

II.H.4 Nanostructured MoS₂ and WS₂ for the Solar Production of Hydrogen

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Objectives

Develop novel nanostructured dichalcogenide materials for photoelectrochemical (PEC) production of hydrogen from water:

- Synthesize nanometer-scaled MoS₂ and WS₂ as (1) nanoparticles, (2) nanowires, and (3) a 3-dimensional bi-continuous network.
- Explore and optimize bandgap and band edge position as a function of size and architecture for water splitting.
- Study photogenerated charge separation and transport in nanostructured materials.
- Investigate catalytic ability for water splitting as a function of surface structure.
- Incorporate optimized nanostructures into a PEC device and determine efficiency and durability.

Technical Barriers

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

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AB) Bulk Materials Synthesis
- (AC) Device Configuration Designs

Technical Targets

The focus of this project is the development of semiconductor materials with strong solar absorption characteristics that efficiently store energy from the sun by splitting water into hydrogen and oxygen. If successful, this project will address the following DOE technical targets as outlined in the HFCIT Multi-Year RD&D Plan:

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

Characteristics	Units	2013 Target	2009 Status
Usable semiconductor bandgap	eV	2.3	1.9
Chemical conversion process efficiency (EC)	%	10	TBD
Plant solar-to-hydrogen efficiency (STH)	%	8	TBD
Plant durability	hr	1,000	TBD

TBD - to be determined

Accomplishments

- Optimized low temperature (150°C) sulfidization of MoO₃.
- Synthesized air-stable nanoscaled MoS₂ nanoparticles in various sizes.
- Achieved quantum confinement of MoS₂ nanoparticles with indirect bandgaps between 1.2–1.9 eV and direct bandgaps between 2.0–2.8 eV.
- Produced p-type MoS₂ to improve PEC stability.
- Produced highly stable RuO₂ counter electrodes for facile oxygen evolution with ~10% performance decrease over 100 cycles at 2 V vs. Ag/AgCl in a 0.1 M H₂SO₄ solution.
- Developed nanoscaled alumina templates for nanowire synthesis with mean pore diameter of 13 nm.



Introduction

PEC water splitting for hydrogen production was first demonstrated by Fujishima and Honda in 1972 using titanium dioxide (TiO₂) [1], a material limited to a maximum solar-to-hydrogen efficiency of 1% due to its large bandgap of 3.0 eV. Since the maximum solar-to-hydrogen efficiency of a material is ultimately determined by its ability to absorb light, research efforts

have primarily focused on improving solar absorption characteristics, including the use of semiconductor doping/alloying [2-6], tandem absorbers [7,8], and dye sensitization [9,10]. However, even the best absorbers to date are compounded by problems following the initial absorption such as poor charge transport and/or poor stability [11,12]. Thus, no material system exists that can yet be considered as a wide-scale deployable solution. The world record device with 12.4% solar-to-hydrogen efficiency was developed by Khaselev and Turner over a decade ago in 1998 [13], but exhibited significant stability problems and extremely high cost [14,15]. New approaches are necessary to accelerate the development of highly efficient, durable, and low cost materials for PEC water splitting.

Approach

The project discussed here aims to improve upon previous material deficiencies through the nanostructuring of low cost semiconductor materials – in particular, molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2). Both materials exhibit a bandgap of ~ 1.2 eV [16-19], which enables the absorption of a significant portion of the solar spectrum. However, this value is too small to provide the photovoltage necessary to drive the water splitting reaction ($\Delta G = 1.23$ eV). The minimum bandgap must encompass that thermodynamic water splitting potential of 1.23 eV in addition to the activation energies required to drive the individual hydrogen and oxygen evolution half reactions. Thus, the optimal bandgap value will likely lie in the range of ~ 1.8 - 2.0 eV [20]. Nanostructuring materials can result in an effect known as quantum confinement [19,21,22], which enables widening of the bandgap to a larger, more useable value for water splitting in the case of MoS_2 and WS_2 . In addition, edge sites at the surface of MoS_2 , which are more prominent when nanostructured, have been documented as centers of high catalytic activity for the hydrogen evolution reaction [23]. This translates into a smaller required bandgap and higher theoretical efficiency.

Lastly, controlling the type of conductivity has important consequences on the material's photoelectrochemical properties. By focusing on synthesizing p-type (rather than n-type) MoS_2 and WS_2 , the possibility of photo-oxidation is minimized and stability can be improved since the material operates as a photocathode and oxidizing holes flow away from the semiconductor-electrolyte interface [24-28].

Results

Our efforts within the first six months of the project have focused on the development of MoS_2 , since it represents a material with a rich history of catalysis and photoactivity [22,29-31]. We have optimized the sulfidization of molybdenum in our laboratory using temperatures as low as 150°C , confirmed using ultraviolet-visible transmission (UV-Vis) spectroscopy and X-ray photoelectron spectroscopy (XPS). Electrochemical testing of MoS_2 also revealed high activity for the hydrogen evolution reaction, in agreement with previous reports [23].

Synthesis of supported MoS_2 nanoparticles in various sizes was accomplished using a reverse micelle encapsulation method [32-34]. The low temperature sulfidization process minimized nanoparticle sintering. The nanoparticles were imaged using atomic force microscopy (AFM) as shown in Figure 1, although exact size measurements are limited due to convolution of the AFM tip. Work is currently underway to precisely determination the size distributions of such nanoparticles using transmission electron microscopy. Despite their small size, these nanoparticles are fully resistant to oxidation from exposure to air, as confirmed using XPS.

UV-Vis spectroscopy of the MoS_2 nanoparticles revealed a blue-shift in their absorption onset. Furthermore, the degree of blue-shifting increased with smaller nanoparticle size. This behavior is expected and is characteristic of the quantum confinement phenomenon. Tauc plots of the direct and indirect bandgaps are shown in Figure 2.

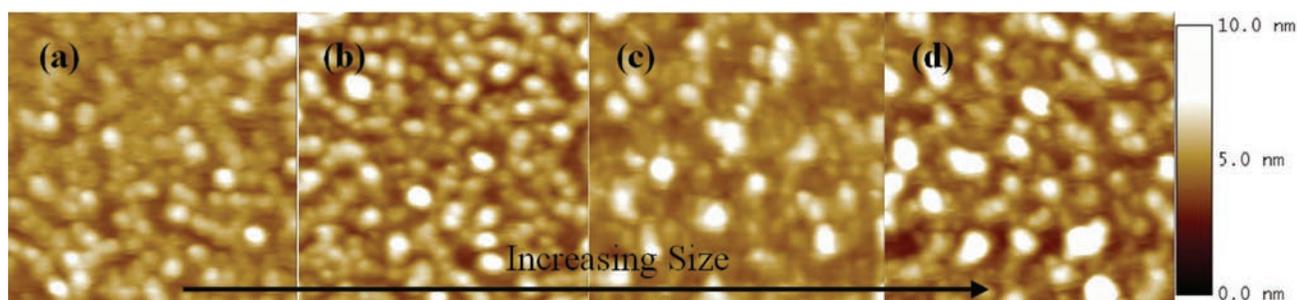


FIGURE 1. Atomic force microscopy of MoS_2 nanoparticles in increasing size from (a)→(d), produced using an inverse micelle encapsulation method, using a poly(styrene-*b*-2-vinylpyridine) polymer and a MoCl_3 precursor.

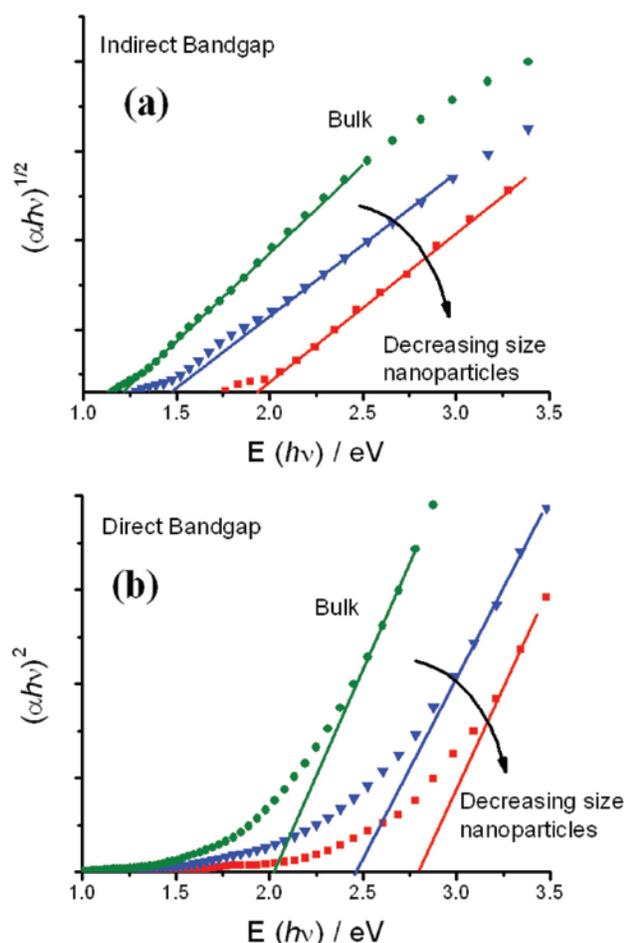


FIGURE 2. MoS₂ absorption shown in (a) allowed indirect and (b) allowed direct Tauc plots. Bulk MoS₂ films show an indirect bandgap of ~1.2 eV and a direct bandgap of ~2.0 eV (green circles). MoS₂ nanoparticles from Figure 1(d) show an indirect bandgap of ~1.5 eV and a direct bandgap of ~2.5 eV (blue triangles), while nanoparticles from Figure 1(c) show an indirect bandgap of ~1.9 eV and a direct bandgap of ~2.8 eV (red squares).

While MoS₂ crystals in nature can be found to have either n-type or p-type conductivity, we have synthesized consistently p-type MoS₂ by the addition of Nb. Conductivity type was assessed using photocurrent measurements under an applied bias in an electrochemical cell, shown in Figure 3. The observed photocurrent was negative in sign, and increased towards negative potentials, characteristic of p-type behavior.

As part of the effort to develop p-type MoS₂, it is necessary to produce counter-electrodes that have low overpotentials for the oxygen evolution reaction. RuO₂ is a material that exhibits high conductivity, chemical and thermal stability, and catalytic activity [35-37]. Using an electrochemical deposition technique followed by a heat treatment, we produced RuO₂ counter-electrodes that exhibit a 400 mV earlier onset for oxygen

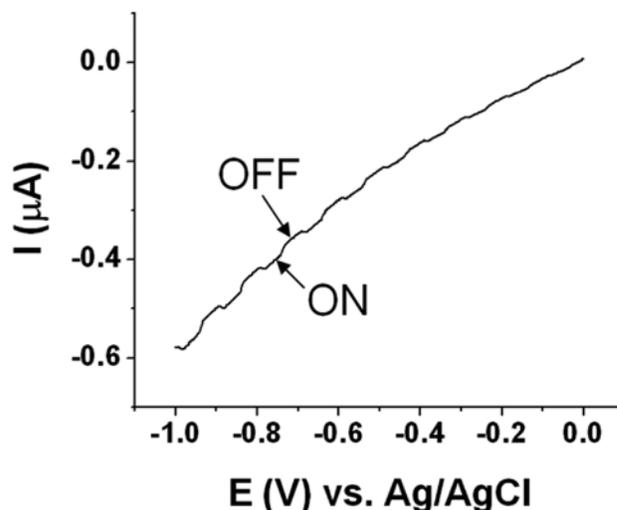


FIGURE 3. PEC response for Nb-doped MoS₂ thin film under chopped illumination from a ~2.5 Sun xenon lamp.

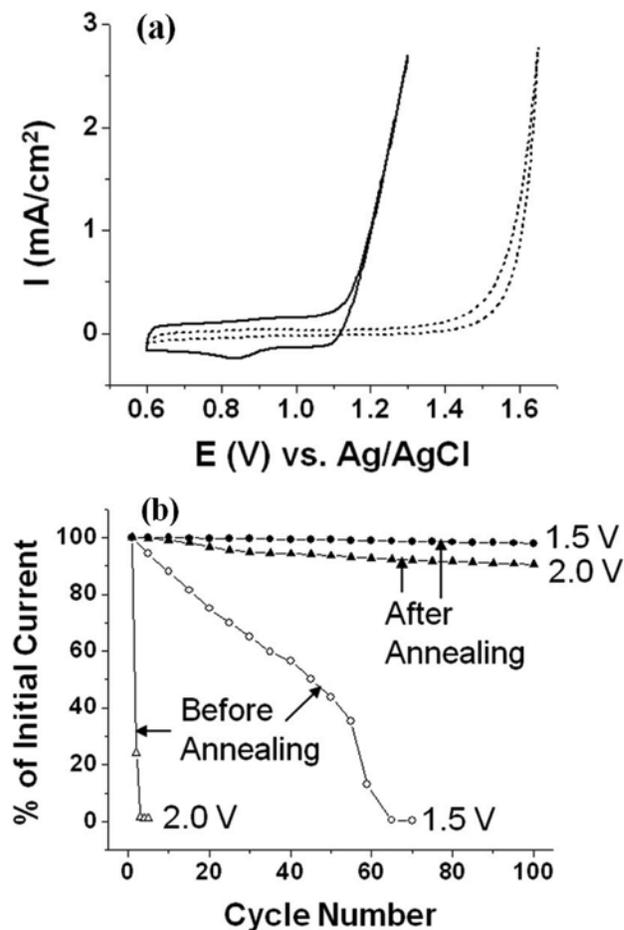


FIGURE 4. (a) Cyclic voltammogram of oxygen evolution reaction for a RuO₂ electrode (solid line) compared to a Pt electrode (dotted line). (b) Stability of RuO₂ electrodes unannealed and annealed at 400°C for 1 hr during 100 cyclic voltammograms between 0.5 V up to 1.5 V or 2.0 V vs. Ag/AgCl.

evolution compared to Pt as shown in Figure 4(a), and demonstrates strong stability over 100 cycles of oxygen evolution, even when subjected to a +2 V bias vs. the Ag/AgCl reference electrode in a highly acidic 0.1 M H₂SO₄ solution as shown in Figure 4(b).

Our efforts to synthesize nanowires have been focused on the development of anodic alumina templates [38-42]. We have achieved the synthesis of templates with 13 nm pores, as imaged by scanning electron microscopy, and are continuing to optimize the synthesis towards even smaller pore sizes. We have also synthesized samples of the bi-continuous network templates using a silica template [43-45] and are continuing with further development. Following the development of these templates, we will synthesize molybdenum and tungsten nanostructures using an electrodeposition process that we optimized in our laboratory.

Conclusions and Future Directions

We have made significant process in developing nanostructured MoS₂ for PEC water splitting:

- Optimized low temperature sulfidization of molybdenum.
- Synthesized air stable nanoparticulate MoS₂ in various sizes.
- Confirmed size-dependent quantum confinement of nanoparticulate MoS₂, widening the bandgap to values of ~2 eV.
- Synthesized p-type MoS₂.
- Developed anodic alumina templates with nanopores.

Our work on this project continues with the assessment of the valence and conduction band edges of our nanostructured MoS₂, using spectroscopic techniques such as ultraviolet photoelectron spectroscopy coupled to inverse photoemission spectroscopy. We plan to assess the flat band potential using electrochemical techniques such as illuminated open circuit potential, Mott-Schottky, and photocurrent onset. This will enable determination of the surface electronic structure of our semiconductor materials and provide insight into their ability to actively split water using sunlight without an applied bias. We will also pursue PEC measurements on the supported nanostructures, measuring photocurrent with and without an applied bias and sampling the gas headspace by gas chromatography.

Work is underway to further develop the anodic alumina templates, as well as the nanoporous bi-continuous networks. The templates will enable the development of MoS₂ and WS₂ nanowires and bi-continuous networks using an electrodeposition process.

Although initial efforts have focused on MoS₂, work is already underway to develop WS₂ nanostructures. WS₂ is an important avenue of study due to its structural and electronic similarities to MoS₂. By studying both MoS₂ and WS₂ in multiple nanostructured forms, we address the challenge of developing a deployable PEC water splitting device using state-of-the-art techniques, with significant potential for producing knowledge that spans a large number of scientific fields, including photovoltaics and heterogeneous catalysis.

FY 2009 Presentations

1. 2009 US DOE Hydrogen Program and Vehicle Technologies Annual Merit Review & Peer Evaluation Meeting, Arlington, VA. "Nanostructured MoS₂ and WS₂ for the solar production of hydrogen" T.F. Jaramillo, May 2009.
2. US DOE Photoelectrochemical Hydrogen Production Quarterly Meeting, San Francisco, CA. "Nanostructured MoS₂ and WS₂ for the solar production of hydrogen" T.F. Jaramillo, April 2009.
3. University of California, Berkeley, Nanosciences and Nanoengineering Institute (BNNI), Nanoscale Science and Engineering (NSE) Seminar, Berkeley, CA. "Designing nano-scaled, non-precious metal catalysts for hydrogen evolution" T.F. Jaramillo, March 2009.
4. Chevron Corporation, Richmond, CA, May 2009. "Solar Fuels by Photoelectrochemistry (PEC)" T.F. Jaramillo, March 2009.
5. US DOE Hydrogen Production Technical Team Review: Photoelectrochemical Hydrogen Production, San Francisco, CA. "Nanostructured MoS₂ and WS₂ for the solar production of hydrogen" T.F. Jaramillo, January 2009.

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