

II.G.2 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 three-dimensional double-gyroid network.
- Explore and optimize bandgap and bandedge position as a function of size and architecture for water splitting.
- Study photo-generated 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 Fuel Cell Technologies 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 FCT 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	1.8
Chemical conversion process efficiency	%	10	TBD
Plant solar-to-hydrogen efficiency	%	8	TBD
Plant durability	hr	1,000	TBD

TBD - to be determined

Accomplishments

- Achieved low temperature (150°C) sulfidization of molybdenum/MoO₃ to produce MoS₂.
- Synthesized tungsten nanoparticles and air-stable nanoscaled MoS₂ nanoparticles in various sizes ranging from 5-25 nm.
- Achieved quantum confinement of MoS₂ nanoparticles with indirect bandgaps up to 1.8 eV.
- Electrochemical testing of the MoS₂ nanoparticles supported on fluorine-doped tin oxide revealed activity for the hydrogen evolution reaction with Tafel slopes of ~200 mV/decade.
- Developed a macroporous indium tin oxide support to allow vertical integration of nanoparticles for increased absorption.
- Synthesized quantum confined nanowebs of MoS₂ with bandgaps up to 1.6 eV.
- Synthesized Nb doped MoS₂ films that produced cathodic photocurrent.
- Produced highly stable nanoscaled double-gyroid RuO₂ counter electrodes for efficient oxygen evolution with over 19 times the exchange current density of a comparable thin film.
- Developed nanoscaled alumina templates for nanowire synthesis with mean pore diameter of 13 nm.

- Investigated sulfidization of MoO₃ nanowires up to 700°C without significant sintering in collaboration with Prof. Mahendra Sunkara at the University of Louisville, Kentucky.



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, the best absorbers to date are often hindered by other issues such as poor charge transport [11], slow kinetics for the hydrogen evolution reaction or oxygen evolution reaction [12], and/or poor stability [13,14]. Thus, no material system exists that can yet be considered as a wide-scale deployable solution. The world record PEC device with 12.4% solar-to-hydrogen efficiency was developed by Khaselev and Turner in 1998 [14], but it exhibited significant material instability and extremely high cost [15,16]. 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 (MoS₂) and tungsten disulfide (WS₂). Both materials exhibit a bandgap of ~1.2 eV [17-20], which enables absorption of a significant portion of the solar spectrum. However, this value is too small to provide the photovoltage necessary to split water, which requires a minimum thermodynamic potential of 1.23 eV in addition to the overpotentials required to drive the kinetics of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The minimum bandgap value will likely lie in the range of ~1.8-2.0 eV [21]. Nanostructuring materials can result in an effect known as quantum confinement [20,22,23], which enables widening of the bandgap to a larger, more useable value for water splitting in the case of MoS₂ and WS₂. In addition, edge sites at the surface of MoS₂, which are more prominent when nanostructured, have been documented as centers of high catalytic activity for

the HER [24]. This translates into a smaller required bandgap and higher theoretical efficiency.

Furthermore, controlling the material conductivity has important consequences on its PEC properties. By focusing on the development of MoS₂ and WS₂ as photocathodes (rather than photoanodes), the possibility of photo-oxidizing the sulfide is minimized and stability can be improved since photogenerated electrons drive the HER at the semiconductor-electrolyte interface while oxidizing holes flow to the counterelectrode to drive the OER [25-29]. One approach to develop a material that exhibits photocathodic behavior with minimum input bias is to increase its work function by the addition of dopants. In the case of MoS₂, doping with niobium can produce a p-type semiconductor [30] that is more likely to behave as a photocathode. Consequently, a photocathode that drives the HER requires a counterelectrode that efficiently drives the OER. Ruthenium dioxide (RuO₂) is a material known to exhibit high conductivity, chemical and thermal stability [31-33] and catalytic activity for the OER [34-36]. By nanostructuring RuO₂ in a double-gyroid geometry [37] it is possible to improve its catalytic ability even further [38].

Results

Our efforts within the project have focused on the development of MoS₂, since it represents a material with a rich history of catalysis and photoactivity [23,39-41]. We achieved 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).

Synthesis of supported MoS₂ nanoparticles in various sizes was accomplished using a reverse micelle encapsulation method [42-44]. The low temperature sulfidization process minimized nanoparticle sintering. The nanoparticles were imaged using atomic force microscopy as shown in Figure 1. Scanning electron microscopy (SEM) revealed size distributions ranging from 5-25 nm. Despite their small size, these nanoparticles are resistant to oxidation from exposure to air, as confirmed using XPS shown in Figure 2. The same reverse micelle encapsulation method was used to synthesize tungsten nanoparticles, which are currently under further development.

UV-Vis spectroscopy of the MoS₂ 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 indirect bandgaps are shown in Figure 3.

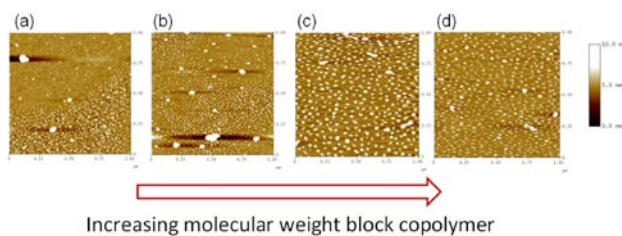


FIGURE 1. Atomic force microscopy of MoS_2 nanoparticles made using a $(\text{Mo}(\text{OCOCH}_3)_2)_2$ precursor. From (a) \rightarrow (d), the molecular weight increases for the poly(styrene-*b*-2-vinylpyridine) polymer used to form the micelles.

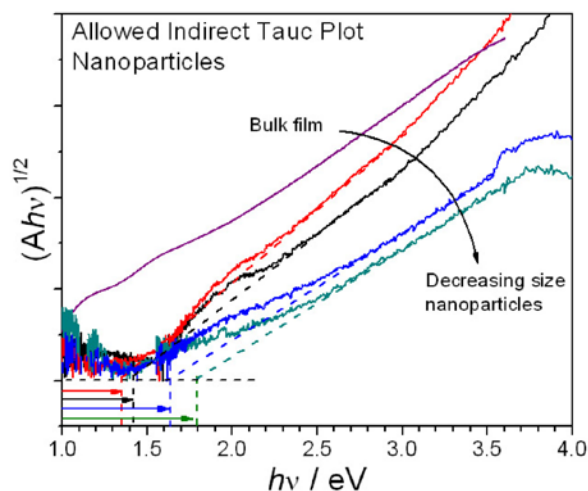


FIGURE 2. Indirect bandgap Tauc plot of supported MoS_2 nanoparticles. The absorption onset increases with decreasing nanoparticle size, up to 1.8 eV.

During attempts to synthesize MoS_2 nanoparticles, we found that using a highly hydrophilic precursor (MoCl_3 instead of $\text{Mo}(\text{OCOCH}_3)_2$) could disrupt the micelle network and form an interconnected web morphology. These nanoweb still exhibited a quantum confined blueshift in the absorption onset up to 1.6 eV, slightly less than the blueshift seen with nanoparticles. One reason for this may be because of a greater degree of electron delocalization in the interconnected structures.

In order to obtain measurable photocurrent from the MoS_2 nanoparticles, they must first be supported in a structure that allows them to absorb a significant number of photons. This is difficult to achieve with a sub-monolayer of nanoparticles supported on a planar surface due to the short absorption path length. One approach is to develop a macroporous transparent conducting oxide which enables the vertical integration of nanoparticles to increase absorption path length without sacrificing absorption or limiting the diffusion of reactants and products to the active sites. Using this approach, we synthesized a macroporous indium tin

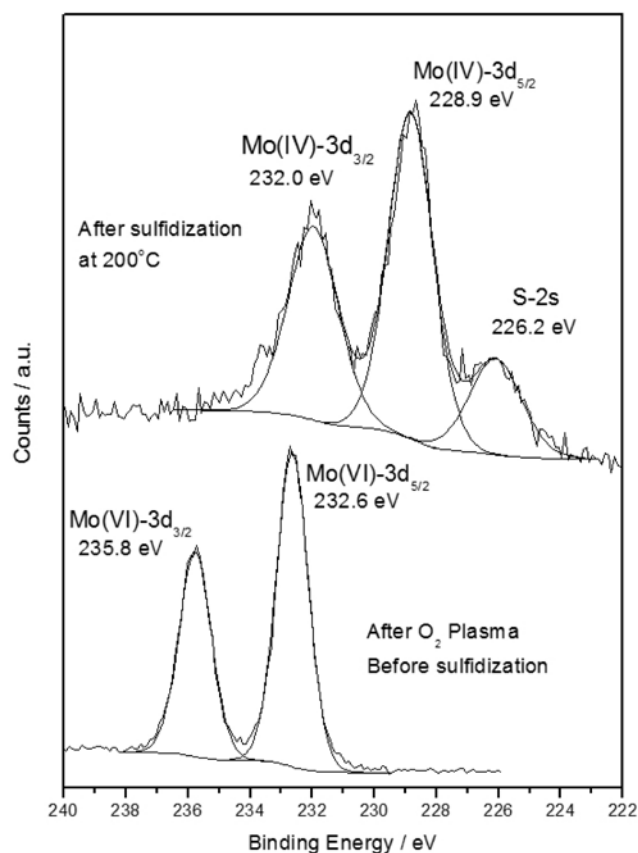


FIGURE 3. X-ray photoelectron spectroscopy of Mo nanoparticles. After sulfidization at 200°C and exposure to air, an S 2s peak appears and the Mo $3d_{5/2}$ peak shifts from 232.6 eV to 228.9 eV, characteristic of a chemical state change from Mo(VI) in MoO_3 to Mo(IV) in MoS_2 .

oxide support structure, and are currently optimizing its conductivity.

While MoS_2 crystals in nature can be found to intrinsically have either n-type or p-type conductivity, leading them towards photoanodic or photocathodic behavior, we synthesized a p-type photocathodic MoS_2 by doping with Nb. Activity was assessed using photocurrent measurements under a negative applied bias in a PEC cell. The observed photocurrent was cathodic and increased with greater negative applied bias.

As part of the effort to develop photocathodes of sulfides, it is necessary to produce counter-electrodes that efficiently drive the oxygen evolution reaction. Using an electrochemical deposition technique followed by a heat treatment, we produced RuO_2 films that exhibit a 320 mV earlier onset for oxygen evolution compared to Pt. The films demonstrated 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 H_2SO_4 solution. To develop even more active RuO_2 , we used a silica template made with a poly(ethylene oxide)-poly(propylene oxide)-alkane tri-

block copolymer surfactant [37,45,46] to form a double-gyroid RuO_2 structure. In comparison to the thin film of RuO_2 , which produced an exchange current density of $3.67 \times 10^{-9} \text{ A/cm}^2$ for the OER, the double-gyroid RuO_2 structure produced an exchange current density of $7.11 \times 10^{-8} \text{ A/cm}^2$, over 19 times greater than the thin film.

To synthesize nanowires, we have focused on the development of anodic alumina templates [47-51]. Using this technique, we have synthesized templates with 13 nm pores, as imaged by SEM, and are continuing to optimize the synthesis towards even smaller pore sizes. We are also working to synthesize double-gyroid MoS_2 structures using the same silica template developed for the double-gyroid RuO_2 . We plan to fill the templates and develop the inverse Mo and W structures using an electrodeposition technique optimized in our laboratory.

We are also working in close collaboration with Mahendra Sunkara, Professor of Chemical Engineering at the University of Louisville, Kentucky. Using a hot-wire chemical vapor deposition technique, Sunkara has successfully formed vertical nanowires of MoO_3 . We convert the nanowires to MoS_2 using our sulfidization furnace and study their physical and PEC properties as a function of sulfidization temperature. Once sulfidized, the nanowires change in color from a transparent blue to an extremely opaque black with imperceptible amounts of reflection and transmission, indicating very high levels of photon absorption, as confirmed by UV-Vis. SEM reveals that our sulfidization process results in minimal sintering of the nanowires, even up to 700°C . Transmission electron microscopy shows the formation of polycrystalline layers of MoS_2 in Figure 4, which is further confirmed by X-ray diffraction. We are continuing to work on the development of substrates that can withstand the effects of higher sulfidization

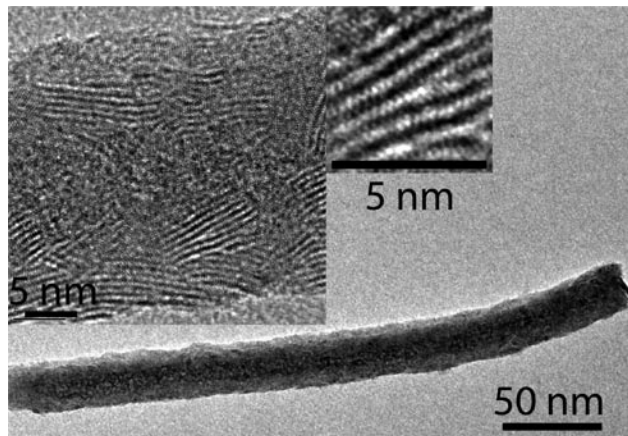


FIGURE 4. Transmission electron microscopy of MoS_2 nanowires made using a hot-wire CVD method, followed by sulfidization in at 500°C . The layered structure possesses intralayer spacings of approximately $6\text{-}7 \text{ \AA}$ and interlayer spacings of approximately 3 \AA , characteristic of MoS_2 [39].

temperatures, yet retain the necessary conductivity and electrochemical inertness for PEC testing.

Conclusions and Future Directions

We have made significant process in developing nanostructured MoS_2 for PEC water splitting, with the most significant results being summarized as follows:

- Synthesized air stable MoS_2 nanoparticles in various sizes that exhibit a size-dependent quantum confinement up to 1.8 eV.
- Developed a highly porous nano-scale double-gyroid structure of RuO_2 with very high activity for the OER.
- Synthesized air stable MoS_2 nanowires in collaboration with the University of Louisville that show extremely high photon absorption.

Our work on this project continues with the development of substrates that will enable PEC testing of nanostructured MoS_2 . In order to achieve this goal, we will:

- Optimize the conductivity and transmissivity of the indium tin oxide macroporous network upon which we will support quantum confined MoS_2 nanoparticles. This will allow vertical stacking of the nanoparticles for improved photon absorption, while retaining the required conductivity for the photogenerated electrons and holes.
- Investigate the use of molybdenum foil and other metals as substrates for MoS_2 nanowires. Unlike the nanoparticles, the nanowires are already excellent absorbers of light, and simply need a substrate that can withstand the sulfidization process and retain good conductivity.

Upon achieving photoresponse from our nanostructures, we will proceed with a full battery of PEC studies, including the determination of the flat-band potential using:

- Illuminated open circuit potential
- Mott-Schottky
- Photocurrent onset

The flat-band potential 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 other PEC measurements on the supported nanostructures, including:

- Monochromatic photoresponse to obtain the incident photon-to-current conversion efficiency.
- Photoresponse under an applied bias to obtain the applied bias photon-to-current conversion efficiency.

- Photoresponse under zero applied bias to obtain the solar-to-hydrogen conversion efficiency.
- Assessing the hydrogen and oxygen products in the headspace to obtain the Faradaic efficiency for water-splitting by gas chromatography.

These studies will help to elucidate fundamental charge transport and interfacial properties of our materials and enable an improved degree of scientific understanding necessary to meet the goals set forth in Table 1. These techniques are explained in further detail in one of our recently published articles that outline proper methods, definitions, and protocols for developing materials for PEC hydrogen production [52].

Lastly, work is underway to further develop the anodic alumina templates, as well as the nanoporous double-gyroid networks. The templates will enable the development of MoS₂ and WS₂ nanowires and double-gyroid 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 2010 Presentations

1. University of California at Berkeley (*invited*). “Nano-scaled materials for the synthesis of fuels from sunlight.” T.F. Jaramillo, December 2009.
2. 2009 American Institute of Chemical Engineers Annual Meeting, Nashville, TN. “Nanostructured MoS₂ for the Photoelectrochemical (PEC) Production of Hydrogen.” T.F. Jaramillo, November 2009.
3. University of Texas at Austin (*invited*). “Nano-scaled materials for the synthesis of fuels from sunlight.” T.F. Jaramillo, October 2009.
4. 2009 Global Climate Energy Project Research Symposium, Stanford, CA. “Nanostructured MoS₂ and WS₂ for the Solar Production of Hydrogen.” T.F. Jaramillo, October 2009.

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