Nanostructured MoS_2 and WS_2 for the solar production of hydrogen

Thomas F. Jaramillo
Dept. of Chemical Engineering
Stanford University
20 May 2009

DOE Hydrogen Review Meeting

Arlington, VA

Project ID # PD_25_Jaramillo

Overview

Timeline

- Start – Dec 2009
- Finish – Dec 2010
- 40% complete

Barriers

- Y. Materials Efficiency
- Z. Materials Durability
- AB. Bulk Materials Synthesis

Budget

- Total project funding
  - DOE - $130k
  - Contractor - $32k
- Funding received in FY08
  - $0k
- Funding for FY09
  - $130k

Targets

Semiconductor	**2006**	**2013**	**2018**
Bandgap	2.8 eV	2.3 eV	2.0 eV
Efficiency	4 %	10 %	12 %
Durability	N/A	1000 hrs	5000 hrs

Collaborations

- NREL
- U. Hawaii
- UNLV
- UC Santa Barbara

Relevance: Objectives

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

Table 3.1.10. Technical Targets: Photoelectrochemical Hydrogen Production [a]					
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

To date, there are no known materials that simultaneously meet these DOE targets.

Relevance: Technology Barriers

Table 1. Materials-related "Technology Barriers" for successful PEC water-splitting: material class challenges and strengths for MoS_2 and WS_2.

Barrier	Challenges	Strengths
Y. Materials Efficiency	- Bandgap is too small at 1.2 eV - Indirect bandgap - C. Band 0.4 eV too low w.r.t. $E^0_{H+/H2}$ - Relatively low charge mobility along the c-axis (0.1 $cm^2/V*sec$)	- Absorbs large fraction of solar photons. - Nanostructuring can improve both bandgap problem and mismatched CB - High charge mobility along the basal plane (100 $cm^2/V*sec$) - Excellent hydrogen evolution catalysis
Z. Materials Durability	- n-type materials are unstable due to photo-oxidation of the sulfide surface.	- p-type materials have demonstrated long-term photo-stability (~ 1000 hrs)
AB. Bulk Materials Synthesis	- Need to do develop low cost and scalable route to synthesize materials.	- Multiple sulfidation routes involving H_2S, elemental sulfur or Na_2S can be used - Mo and W are inexpensive and abundant. - Low temperature processing (< 250 °C)
A.C. Device Configuration Designs	- Bulk MoS_2 or WS_2 would require a tandem/multijunction device configuration to account for band mismatch and small bandgap.	- Nanostructuring can overcome bandgap and band mismatch problems

Approach: Addressing the Challenges

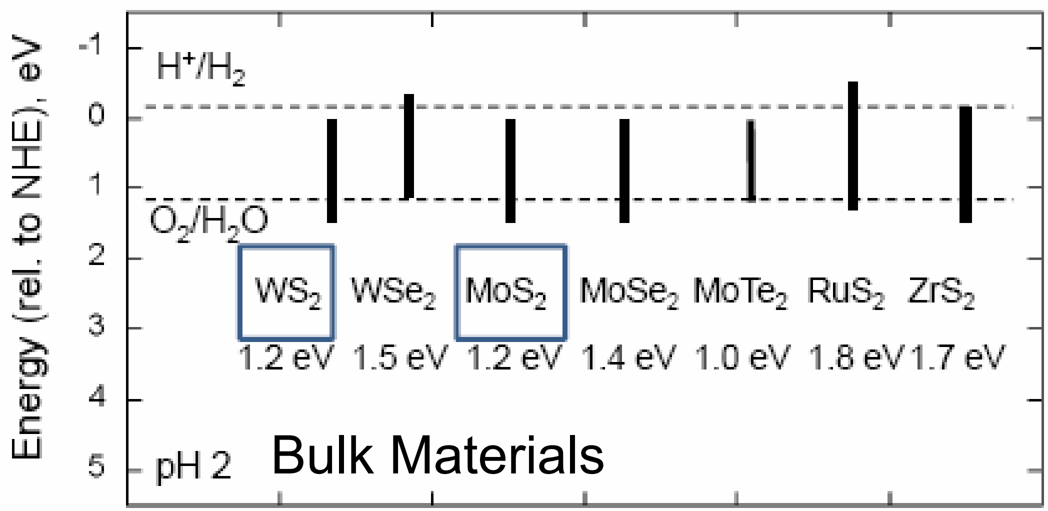
- **Y. Efficiency**
  - Electronic band structure can be widened via nanostructuring to achieve the desired 2.0 eV – 2.3 eV bandgap.

- **Z. Durability**
  - Targeting p-type materials for photocathodic operation, which improves stability.

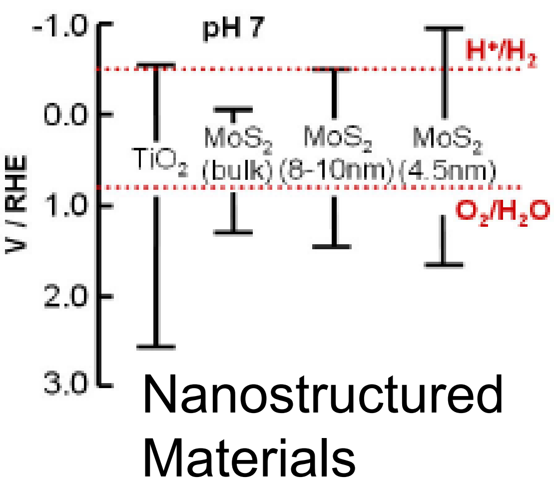
- **AB. Bulk materials synthesis**
  - Developing low-cost wet-chemical based routes to nanostructures.
  - All elements are inexpensive and earth-abundant.

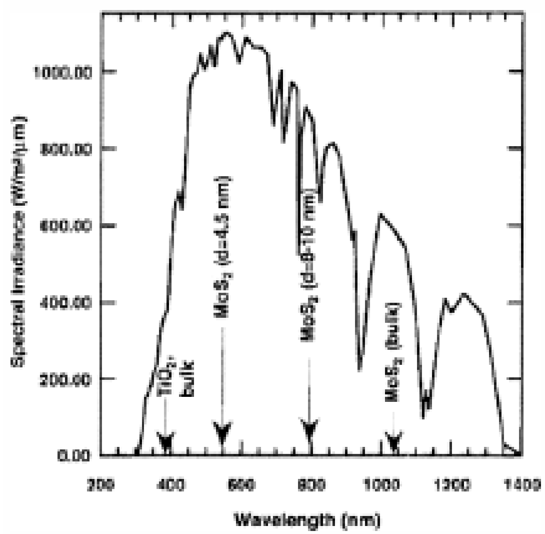
- **AC. Device configuration designs**
  - Tuning the bandstructure (see Y. Efficiency above) appropriately may prevent the need for tandem/multijunction devices.

Approach: Tuning Electronic Band Structure by Quantum Confinement



Jaegermann, W.; Tributsch, H. *Progress in Surface Science* 1988, *29*, 1.



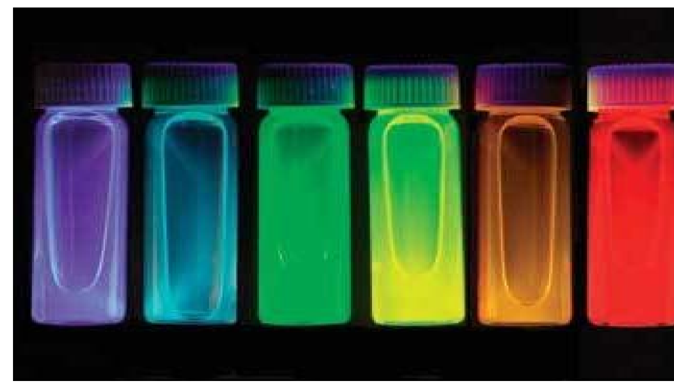


Thurston, T. R.; Wilcoxon, J. P. *Journal of Physical Chemistry B* 1999, *103*, 11.

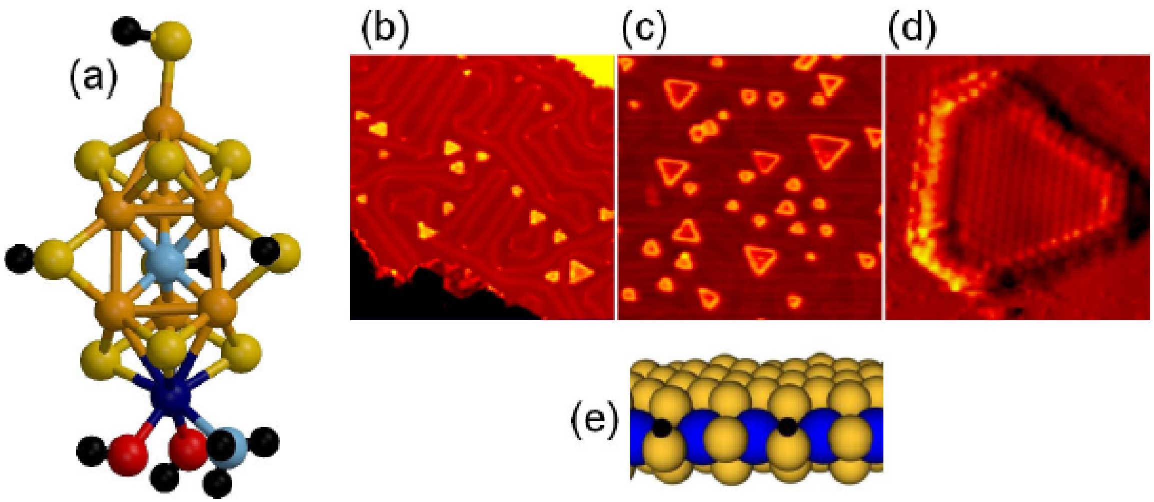
This is a unique approach that diverges from the standard doping/alloying methodology that is commonplace in the field of PEC.

CdSe: a "classic" example of quantum confinement

2 nm CdSe ← 8 nm CdSe



Approach: Enhancing the rate of H_2 production at the surface



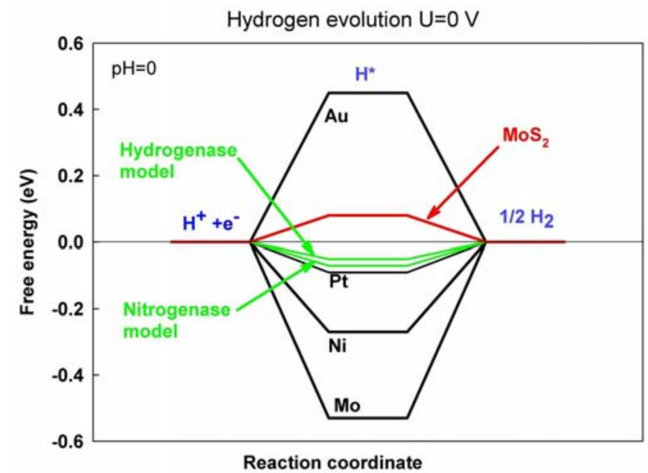


Figure 7. *(a) DFT-calculated active center in the Nitroger evolve H_2. (b, c, d) STM images of nanoparticulate MoS_2, enzyme (b = 470 Å x 470 Å, c = 470 Å x 470 Å, d = 60 Å : geometry for nanoparticulate MoS2's active site [39, 40].*

T.F. Jaramillo, K.P. Jørgensen, J. Bonde, J.H. Nielsen, S. Horch, I. Chorkendorff; *Science* **317** (2007) 100.

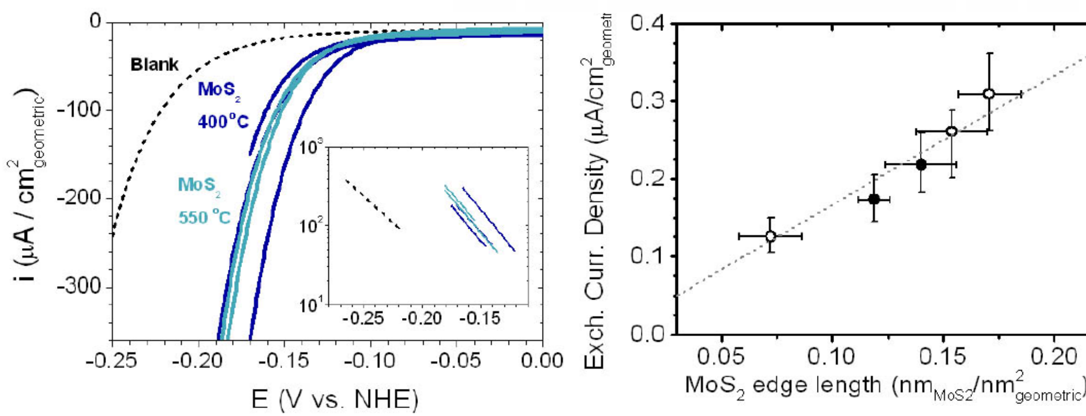
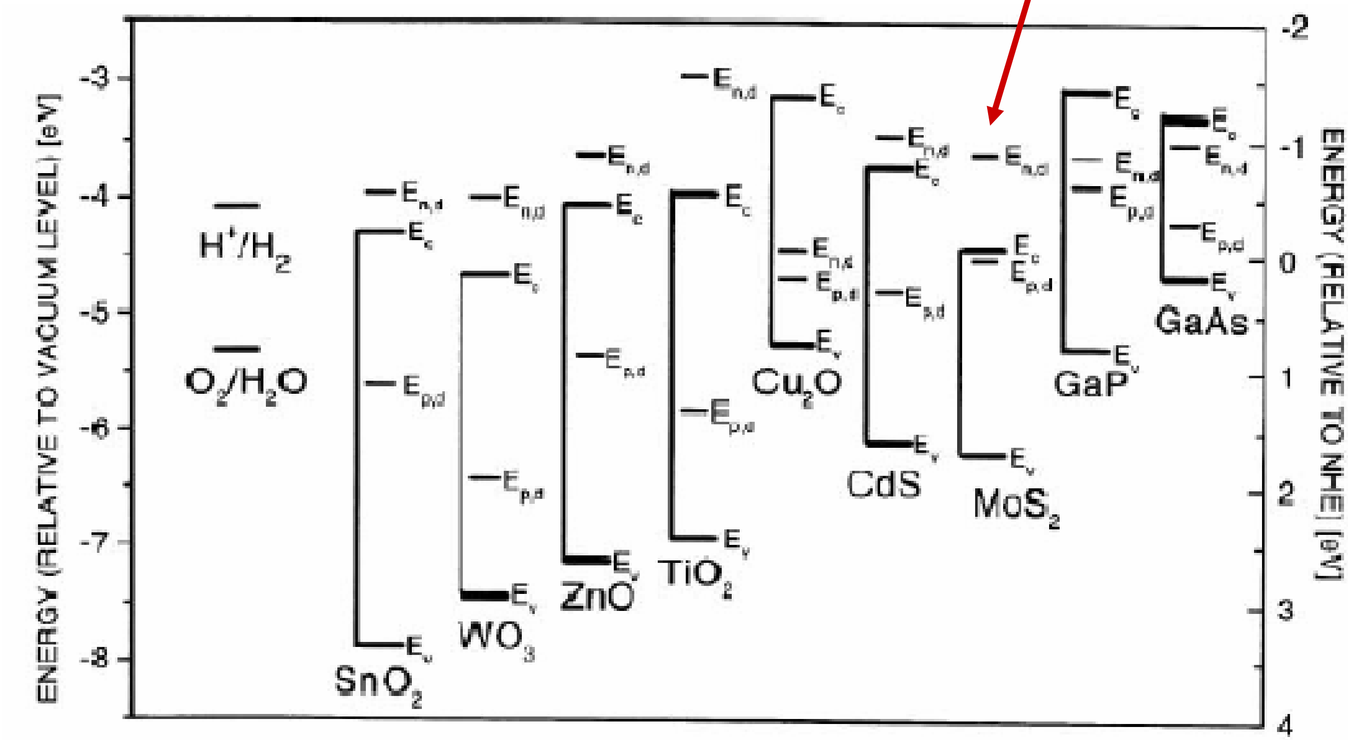


Figure 8. *Electrocatalytic hydrogen evolution on nanoparticulate MoS_2. (left) Polarization curves in sulfuric acid (pH 0.24) exhibiting catalytic activity (inset: Tafel plots). (right) Exchange current density correlates linearly with edge state length of the nanoparticles, not their area [40].*

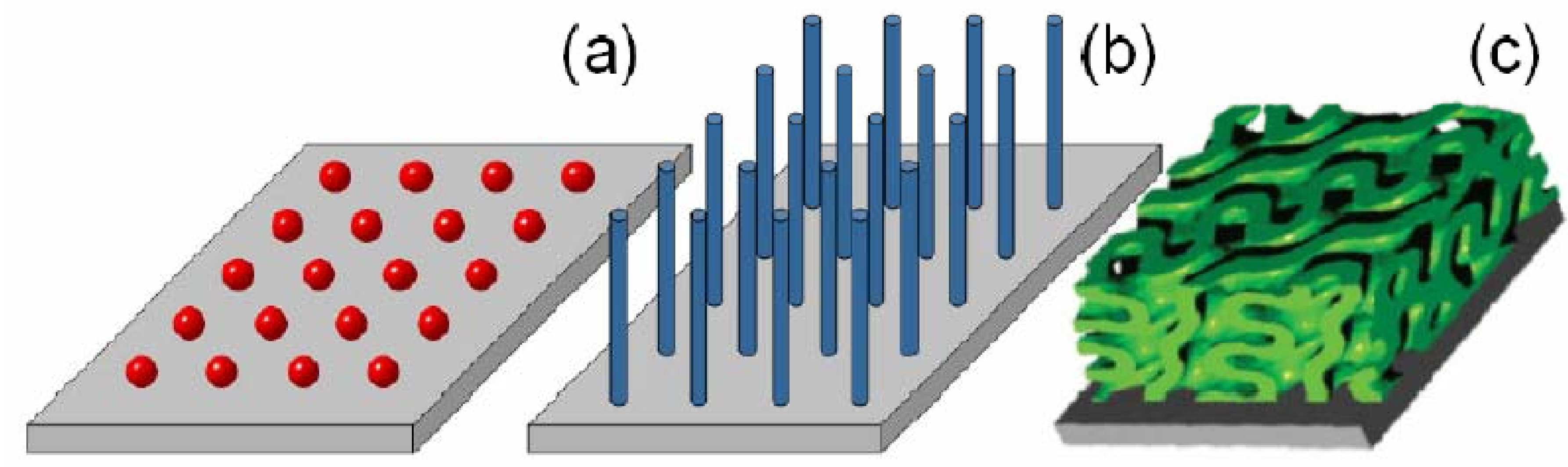
Approach: Improving durability

Cathodic corrosion potential lies above $E^0_{H+/H2}$. Photocathodes (p-type) should be stable.



Bak, T.; Nowotny, J.; Rekas, M.; Sorrell, C. C. *International Journal of Hydrogen Energy* **2002**, *27*, 991.

Approach: Targeted Nanostructures



<u>Nanoparticles</u>
- Improve monodispersity
- Establish size-control
- Correlate bandgap to size
- CB and VB positions

<u>Nanowires</u>
- Develop synthesis route to achieve the appropriate dimensions

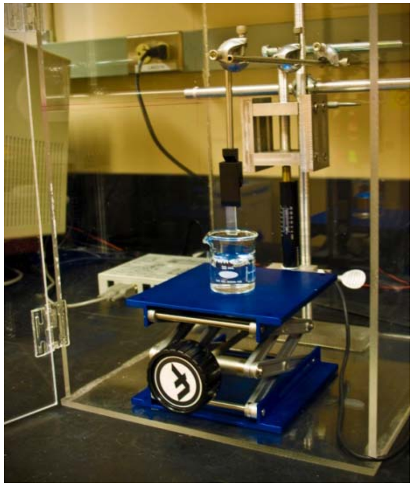
<u>3-D Mesoporous</u>
- Develop synthesis route to achieve the appropriate dimensions

Approach: Milestones

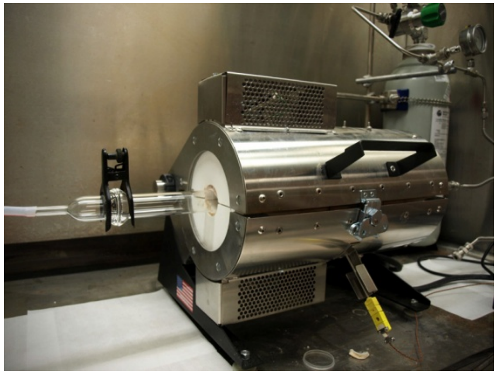
Milestones	Progress Notes	Comments	% Comp.
Plan, develop, and perform synthesis and characterizations, both physical and photoelectrochemical, of nanoscale transition metal dichalcogenides.	Synthesized and characterized monodisperse nanoparticles. Other morphologies underway.	Demonstrated bandgap enlargement to 1.7 eV.	50 %
Correlate physical characterization test results with photoelectrochemical performance to tune subsequent syntheses in an effort to optimize water splitting efficiency and photoelectrode stability.	Initial tests on nanoparticles underway.	Need to increase loading of supported nanoparticles to achieve better signal-to-noise.	10 %

Accomplishments: Synthesis & Characterization Methodology

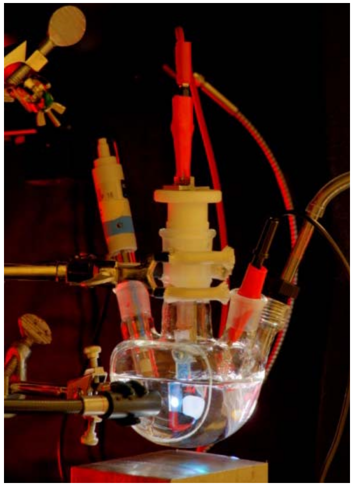
Wet-chemical synthesis of nanostructures



Dip-coat onto substrates

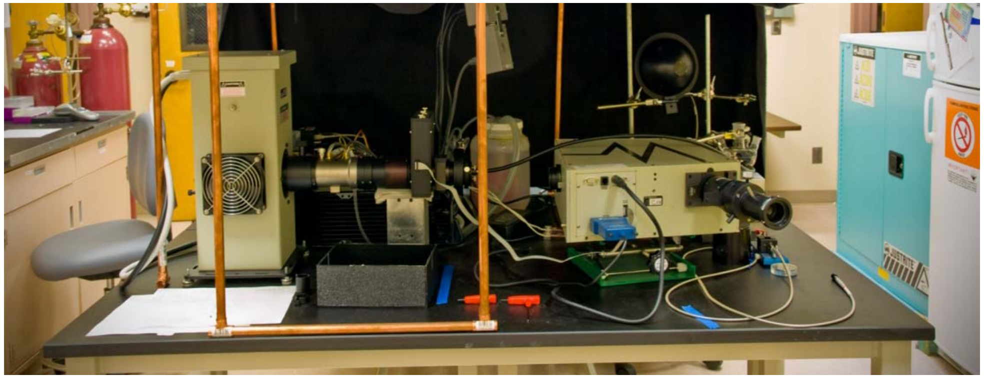


Sulfidize: 10% H_2S 90% H_2 (150 °C < T < 400 °C)



PEC

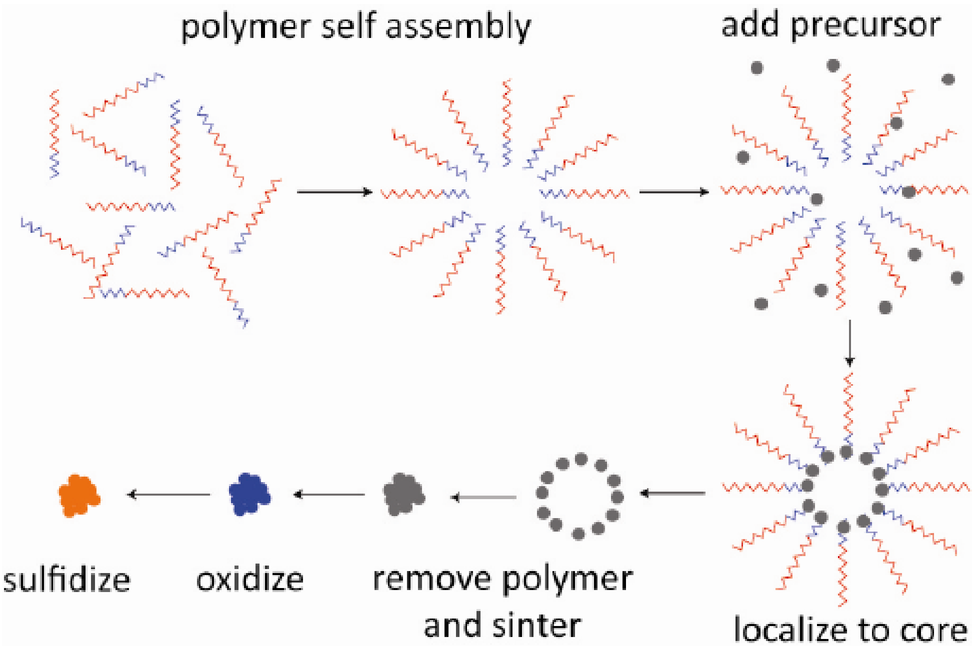
<u>Take home message</u>:
We have developed a methodology by which we can synthesize well-defined nanoparticles, support them onto an inert electrode, and characterize them photoelectrochemically.

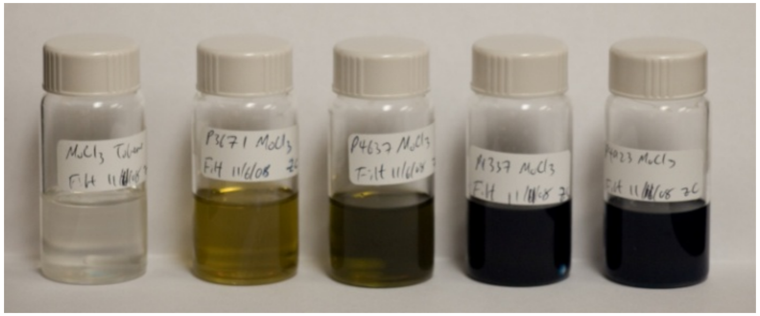


Accomplishments: Synthesis of MoS_2 nanoparticles

Nanoparticle synthesis by wet chemistry

- Reverse micelle encapsulation process
- Poly(styrene-b-2-vinylpyridine) in toluene
- Precursors: $MoCl_3$, $W(CO)_6$

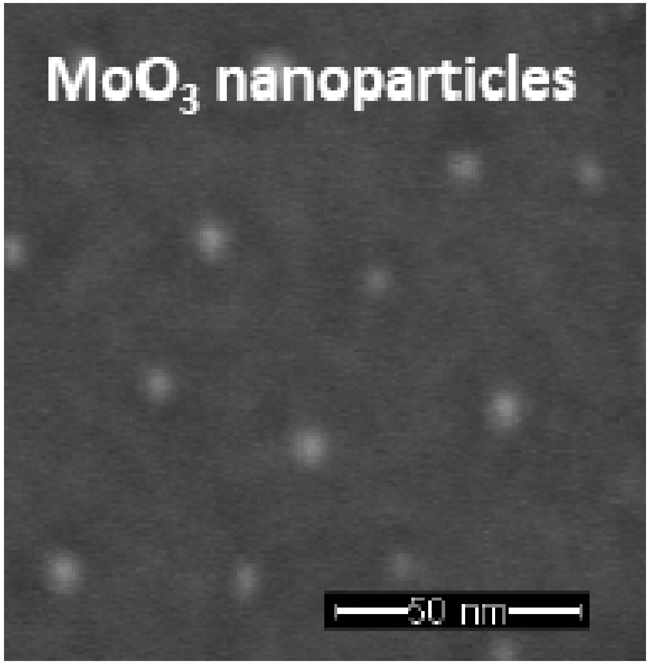


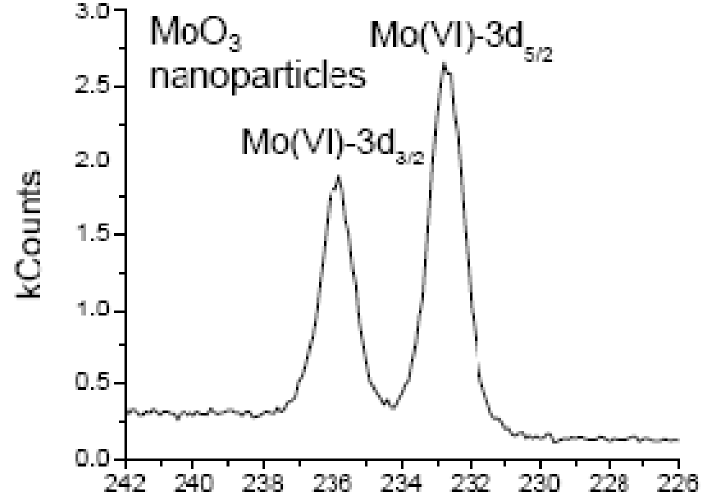


- PS/P2VP ratios (m.w.):
  - 27700/4300
  - 32500/7800
  - 81000/21000
  - 172000/42000
- $MoCl_3$:P2VP
  - 0.05-1.0

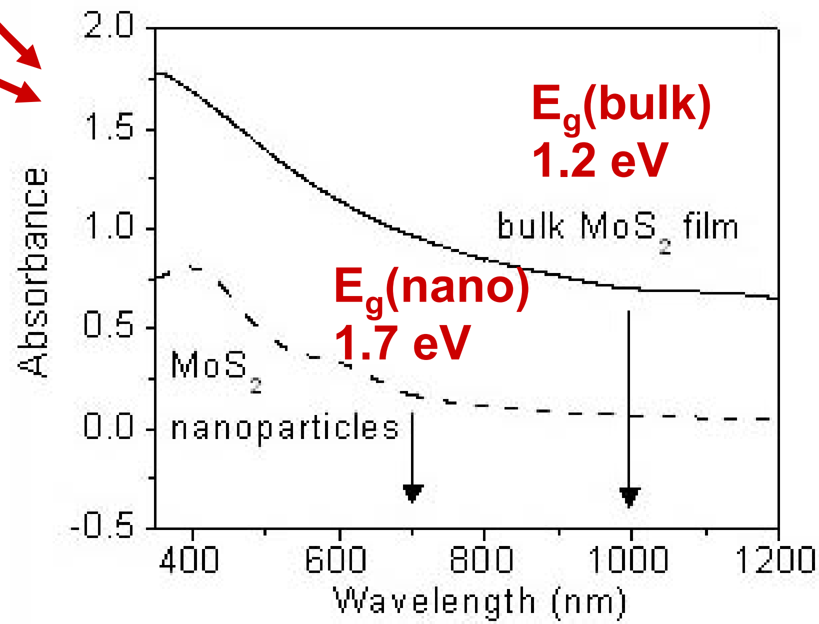
<u>Take home message</u>:
We have developed a synthetic route that leads to well defined molybdenum or tungsten nanoparticles in the 1-15 nm diameter range.

Accomplishments: MoS_2 n.p. deposition & characterization





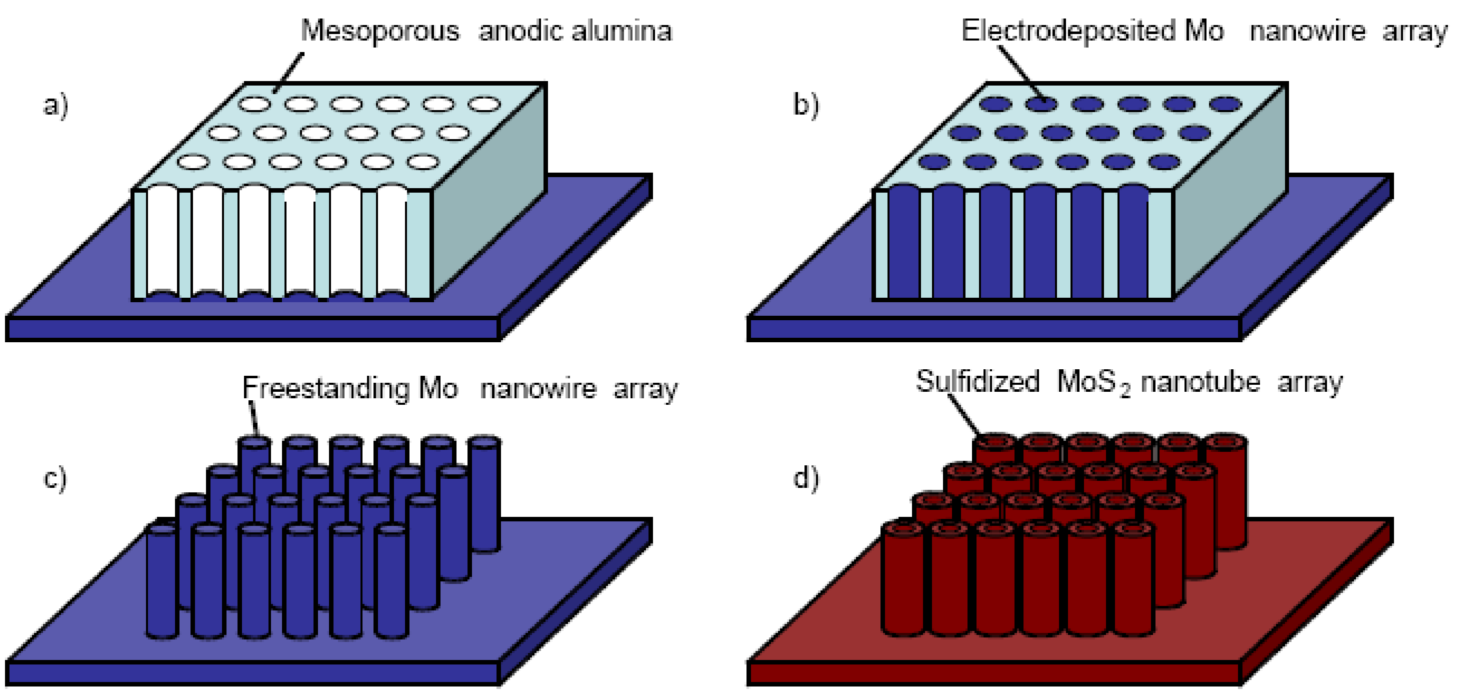
After sulfidation



<u>Take home message</u>:
Nanoparticles of approx. 5 nm diameter exhibited a bandgap enlargement from 1.2 eV (bulk) to approx. 1.7 eV, very close to the 2013 and 2018 DOE targets of 2.0 eV - 2.3 eV.

Accomplishments: Developed strategy for vertical nanowires

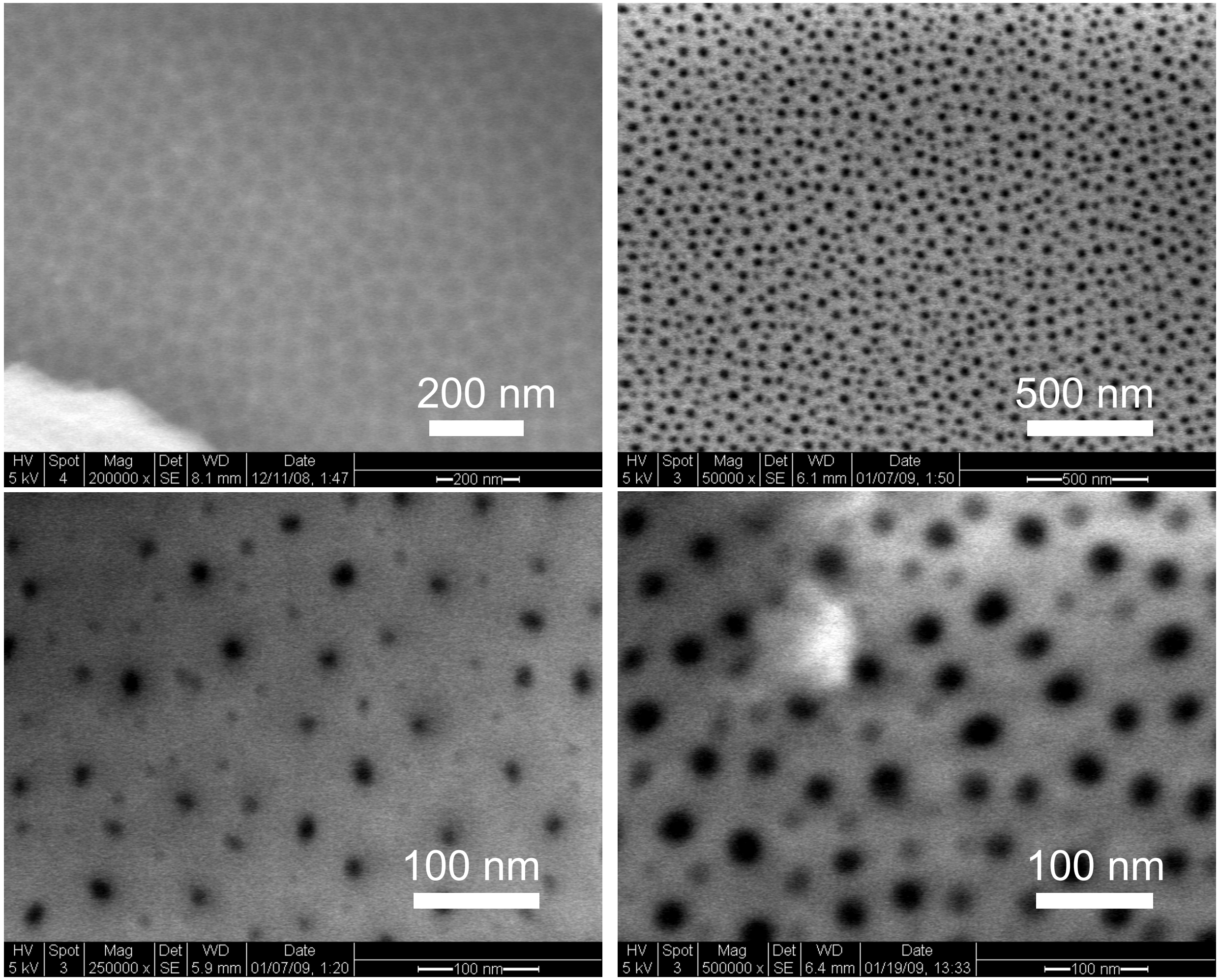
- Templating process using anodic alumina (a), followed by electrodeposition of desired material (b), etching of alumina template (c), and subsequent sulfidization (d)



Take home message:
We have devised a strategy by which we can synthesize well-defined nanorods, nanowires, and nanotubes for photoelectrochemical studies.

Accomplishments: Al_2O_3 template synthesis

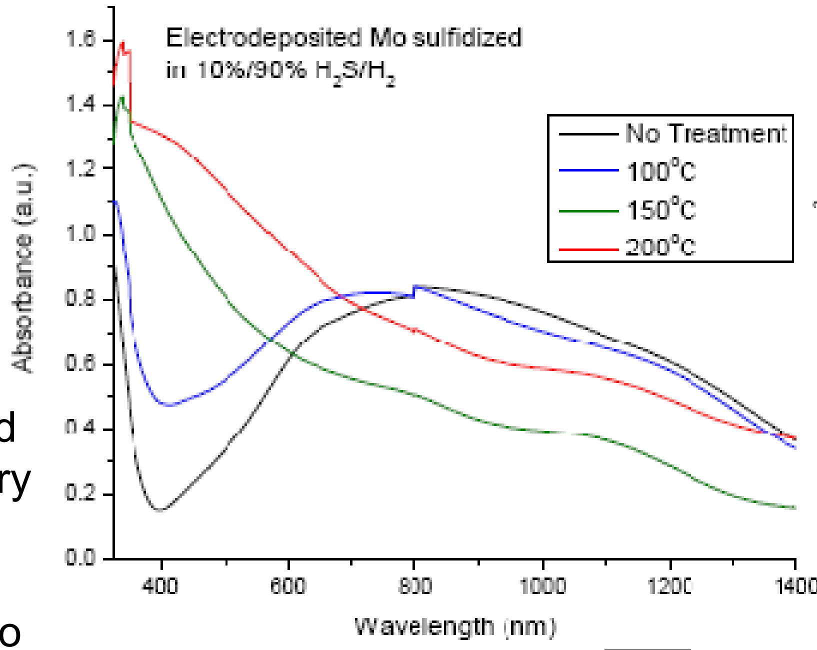
Other researchers in the literature have shown uniform pores of diameter > 20 nm. We are developing a route which can produce uniform pores of diameter < 10 nm.

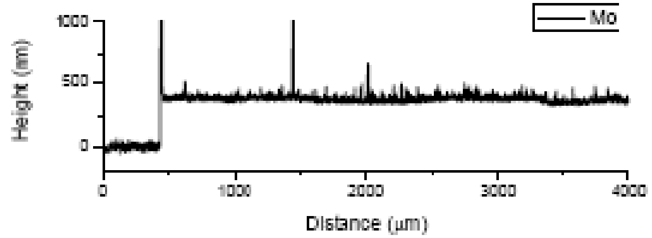


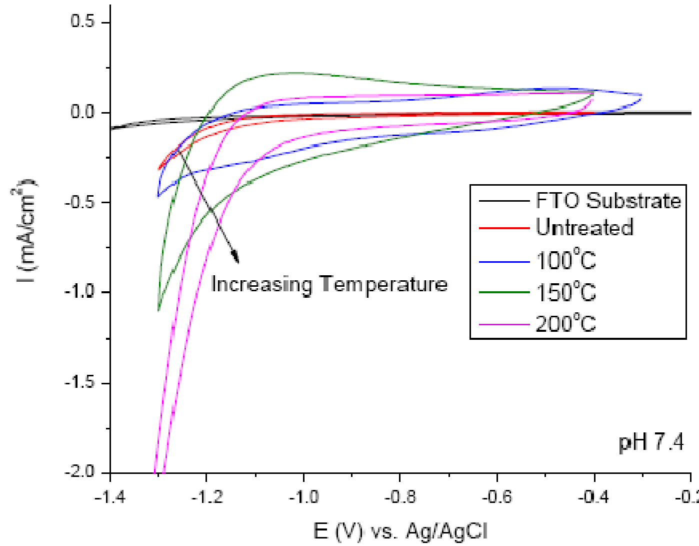
<u>Take home message</u>:
We have developed Al_2O_3 templates with small diameter pores approx. 7 nm diameter. They are not uniform, however; uniformity is the goal of current work.

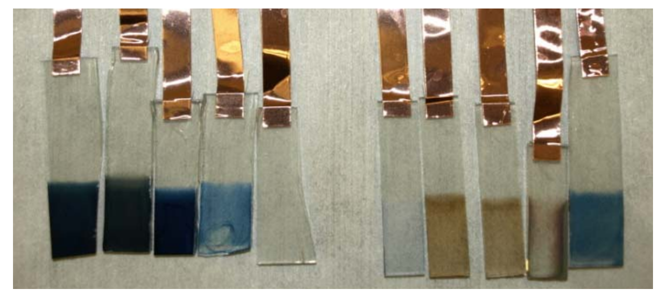
Accomplishments: Electrodeposition of MoS_2 films

UV-Vis spectroscopy and cyclic voltammetry show that electrodeposited Mo is sulfidized to MoS2 at termperatures as low as 150-200 °C.









Take home message: We have developed a synthetic route involving electrochemical deposition and low temp. processing to produce MoS_2 and WS_2 films. The current goal is to modify this process to deposit inside the aforementioned Al_2O_3 templates.

Collaborations

- NREL, UCSB, UNLV, U. Hawaii.
  - Development of standardized testing and reporting protocols for PEC material/interface evaluation.
    - all supported by DOE H_2 program.
- NREL, UCSB, U. Hawaii, Directed Technologies, Inc.
  - Techno-economic analysis of PEC Hydrogen production systems
    - all supported by DOE H_2 program.
- UCSB
  - Sample-swapping for PEC measurement validation
    - supported by DOE H_2 program.
- UNLV
  - Collaboration with Prof. Clemens Heske for bulk and surface materials characterization by electronic spectroscopies
    - supported by DOE H_2 program.

Future Research

- **Synthesis – control over morphologies**
  - Synthesize monodisperse MoS_2 and WS_2 nanoparticles in the 1-15 nm diameter range (~ 5 nm has been accomplished already).
  - Synthesize Al_2O_3 mesoporous template with uniform pores < 10 nm.
  - Develop electrochemical deposition route to fill < 10 nm pores with Mo and W to produce nanowires or nanotubes.
  - Synthesize a bicontinuous mesoporous structure of MoS_2 and WS_2.

- **Synthesis – control over composition**
  - Identify and explore dopants to create p-type MoS_2 and WS_2.
  - Controlled synthesis of p-type nanostructured MoS_2 and WS_2 in the three different aforementioned morphologies.

- **Opto-electronic characterization** to identify structures with optimal electronic band structure.

- **Electrochemical & PEC characterization** for flat-band potentials, hydrogen evolution catalysis, solar-to-hydrogen efficiency, durability, etc.

- **Collaboration with PEC Working Group partners** to elucidate any material shortcomings (carrier lifetime, mobility, defects, etc.)

Summary

- **Relevance** — The **main objective** of the project is to develop new photoelectrode materials that can potentially meet DOE targets (2013 and 2018) for usable semiconductor bandgap, chemical conversion process efficiency, and durability.

- **Approach** — The approach is different from previously published approaches in PEC. We aim to quantum confine semiconductors through nanostructure to tailor their bulk and surface properties for PEC.

- **Technical Accomplishments & Progress** — By synthesizing ~ 5 nm diameter MoS_2 nanoparticles, we have tuned the band gap from 1.2 eV to 1.7 eV, a value very close to DOE's 2013 and 2018 targets of 2.3 eV and 2.0 eV, respectively.

- **Collaborations** — Collaborations with NREL, UCSB, U. Hawaii, UNLV, and Directed Technologies, Inc. have been fruitful in terms of knowledge exchange and sample-swapping for efficiency validation.

- **Future Research** — Improving control over various morphologies, sizes, and compositions of nanostructures is currently underway. Characterization for physical, opto-electronic, and electrochemical properties, as well as for PEC efficiency and durability is underway.