Nanostructured MoS_2 and WS_2 for the solar production of hydrogen

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DOE Hydrogen Review Meeting

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Project ID # PD033

Overview

Timeline

- Start – Dec 2008
- Finish – Dec 2009
- 100% complete

Budget

- Total project funding
  - DOE - $130k
  - Contractor - $32k
- Funding received in FY09
  - $130k
- Funding for FY10
  - TBD

Barriers

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

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
- U. Louisville
- UNLV
- UC Santa Barbara
- The PEC WG

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

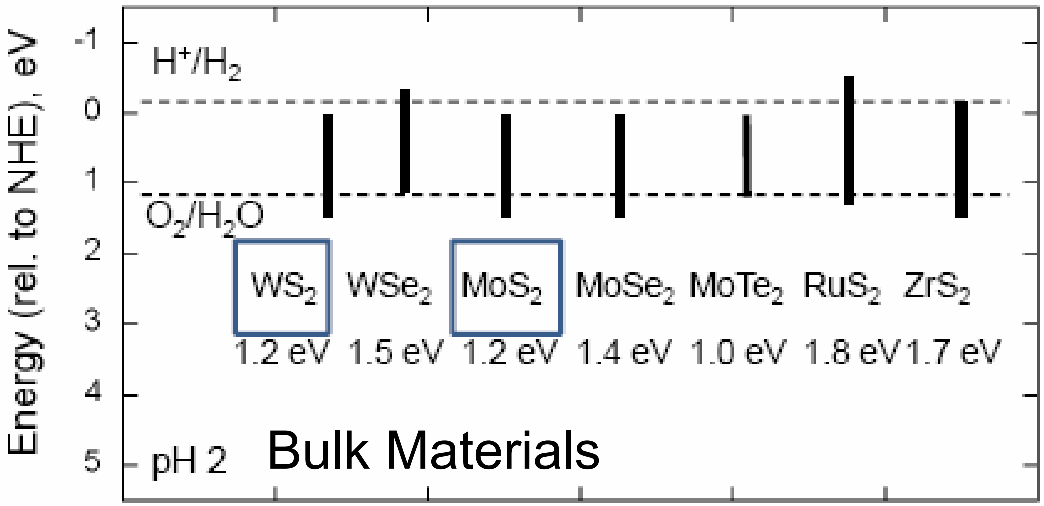
Table 1. Materials-related “Technology Barriers” for successful PEC water-splitting: material class challenges and strengths for MoS_2 and WS_2.

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

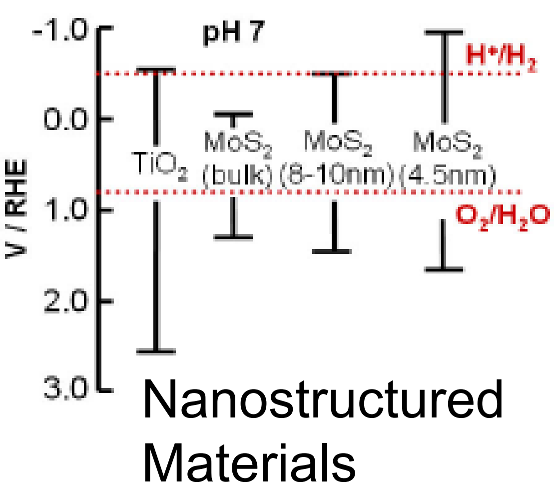
Approach: Addressing the Challenges

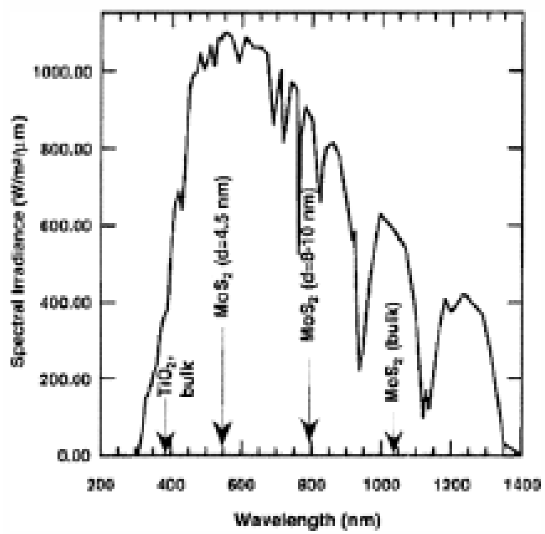
- **Y. Efficiency**
  - **Electronic band structure can be widened via nanostructuring to achieve the desired 1.8 eV – 2.3 eV bandgap.**
- **Z. Durability**
  - **Targeting p-type materials for photocathodic operation, which improves stability.**
- **AB. Bulk materials synthesis**
  - **Developing low-cost 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.



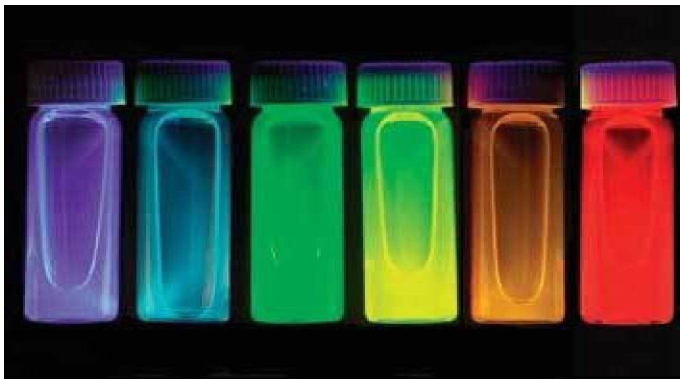


Thurston, T. R.; Wilcoxon, J. P. *Journal of Physical Chemistry B* 1999, *103*, 11.

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

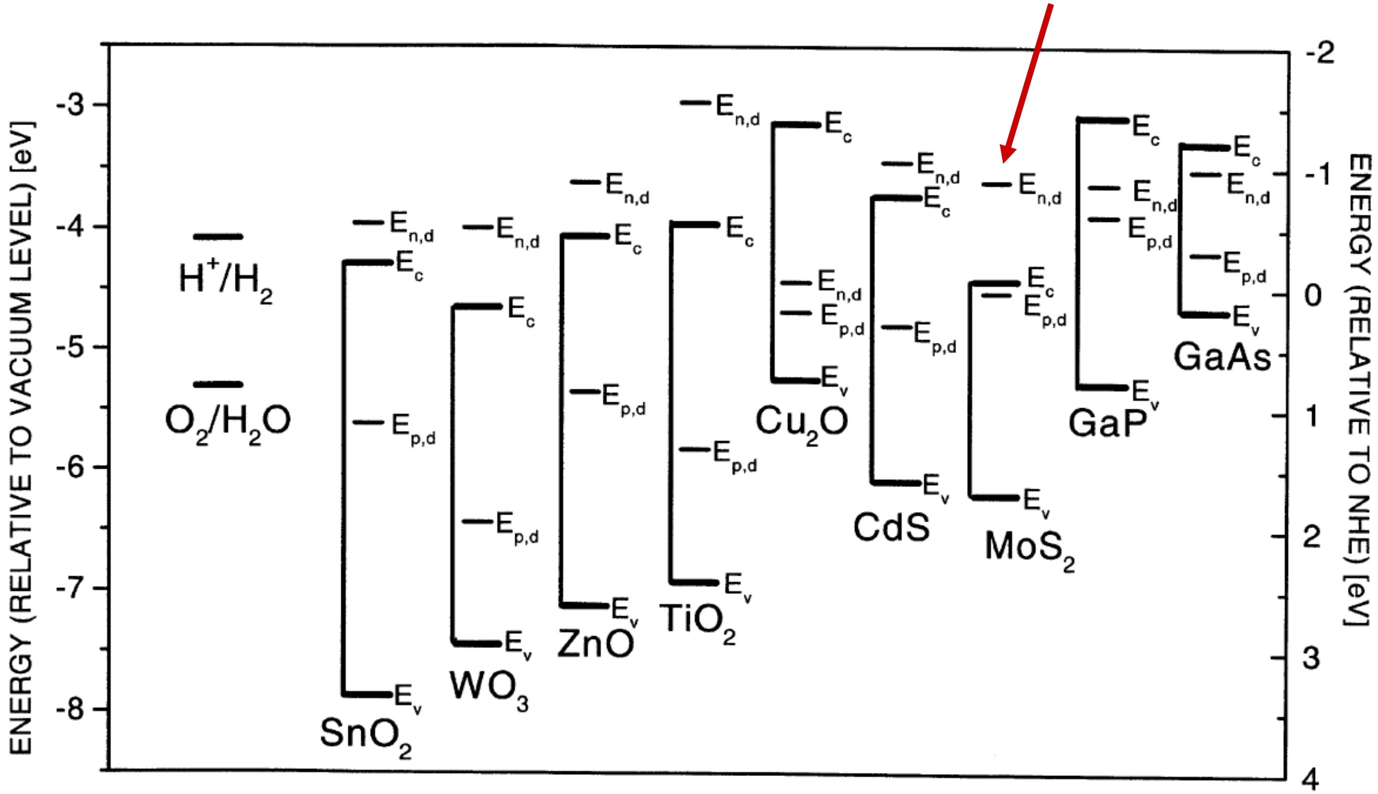
2 nm CdSe ← 8 nm CdSe



Bawendi et. al. (MIT)

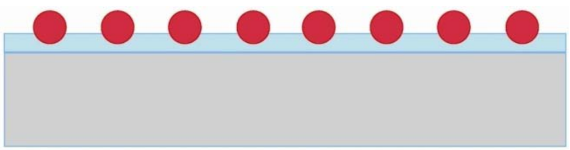
Approach: Improving durability

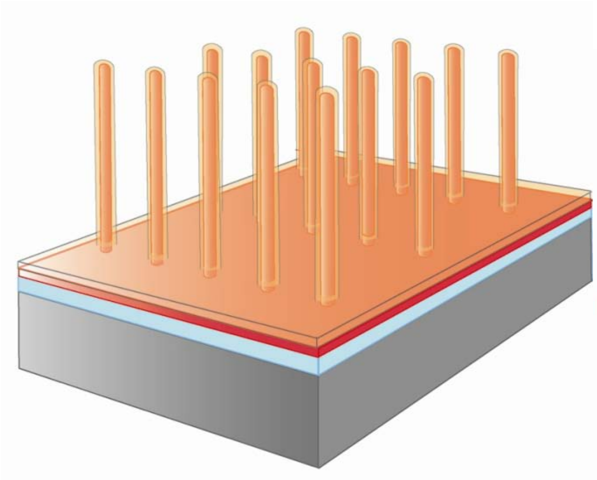
Cathodic corrosion potential lies above $E^0_{H+/H2}$. Photocathodes (p-type) should be stable.

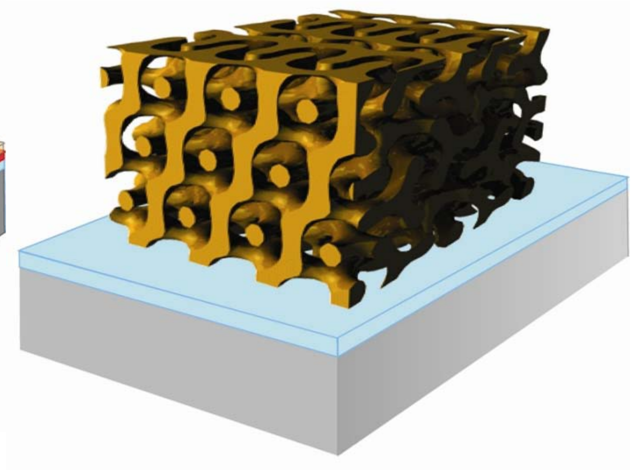


Bak, T.; Nowotny, J.; Rekas, M.; Sorrell, C. C. *International Journal of Hydrogen Energy* **2002**, *27*, 991.

Approach: Targeted Nanostructures







<u>Nanoparticles</u>

- Establish monodispersity (size-control)
- Correlate bandgap to size
- Measure PEC

<u>Nanowires</u>

- Develop synthesis route to achieve the appropriate dimensions

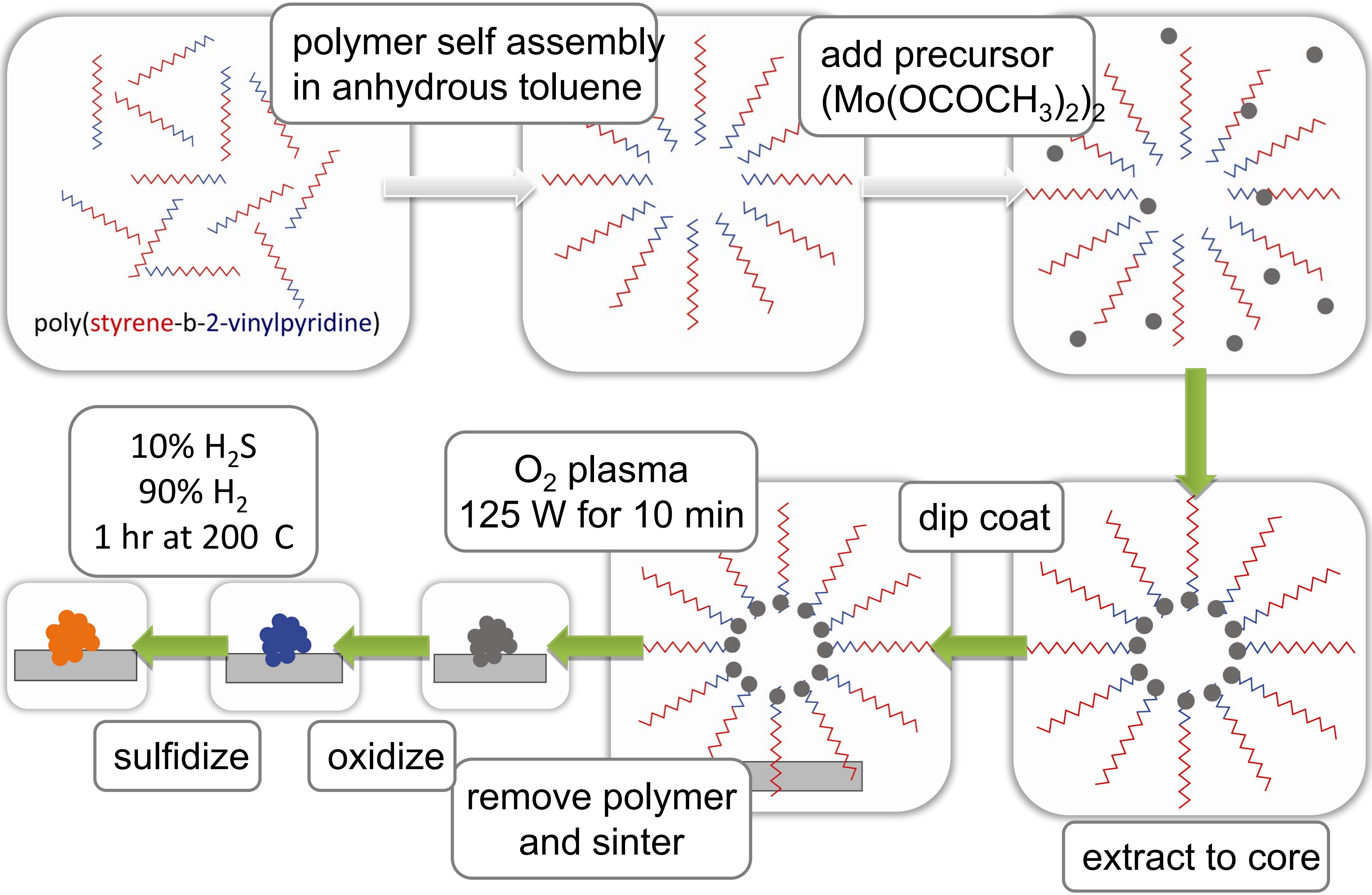
<u>3-D Mesoporous</u>

- Develop synthesis route to achieve the appropriate dimensions

Accomplishments: 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 and other nano-scale morphologies.	Demonstrated bandgap enlargement to 1.8 eV.	100 %
Correlate physical characterization test results with photoelectrochemical performance to tune subsequent syntheses in an effort to optimize water splitting efficiency and photoelectrode stability.	Nanoparticles show photo-electrochemical activity.	Require support onto 3-D transparent conducting scaffolds.	100 %

Accomplishments: Monodisperse MoS_2 nanoparticle synthesis



Accomplishments: Low temperature sulfidization

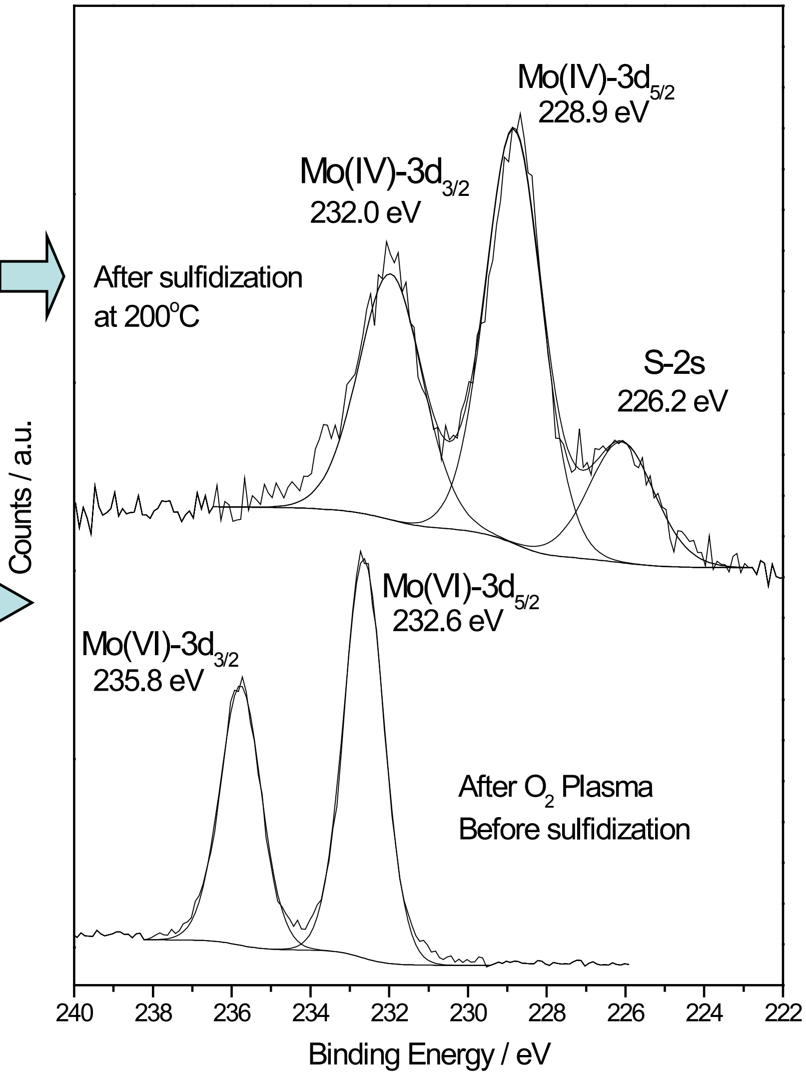
MoO_3 nanoparticles

H_2/H_2S at 200 C

MoS_2 nanoparticles

Atomic Force Microscopy

X-ray Photoelectron Spectroscopy

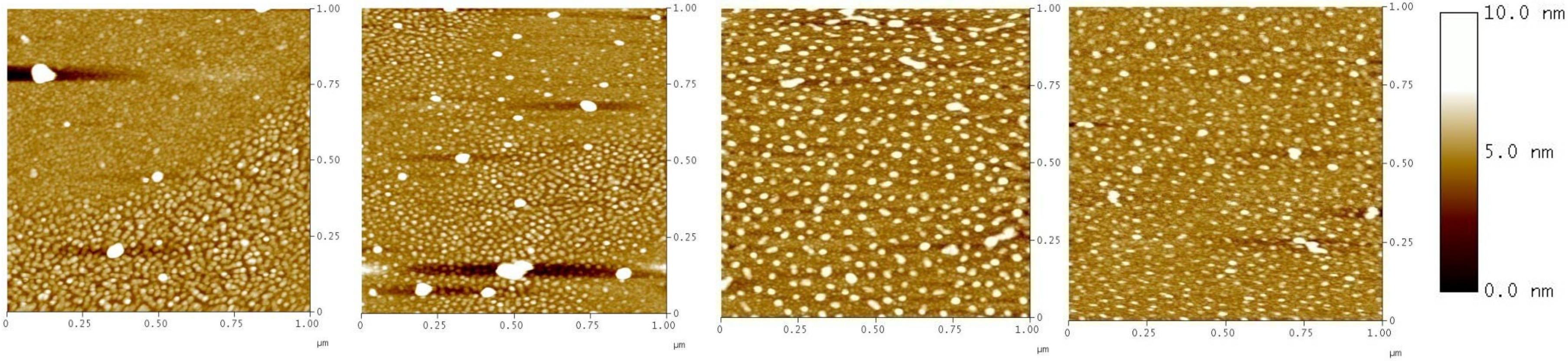


Take home messages:

(1) We have developed a synthetic route to synthesize well-defined, supported MoS_2 nanoparticles, with minimal sintering.

(2) XPS shows that the MoS_2 nanoparticles are stable (not oxidized) in air.

Accomplishments: Tuning nanoparticle size (AFM)



27700/4300	32500/7800	81000/21000	172000/42000
PS(266)-*b*-P2VP(41)	PS(313)-*b*-P2VP(74)	PS(779)-*b*-P2VP(200)	PS(1654)-*b*-P2VP(400)

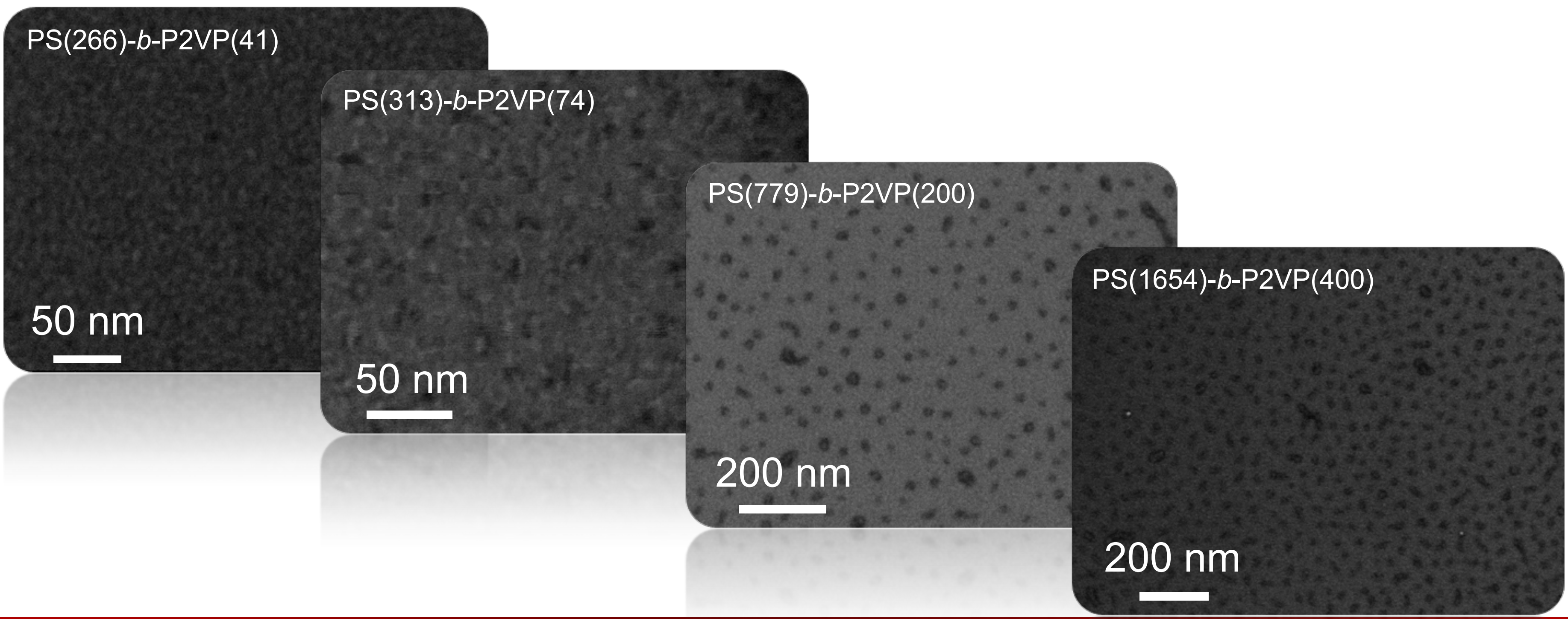
Increasing molecular weight block copolymer (PS/P2VP, units: Da)

Take home message:
We can tailor MoS_2 nanoparticle diameter from 5-25 nm by choosing the appropriate block co-polymer and Mo precursor loading.

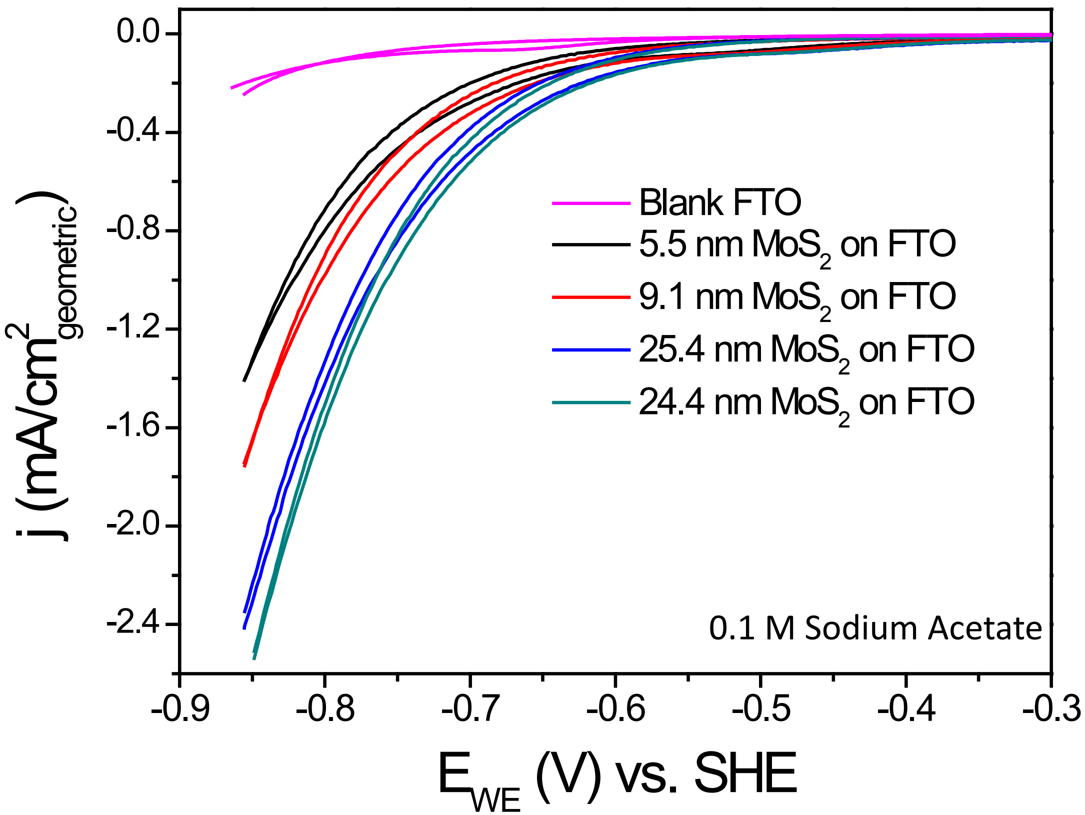
Accomplishments: Tuning nanoparticle size (SEM)

	Average diameter (nm)	Standard deviation (nm)
PS(266)-*b*-P2VP(41)	5.5*	1.0
PS(313)-*b*-P2VP(74)	9.1	2.1
PS(779)-*b*-P2VP(200)	25.4	7.3
PS(1654)-*b*-P2VP(400)	24.4	5.7

*Measurement limited to microscope resolution



Accomplishments: Catalysis for hydrogen evolution

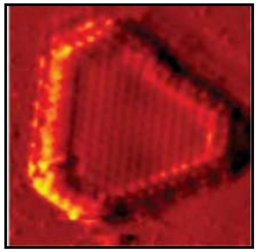


	j_0 (A/cm$^2_{geometric}$)	b (mV/decade)
PS(266)-*b*-P2VP(41)	7.3×10^{-8}	200
PS(313)-*b*-P2VP(74)	7.5×10^{-8}	197
PS(779)-*b*-P2VP(200)	1.3×10^{-7}	200
PS(1654)-*b*-P2VP(400)	1.0×10^{-7}	192

<u>Take home message</u>:

Nanoparticles are active catalysts for the hydrogen evolution reaction (HER).

However, the data suggest that the HER may not be taking place at edge sites.



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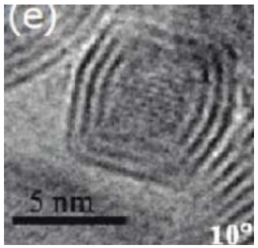
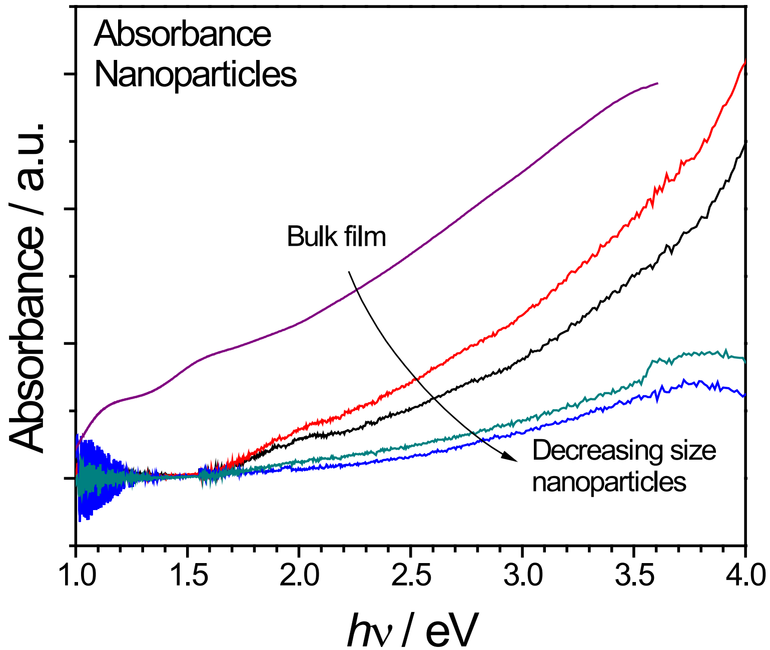


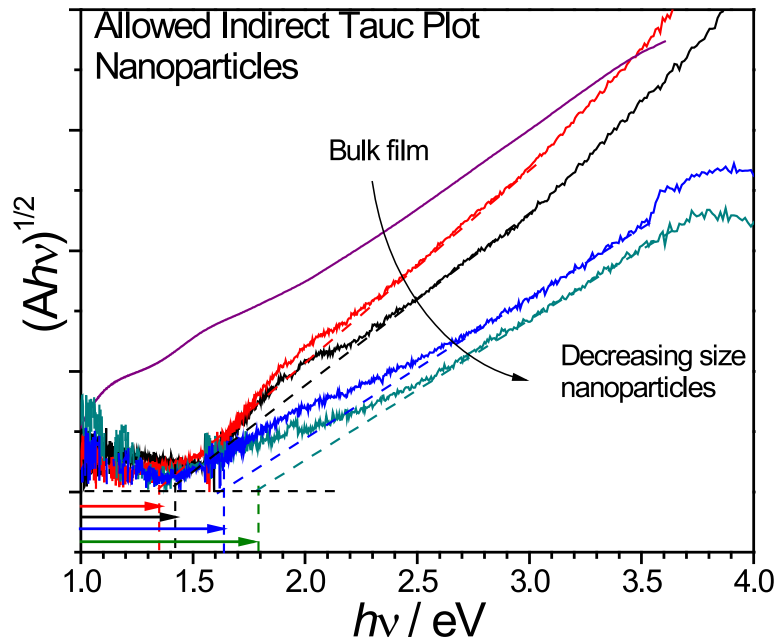
2

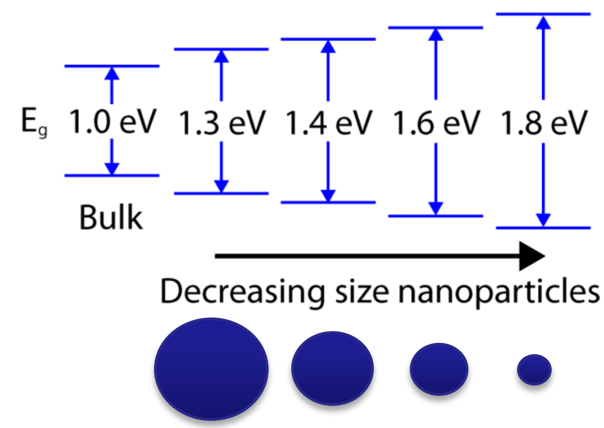
[1]Jaramillo, et al. *Science* **2007**, 317, 100

[2]Seifert, et al. *Chem. Mater.* **2009**, 21, 5629

Accomplishments: Bandgap tuning through size control



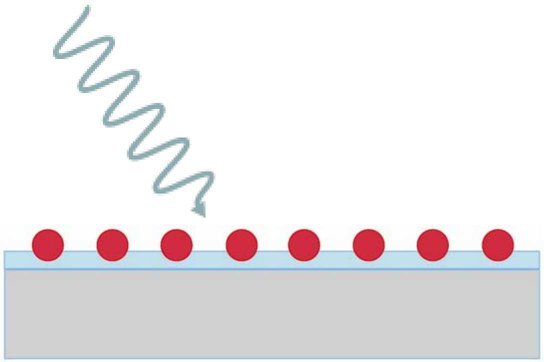


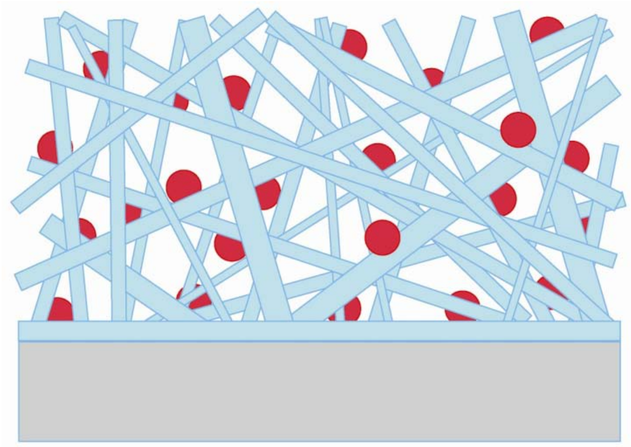


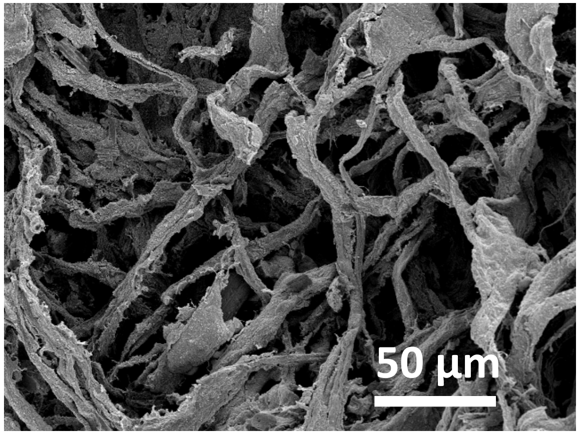
Take home message:
Nanoparticles of approx. 5 nm diameter exhibited a bandgap enlargement from 1.2 eV (bulk) to approx. 1.8 eV, very close to the 2013 and 2018 DOE targets of 2.0 eV - 2.3 eV.

Blueshift in bandgap with decreasing size.

Accomplishments: Macroporous scaffold for nanoparticles





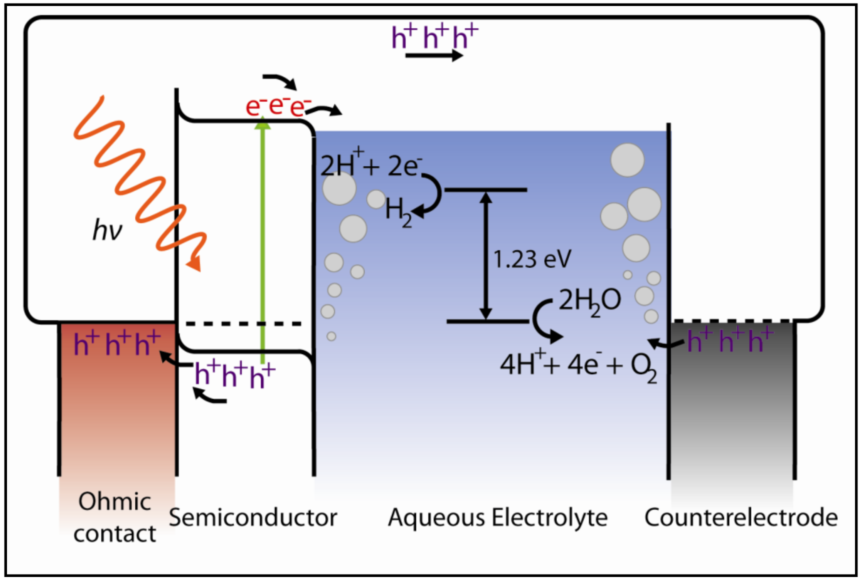


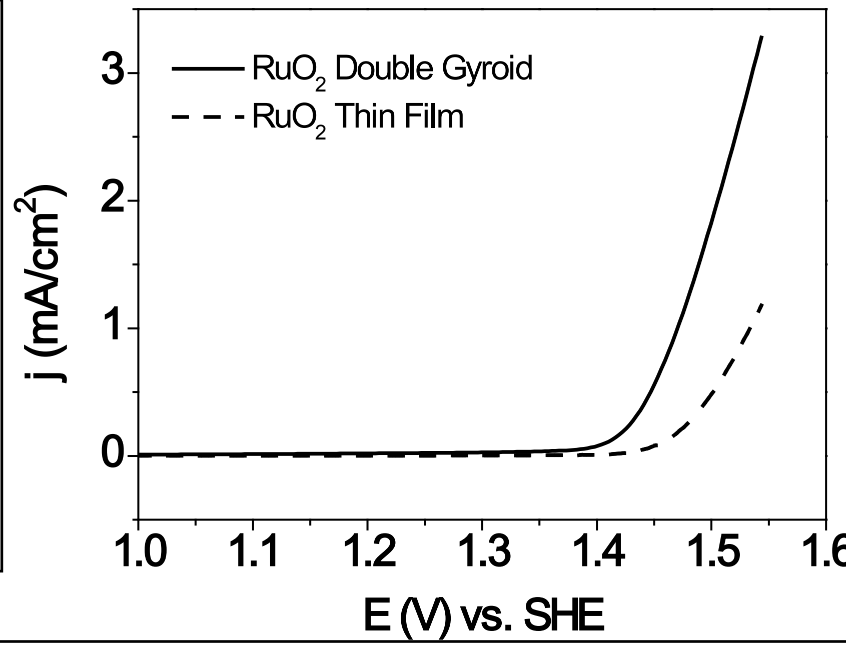
Courtesy of Yen-Chu Yang

Take home message:
In order to increase light absorption, we have initiated the development of a macroporous scaffold consisting of a transparent conducting oxide (TCO) – indium-tin oxide – upon which the MoS_2 nanoparticles can be vertically integrated.

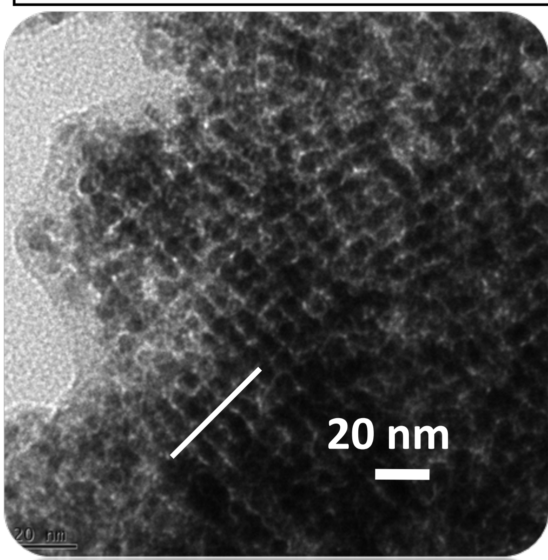
Y. Aoki, J. Huang, T. Kunitake, *J. Mater. Chem.*, 2006, **16**, 292-297

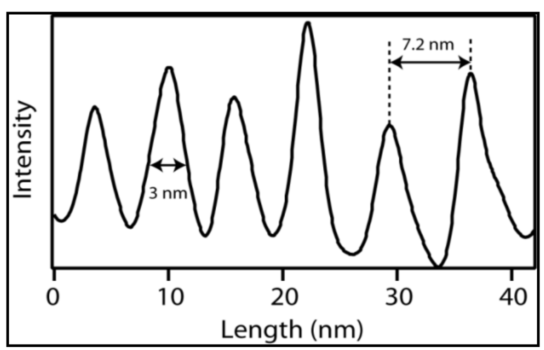
Accomplishments: Development of a high surface area active counter electrode for water oxidation





	j_0 (A/cm^2)	C_{dl} (mF)
RuO_2 Thin film	3.7×10^{-9}	0.34
RuO_2 Double-Gyroid	7.1×10^{-8}	3.15

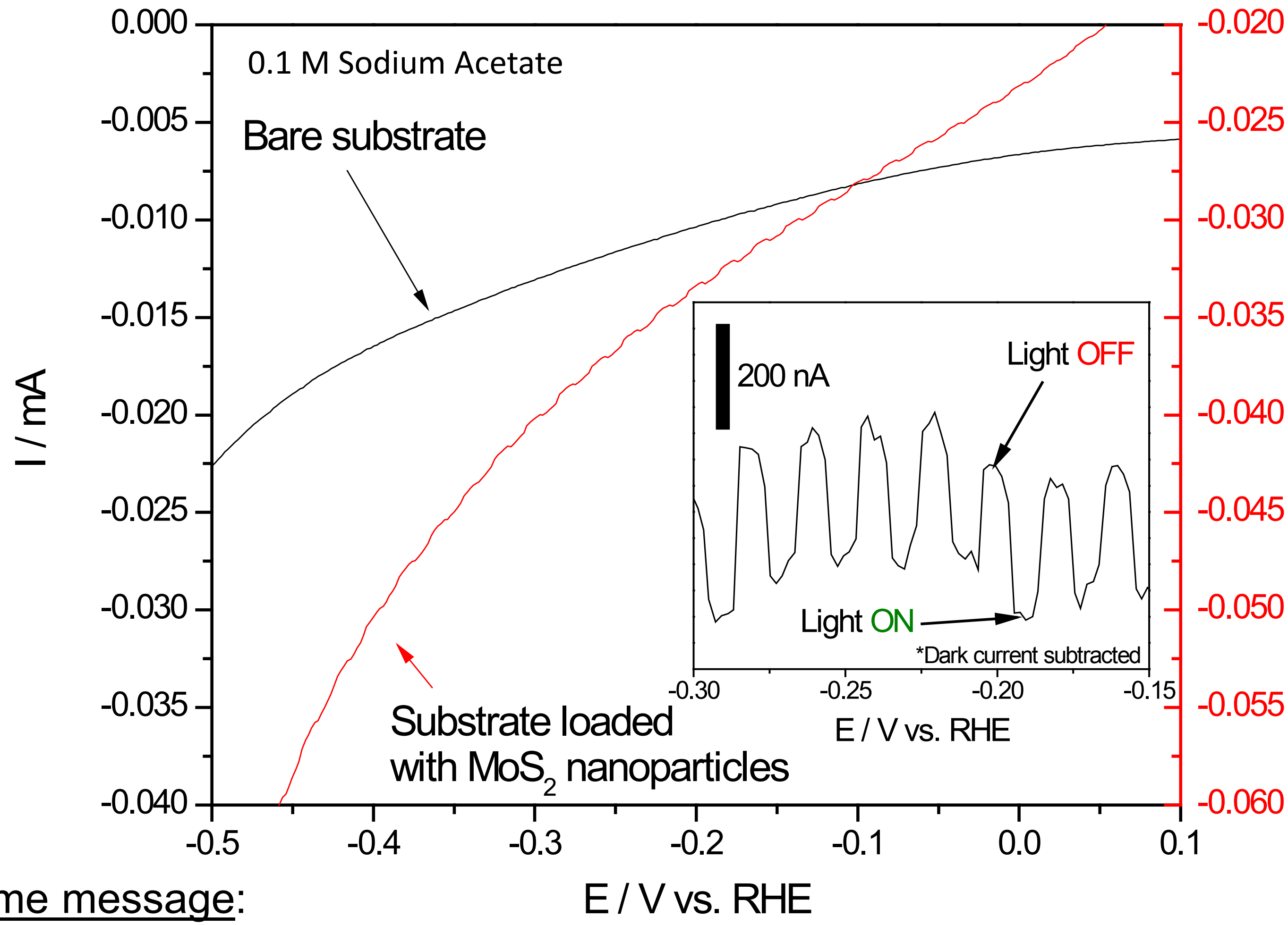




Take home message:

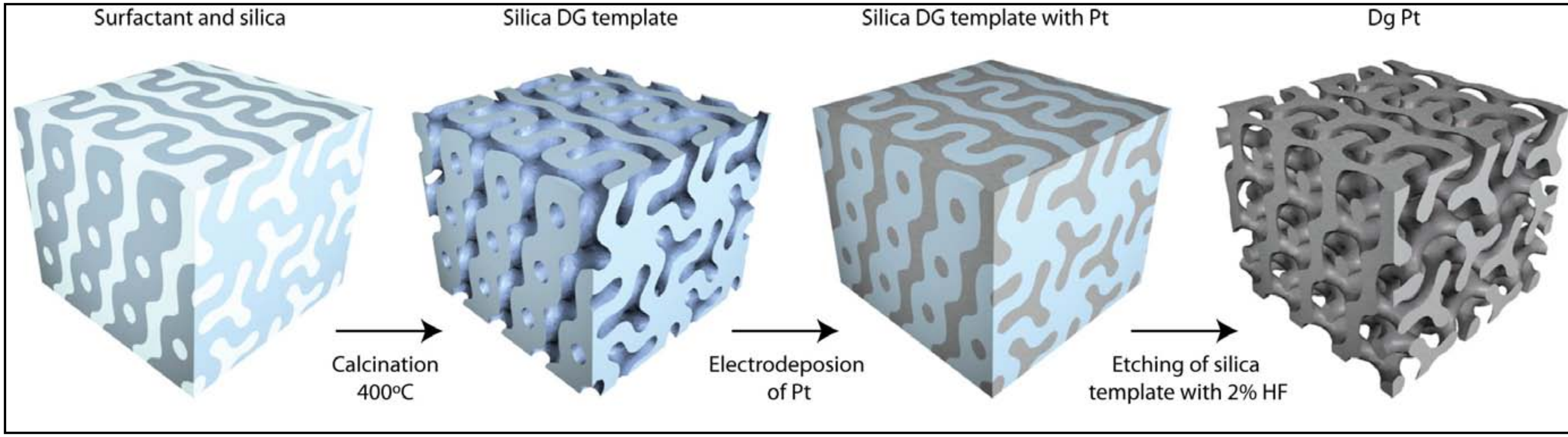
P-type PEC semiconductors (such as p-MoS_2) require a good water oxidation catalyst for the counter electrode. We have developed a highly active RuO_2 for this purpose.

Accomplishments: Photocurrent measurements from nanoparticulate MoS_2 loaded onto macroporous scaffolds



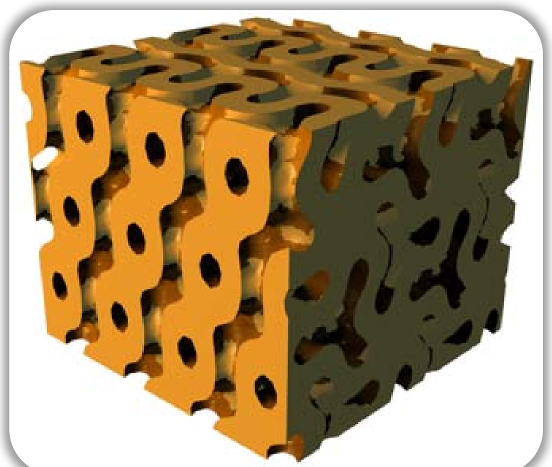
Take home message:
We have measured p-type photoelectrochemical activity from the MoS_2 nanoparticles. They were loaded onto the TCO scaffold described previously, along with the RuO_2 counter electrode. These measurements inspire continued research in this area (go no-go).

Accomplishments: The development of mesoporous double-gyroid materials for PEC



$H(CH_2CH_2O)_{17}$-$(CH(CH_3)CH_2O)_{12}$-$C_{14}H_{29}$
+ Tetraethyl orthosilicate

Artist: Jakob Kibsgaard

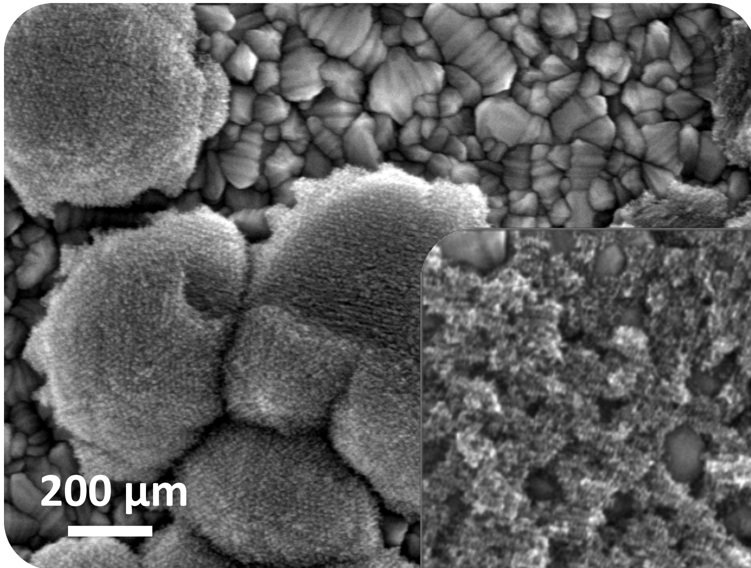


Take home message:
We are pursuing this mesoporous structure for active counter electrode catalysts (Pt for hydrogen evolution, RuO_2 for oxygen evolution) as well as for quantum confined photoelectrode materials (MoS_2).

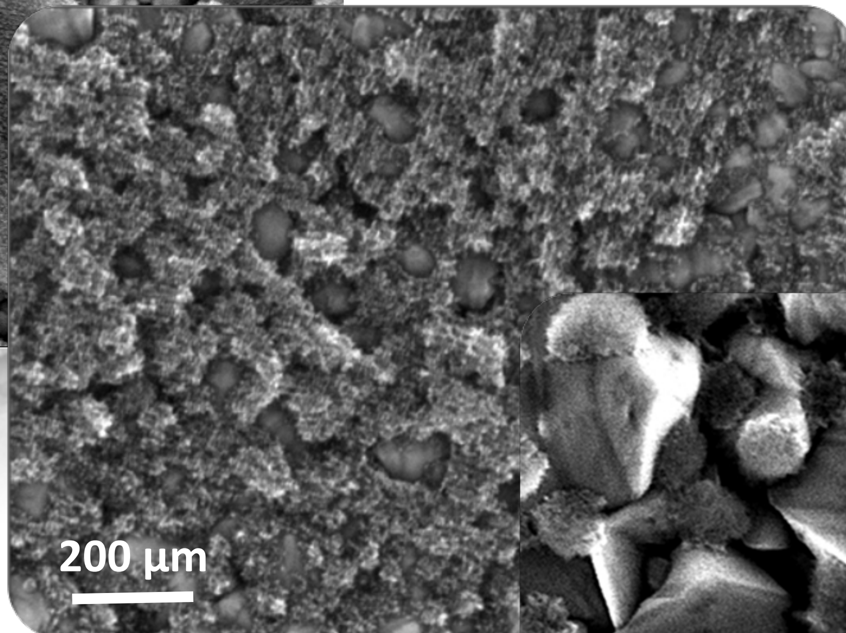
V. Urade, T.-C. Wei, M. Tate, J. D. Kowalski, H. Hillhouse, *Chem. Mater.*, 2007, **19**, 768-

Accomplishments: Mesoporous double gyroid (DG) Pt, RuO_2 and potentially Mo

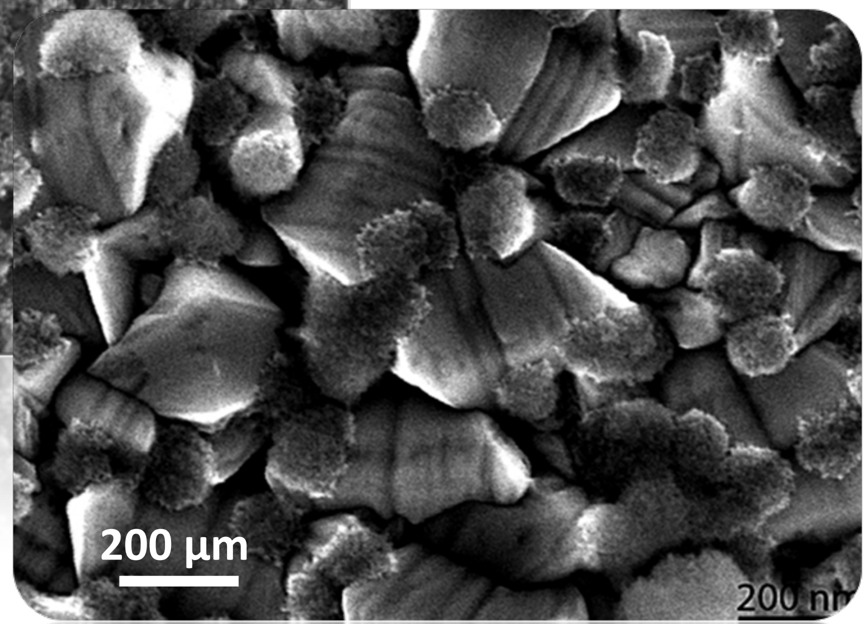
Pt DG



Ru DG

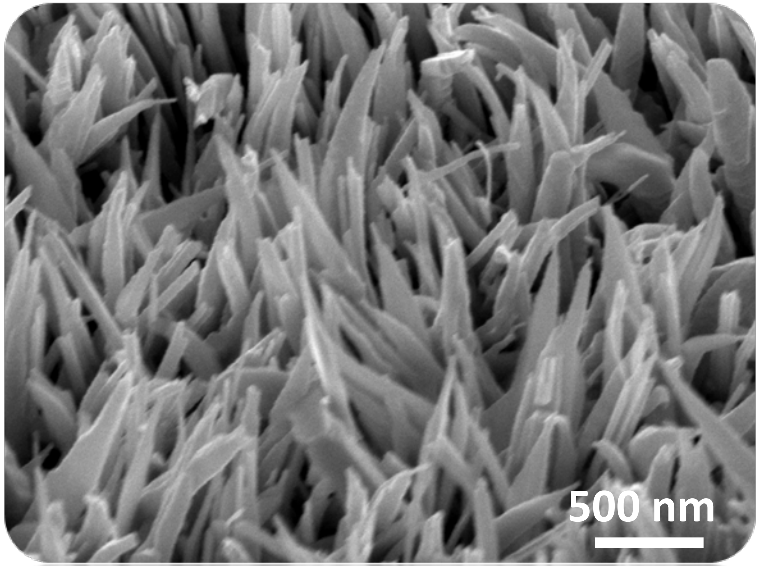


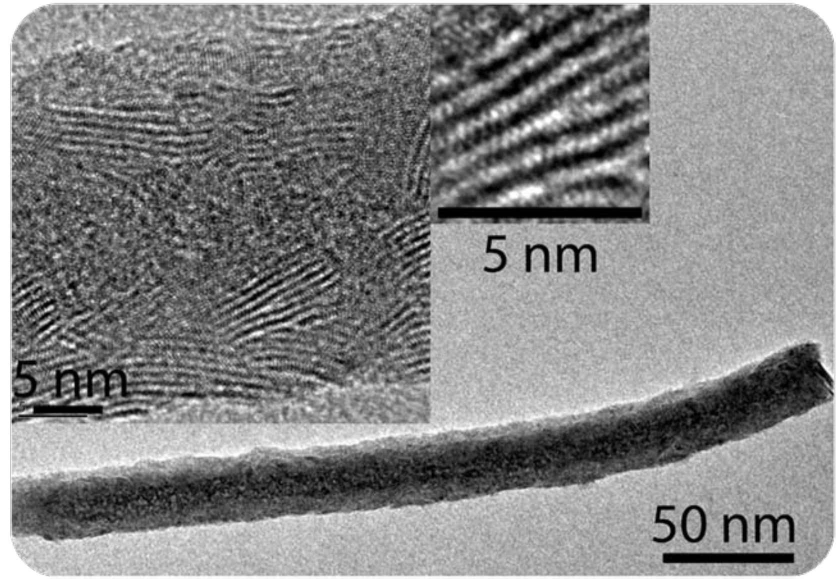
Mo DG(?)



<u>Take home message</u>:
Microscopy confirms the mesoporous double-gyroid structure for Pt and RuO_2, though continued work is necessary for the case of Mo.

Accomplishments: Nanowire MoS_2 synthesis and characterization in collaboration with the University of Louisville, Kentucky





Courtesy: Ben Reinecke

Take-home message:

MoS_2 nanowires were developed in collaboration with Prof. Mahendra Sunkara and student Dustin Cummins at the University of Louisville, Kentucky. MoO_3 nanowires were prepared by hotwire chemical vapor deposition in Louisville, and then sent to Stanford for sulfidization and characterization by TEM. The TEM image above (right) shows the layered MoS_2 structure after sulfidization.

Collaborations

- Univ. of Louisville, Kentucky
  - Development of MoS_2 nanowires for PEC.
    - supported by DOE H_2 program.
- 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.

Proposed Future Research

- **Synthesis – morphologies**
  - Continue research on the double-gyroid mesoporous structure of MoS_2.
  - Develop ultra-thin films of MoS_2 (1-15 nm). Deposit onto:
    - Flat substrates
    - High surface area nanowires – metals and transparent conducting oxides.

- **Synthesis – control over composition**
  - Identify and explore dopants to create p-type MoS_2.
  - Controlled synthesis of p-type nanostructured MoS_2.

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

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

- **Continued 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 MoS_2 nanoparticles of various sizes, we have tuned the band gap from 1.2 eV to 1.8 eV, a value very close to DOE's 2013 and 2018 targets of 2.3 eV and 2.0 eV, respectively.
- **Collaborations** — Collaborations with the U. Louisville, NREL, UCSB, U. Hawaii, UNLV, and Directed Technologies, Inc. have been fruitful in terms of material development, 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 will continue.