University, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001060.

8. H. Tributsch and J.C. Bennett: Electrochemistry and photochemistry of MoS₂ layer crystals. *J. Electroanal. Chem.* **81**, (1977).

9. J.P. Wilcoxon and G.A. Samara: Strong quantum-size effects in layered semiconductor - MoS₂ nanoclusters. *Phys. Rev. B* **51**, (1995).

10. J.P. Wilcoxon, P.P. Newcomer and G.A. Samara: Synthesis and optical properties of MoS₂ and isomorphous nanoclusters in the quantum confinement regime. *J. Appl. Phys.* **81**, (1997).

11. T.F. Jaramillo, K.P. Jørgensen, J. Bonde, J.H. Nielsen, S. Horch and I. Chorkendorff: Identification of active edge sites for electrochemical H₂ evolution from MoS₂ nanocatalysts. *Science* **317**, (2007).

12. Z. Chen, D. Cummins, B.N. Reinecke, E. Clark, M.K. Sunkara and T.F. Jaramillo: Core-shell MoO₃-MoS₂ Nanowires for Hydrogen Evolution: A Functional Design for Electrocatalytic Materials. *Nano Lett.* (2011).

13. G. Wang, Y. Ling, D.A. Wheeler, K.E.N. George, K. Horsley, C. Heske, J.Z. Zhang and Y. Li: Facile Synthesis of Highly Photoactive α -Fe₂O₃-Based Films for Water Oxidation. *Nano Lett.* **11**, (2011).

14. Y. Liang, T. Tsubota, L. P. A. Mooij and R. van de Krol: Highly Improved Quantum Efficiencies for Thin Film BiVO₄ Photoanodes. *The Journal of Physical Chemistry C* **115**, (2011).

15. T. Hisatomi, H. Dotan, M. Stefik, K. Sivula, A. Rothschild, M. Grätzel and N. Mathews: Enhancement in the Performance of Ultrathin Hematite Photoanode for Water Splitting by an Oxide Underlayer. *Adv. Mater.* **24**, (2012).

16. Y. Liang, C. S. Enache and R. van de Krol: Photoelectrochemical Characterization of Sprayed α -Fe₂O₃ Thin Films: Influence of Si Doping and SnO₂ Interfacial Layer. *International Journal of Photoenergy* **2008**, (2008).

17. W. Kautek and H. Gerischer: Photoelectrochemical Reactions and Formation of Inversion Layers at n-Type MoS₂-, MoSe₂-, and WSe₂-Electrodes in Aprotic solvents. *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* **84**, (1980).