Nano-architectures for 3rd generation PEC devices: A study of MoS_2, fundamental investigations and applied research

Prof. Thomas F. Jaramillo,
Zhebo Chen, Arnold Forman, Jesse Benck, Jakob Kibsgaard
Dept. of Chemical Engineering
Stanford University

Project ID: PD033

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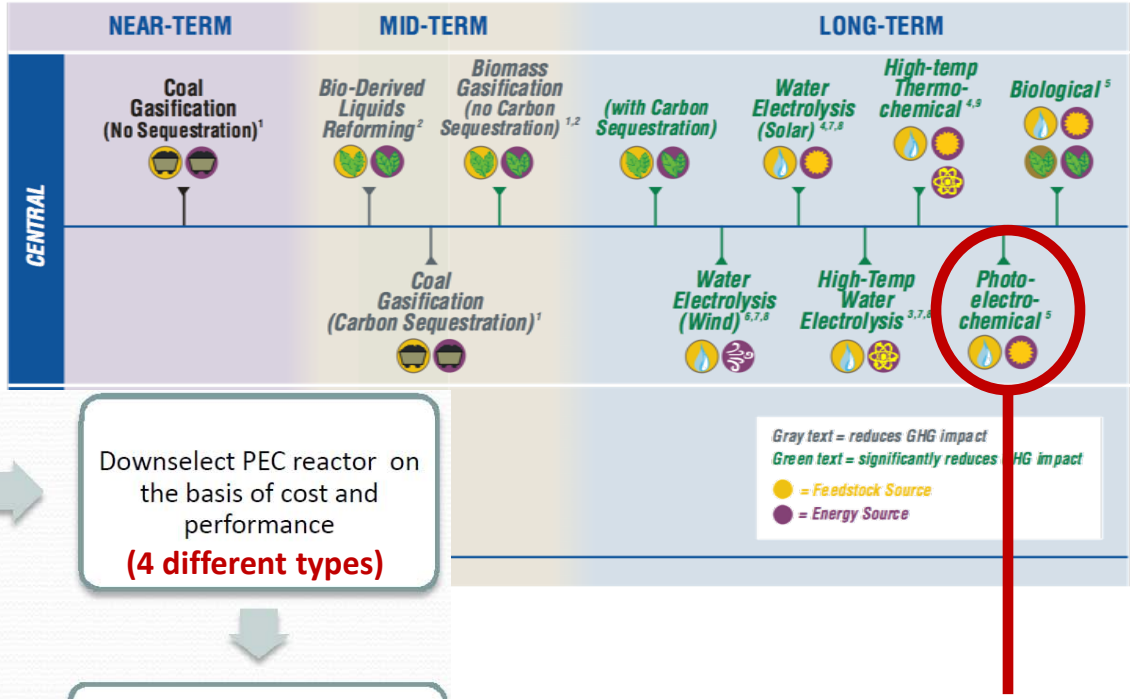
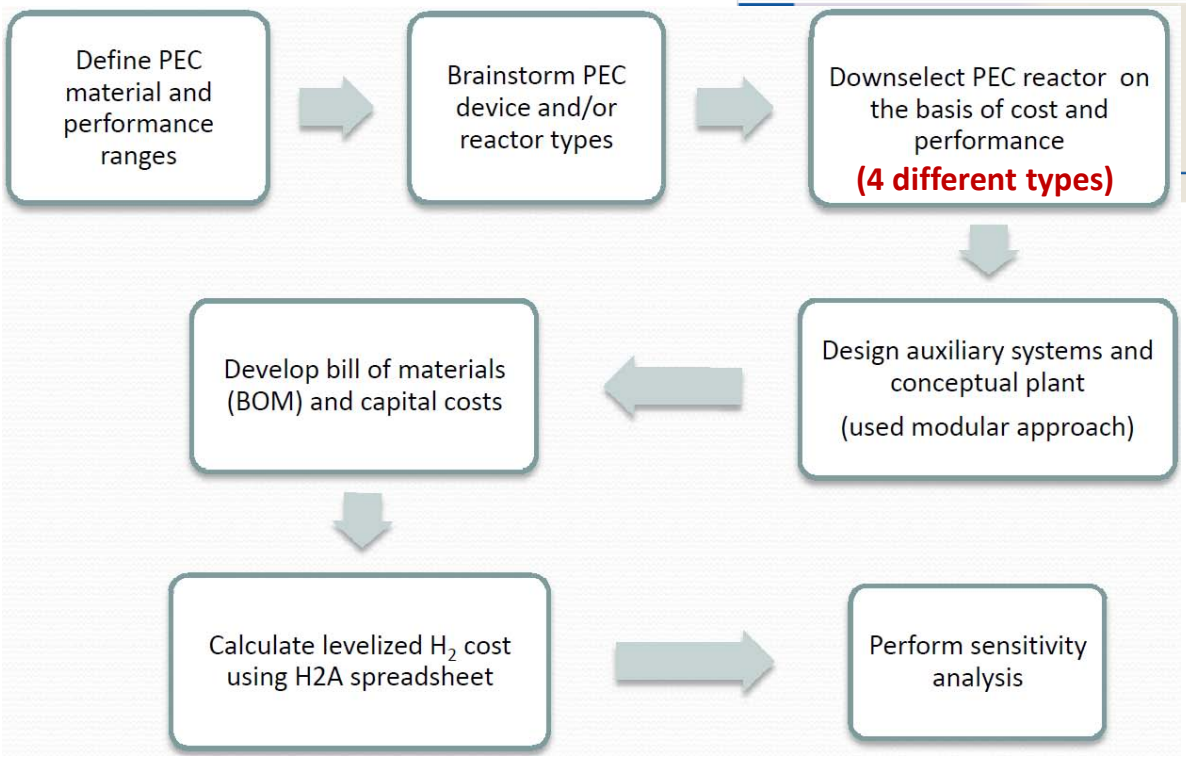
The importance of PEC H_2 production

DOE Hydrogen Production Roadmap
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/h2_production_roadmap.pdf

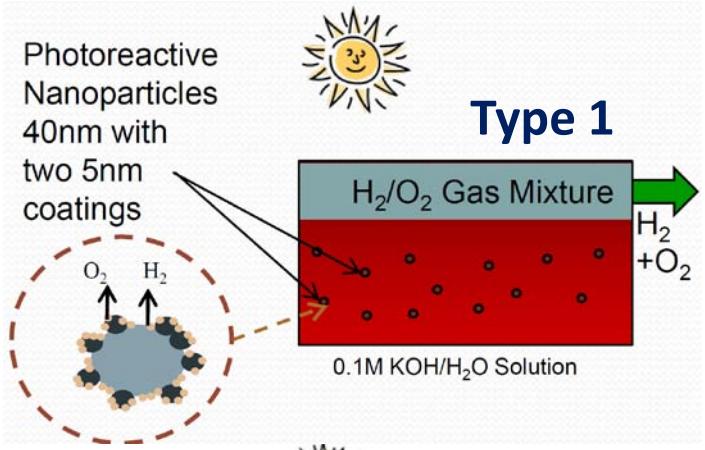


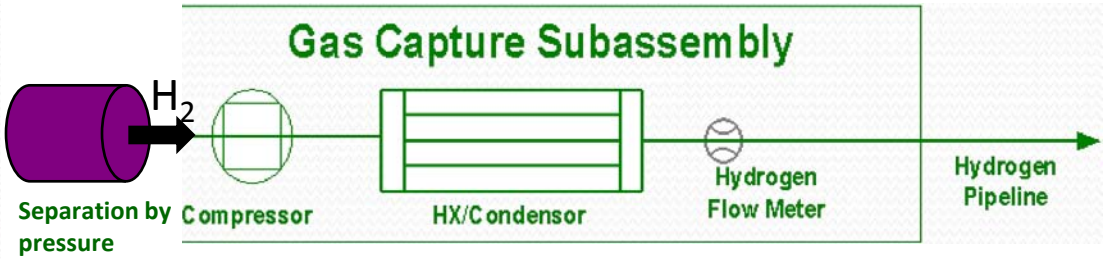


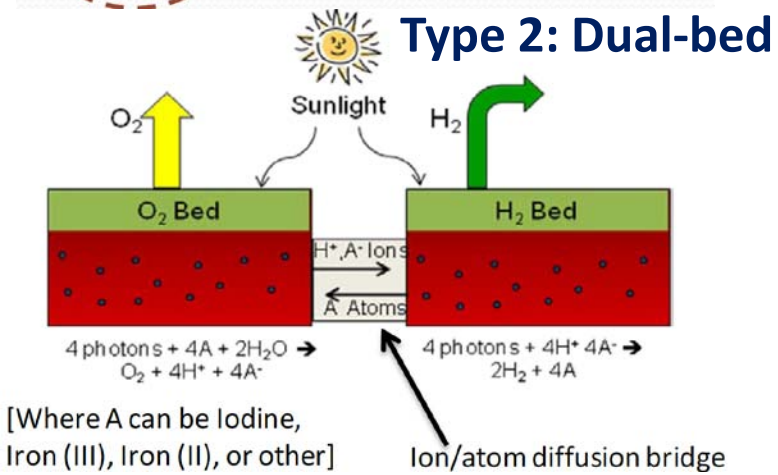
PEC

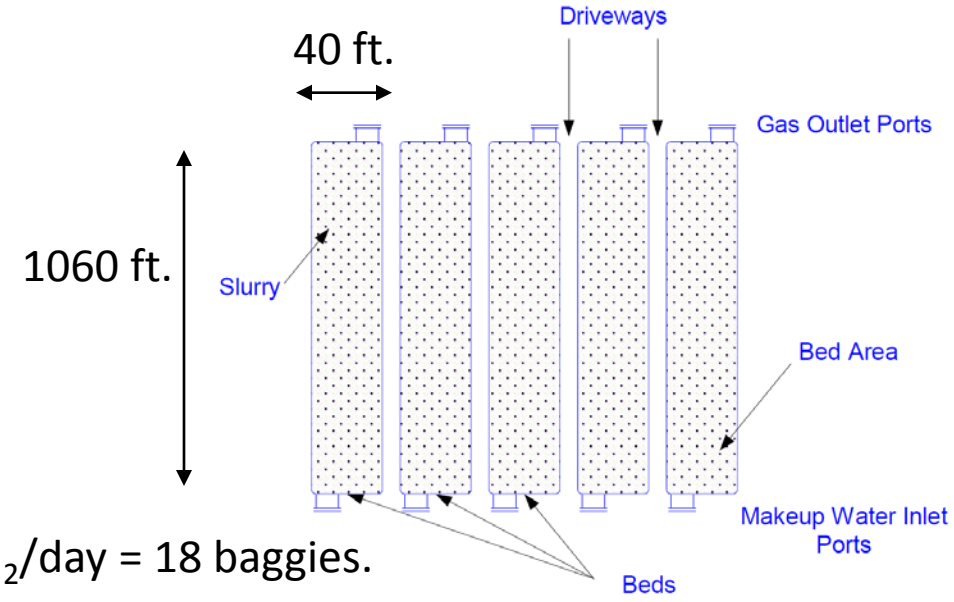
B.D. James, G.N. Baum, J. Perez, K.N. Baum, DTI Technologies, Inc. "**Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production**," DOE Report (2009) Contract # GS-10F-009J.

Reactor Types 1 & 2: Colloidal Suspensions

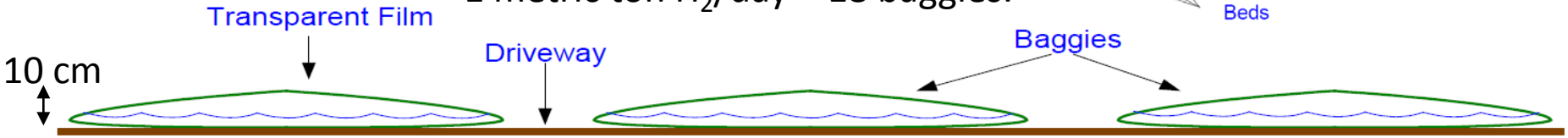




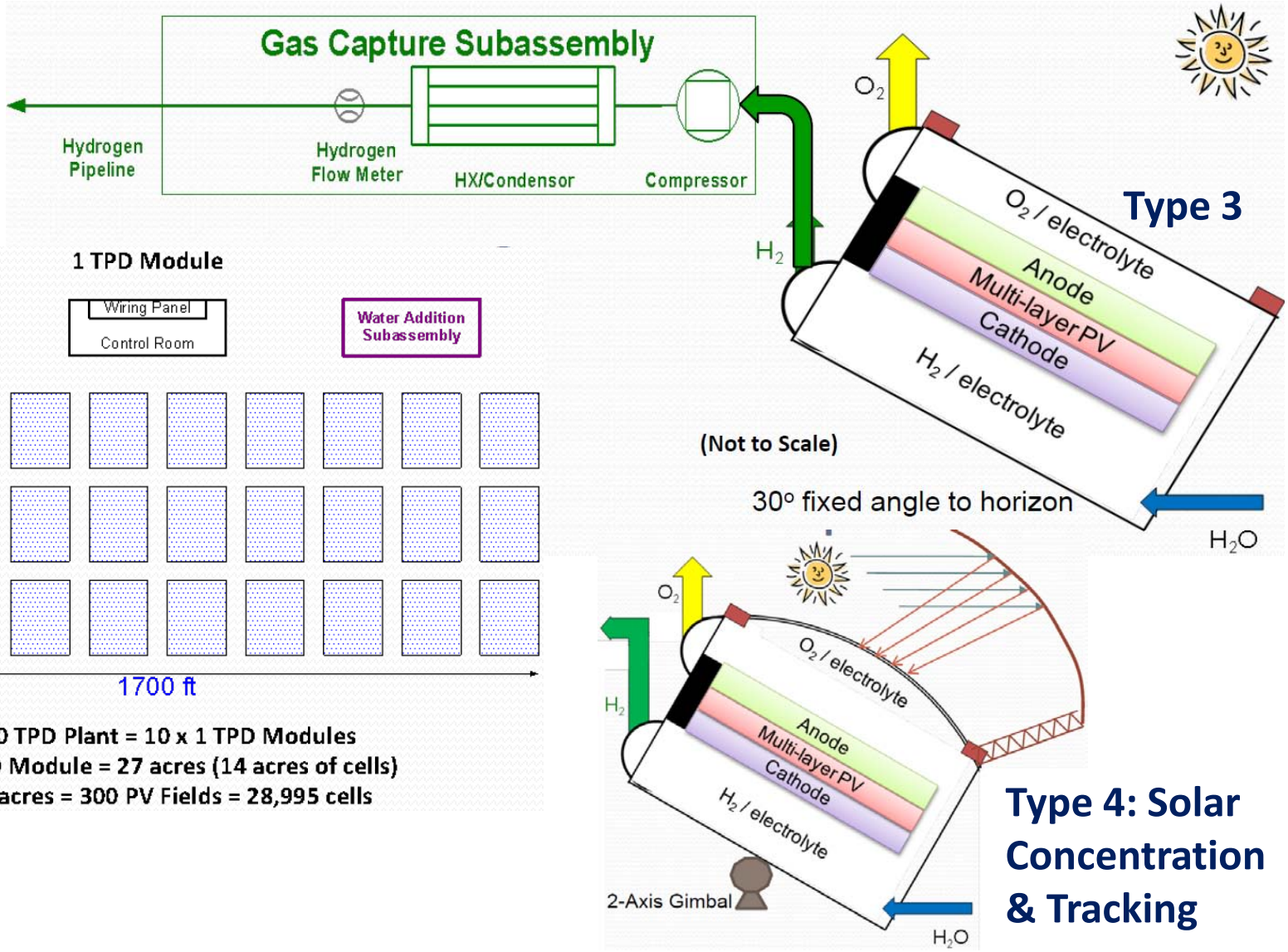




1 metric ton H_2/day = 18 baggies.



Reactor Types 3 & 4: Planar PEC Array



The Bottom Line: Costs of PEC-derived H_2

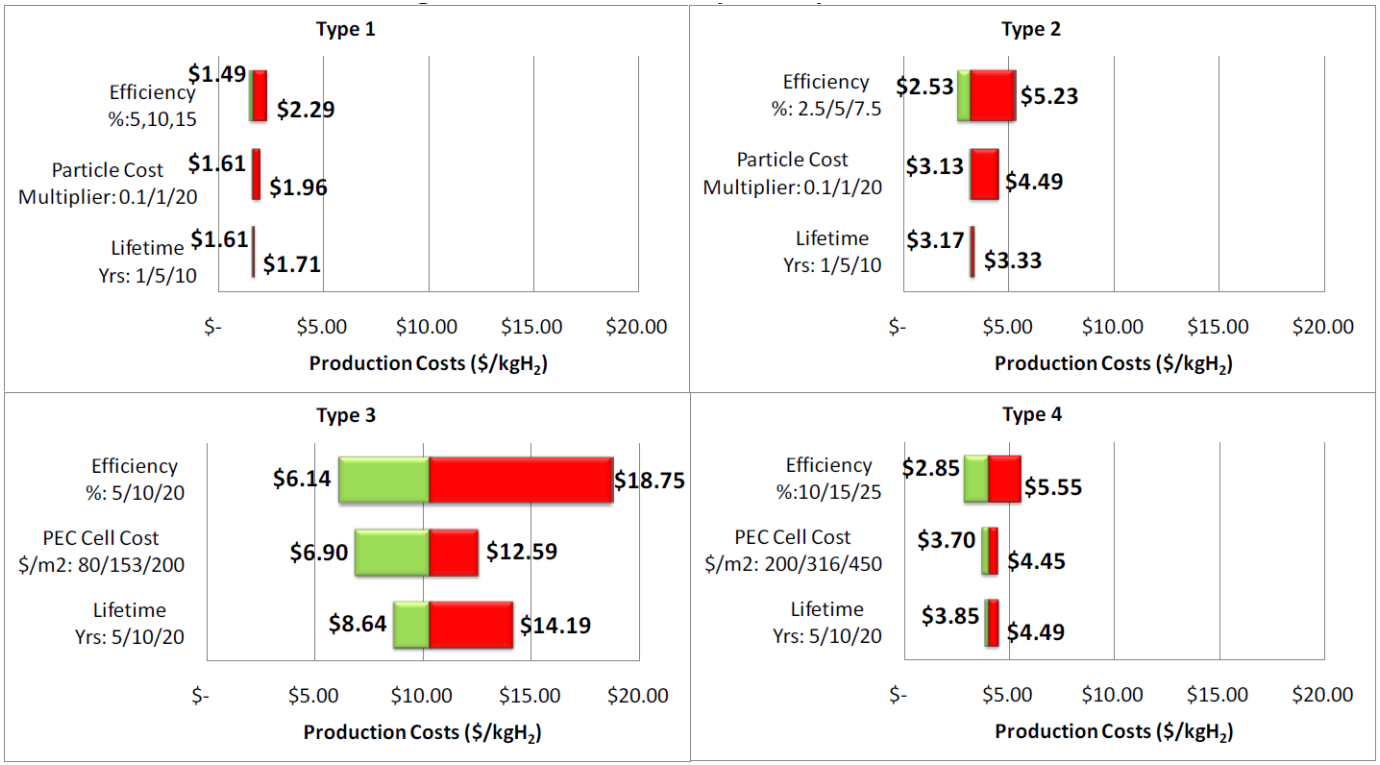
Recall that 1 kg H_2 is the energy equivalent to 1 gallon of gasoline.

Type 1 Sensitivity Analysis Parameters		
Efficiency	Particle Cost	Particle Lifetime
5%	0.1x	1 Year
10%	1x	5 Year
15%	20x	10 Year

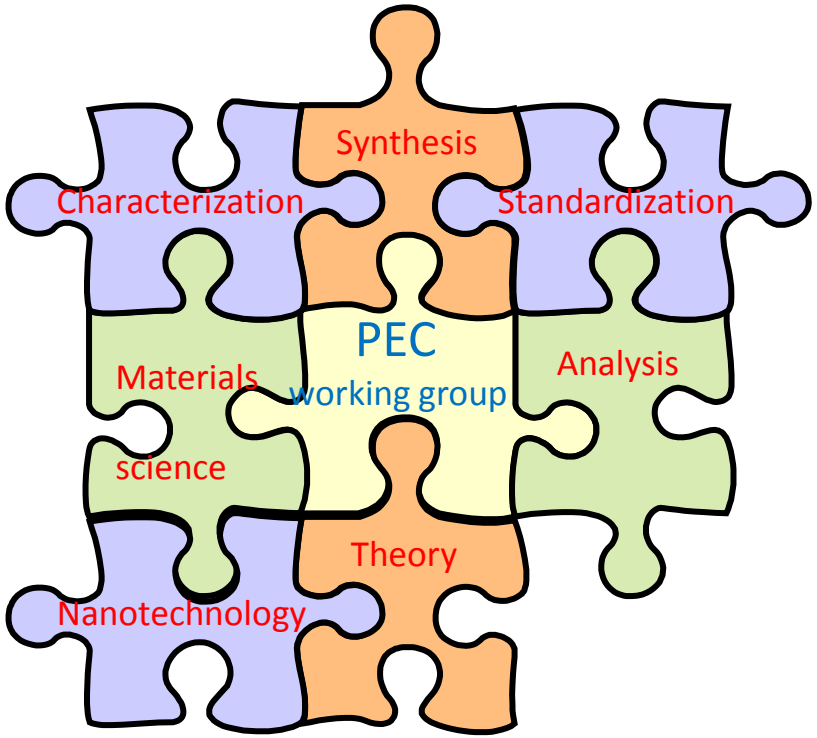
Type 2 Sensitivity Analysis Parameters		
Efficiency	Particle Cost	Particle Lifetime
2.5%	0.1x	1 Year
5%	1x	5 Year
7.5%	20x	10 Year

Type 3 Sensitivity Analysis Parameters		
Efficiency	PEC Cell Cost	PEC Cell Lifetime
5%	$80/m^2	5 year
10%	$153/m^2	10 year
20%	$200/m^2	20 year

Type 4 Sensitivity Analysis Parameters		
Efficiency	PEC Cell Cost	PEC Cell Lifetime
10%	$200/m^2	5 year
15%	$316/m^2	10 year
25%	$450/m^2	20 year



Take-home message from the techno-economic analysis:
Cost-competitive H_2 ($2/kg-$5/kg) can be produced by photocatalysis & PEC *if* appropriate materials can be developed. This motivates the need for research to overcome materials challenges.

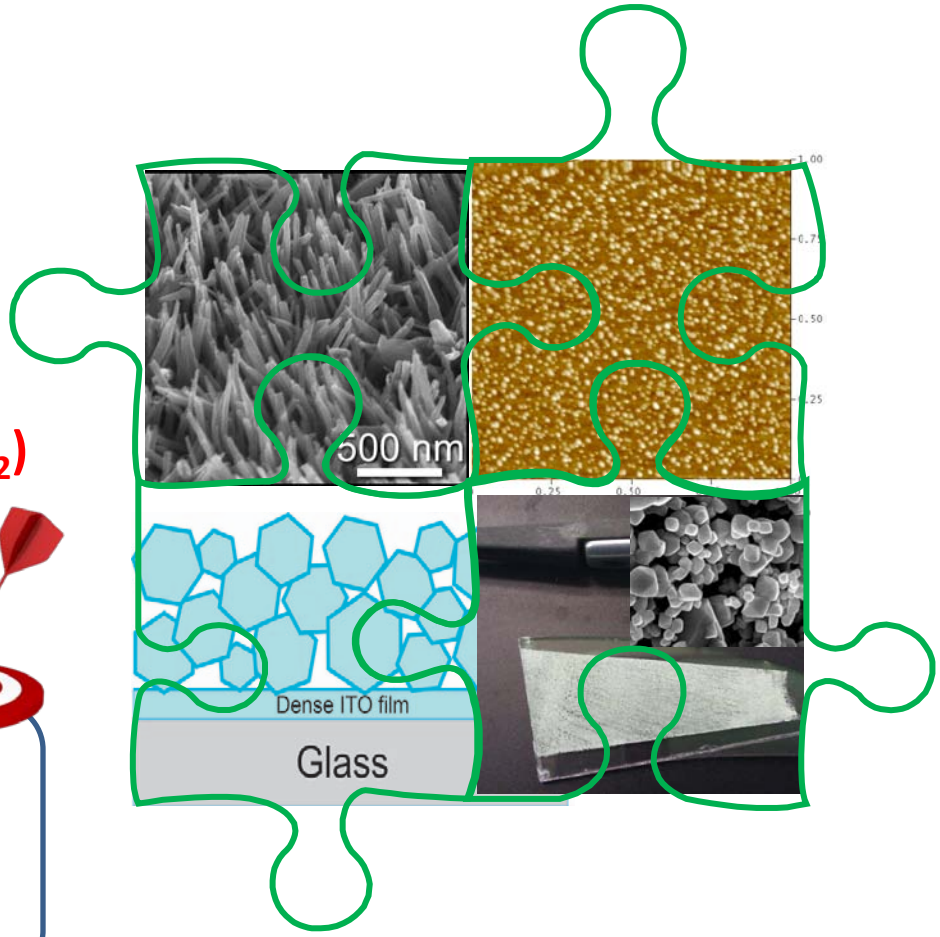


PEC Working Group:

Evaluating working directions

Sharing and building-up knowledge

Accelerating research progress



- **3rd Generation PEC materials (nano-MoS_2)**
- **Transparent conducting oxide (TCO) scaffolds/substrates for PEC**

DOE Targets: >1000h @STH > 8% (2013)

$2 - 4/kg H_2 projected PEC cost

(beating >$10/kg H_2 for PV-electrolysis)

Overview

Timeline

- Start Date: Dec 2008
- End Date: Oct 2011*
- 75% complete

Barriers

- Y. Materials Efficiency
- Z. Materials Durability
- AA. PEC Device and System Auxiliary Material

Budget

- Total project funding
  - DOE - $258k
  - Contractor - $64k
- Funding received in FY10
  - $128k
- Funding for FY11
  - *Project continuation and direction determined annually by DOE

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. Louisville, U. Hawaii, UNLV, UCSB, MV Systems, The PEC WG
- Project Lead: Thomas F. Jaramillo

Project Relevance

The **main objective** of this 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)
AA. PEC Device and System Auxiliary Material	- Need a transparent, conducting, high surface area scaffold for nanomaterials.	- Such a photoelectrochemical substrate could be applicable to a wide range of PEC materials.

Relevance: Project Objectives

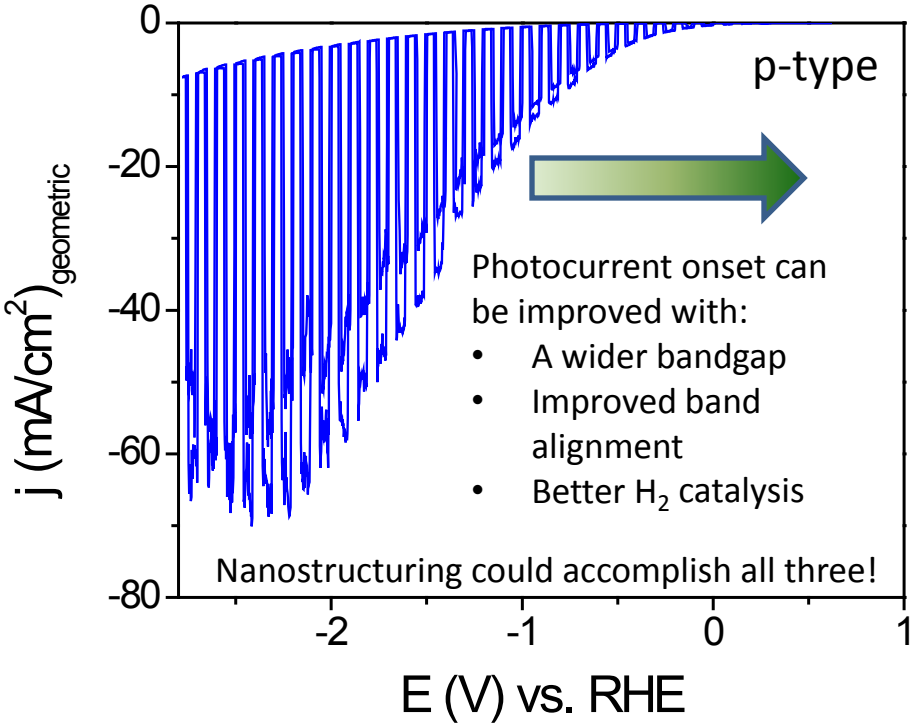
1. Fundamental Science of MoS_2 (primarily funded through DOE BES as part of an EFRC @ Stanford "CNEEC")
   - Barrier Y. To develop **efficient** PEC materials consisting of nanostructured MoS_2 with:
     - a wider bandgap
     - improved band alignment with respect to H_2 and O_2 evolution potentials
     - improved surface catalytic properties
   - Barrier Z. To develop **durable** MoS_2 photo-cathodes

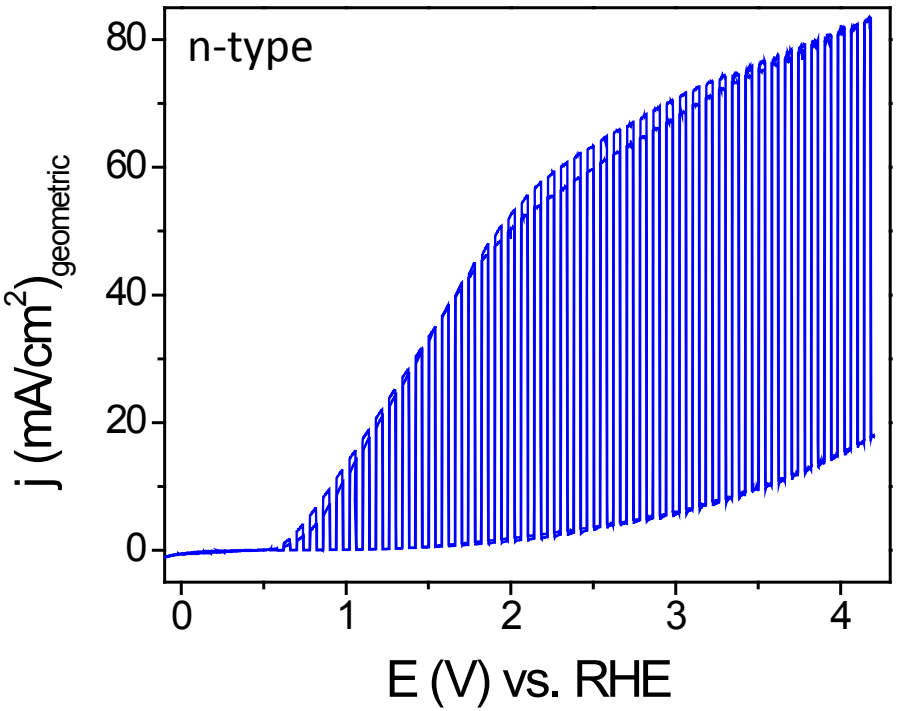
2. Applied research in PEC (funded entirely through DOE EERE Hydrogen and Fuel Cells program)
   - Barrier AA. To develop **photoelectrode substrates** with:
     - Macro-porosity (> 50 nm)
     - High surface area
     - Optical transparency
     - Excellent conductivity

Relevance: Improving PEC Efficiency (MoS_2)

PEC measurements of bulk MoS_2 crystals

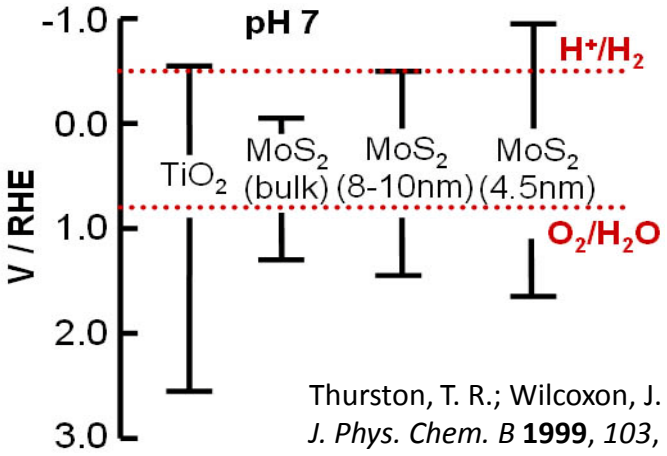
- Up to ~60 mA/cm^2 under ~ 10 suns illumination
- However, a large bias is required!
- Different types of MoS_2 conductivity
  - p-type: photo-cathodic H_2 evolution.
  - n-type: photo-anodic corrosion.





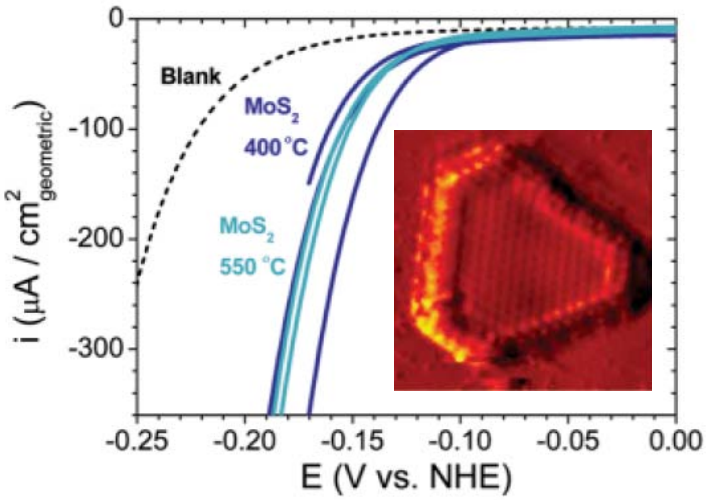
Approach: Bulk MoS_2 vs. Nano MoS_2

- Bulk MoS_2
  - Mismatched bands
  - Poor charge transport
  - Poor catalytic activity



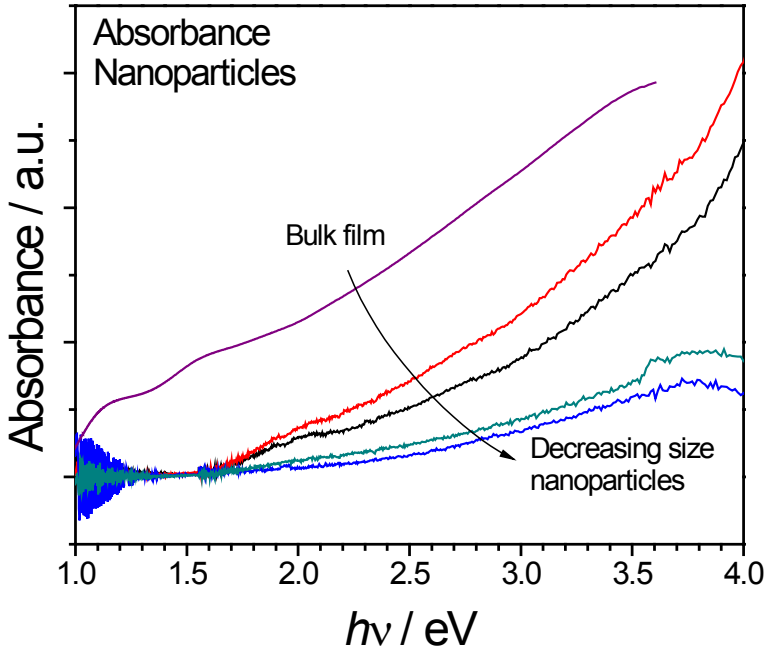
Thurston, T. R.; Wilcoxon, J. P. *J. Phys. Chem. B* **1999**, *103*, 11

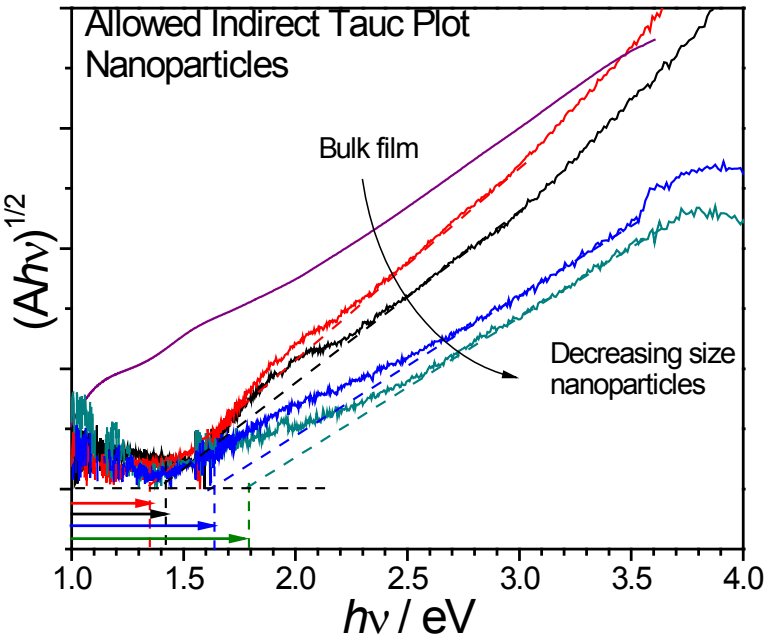
- Nano-MoS_2
  - Bands straddle water splitting
  - Shorter charge transport distances
  - High catalytic activity



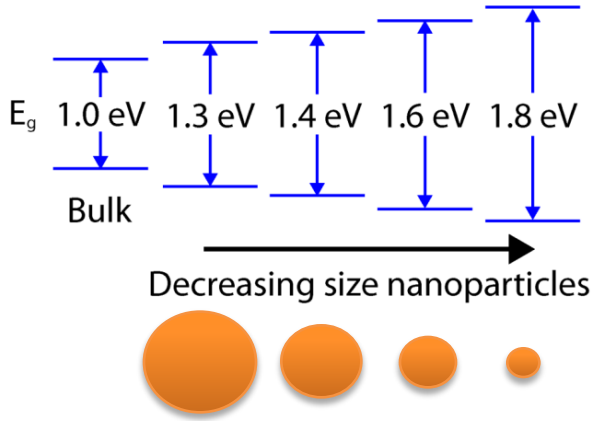
Jaramillo, et al. *Science* **2007**, 317, 100

Technical Accomplishments: Previous Work on Bandgap Engineering of MoS_2 nanoparticles





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.

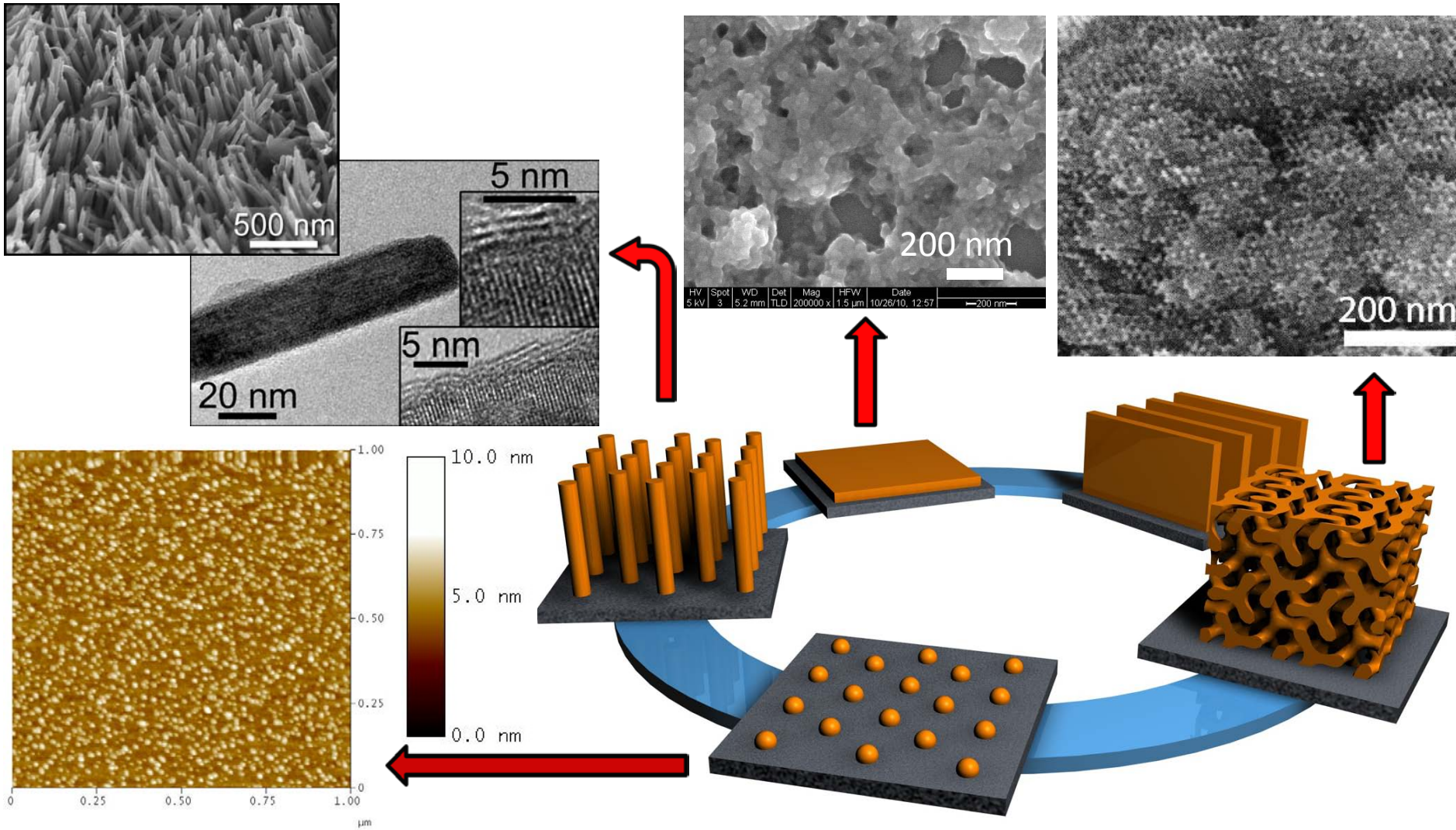


Blueshift in bandgap with decreasing size.

Approach: Milestones

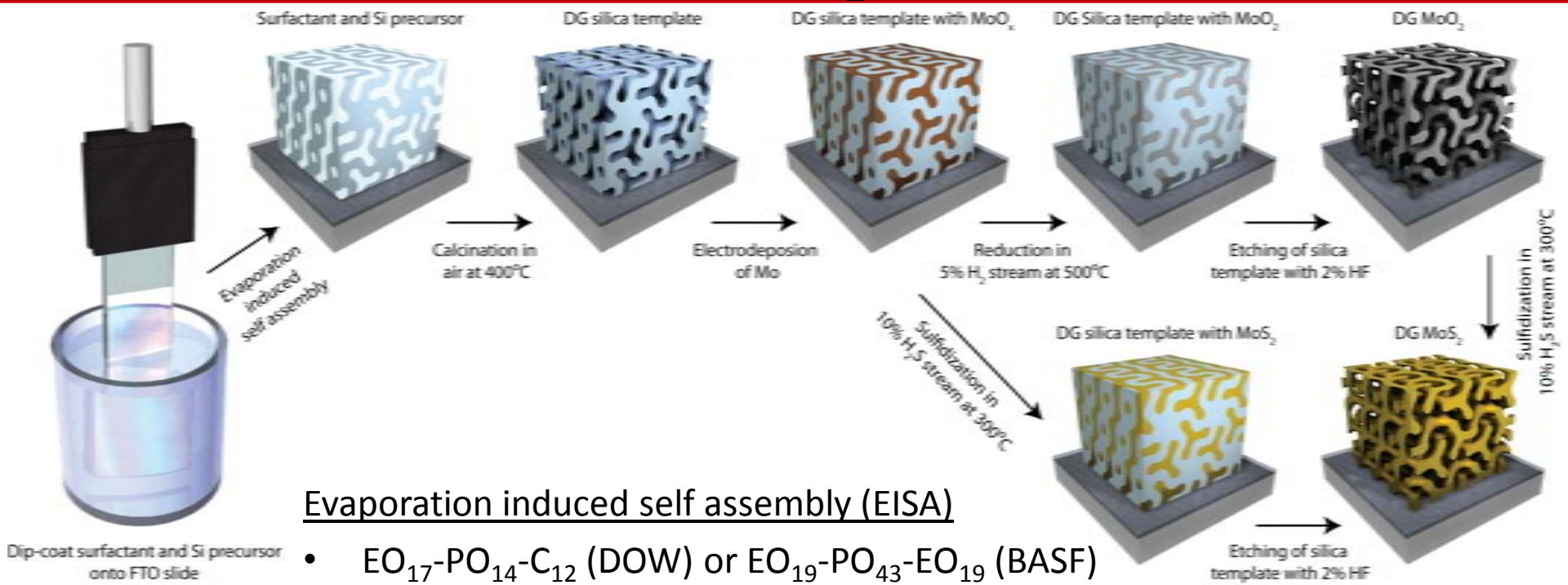
Milestones	Progress Notes	Comments	% Comp.
Develop a transparent conducting oxide (TCO) 3-D scaffold upon which MoS_2 and WS_2 nanostructures can be deposited, and characterize resulting devices.	A high surface area 3-D TCO scaffold has been developed.	Next step is to incorporate PEC materials such as MoS_2.	80 %
Correlate physical characterization test results with photoelectrochemical performance to tune subsequent syntheses in an effort to optimize water splitting efficiency and photoelectrode stability.	Nanostructures show PEC activity.	3-D TCO scaffolds will soon be used to enhance activity and efficiency.	70 %

Technical Accomplishments & Progress: Synthesis of MoS_2 Nanostructures



Take-home message: We have synthesized and studied a wide range of MoS_2 nanostructures.

Technical Accomplishment: Synthesis of a nano-structured MoS_2 Double Gyroid



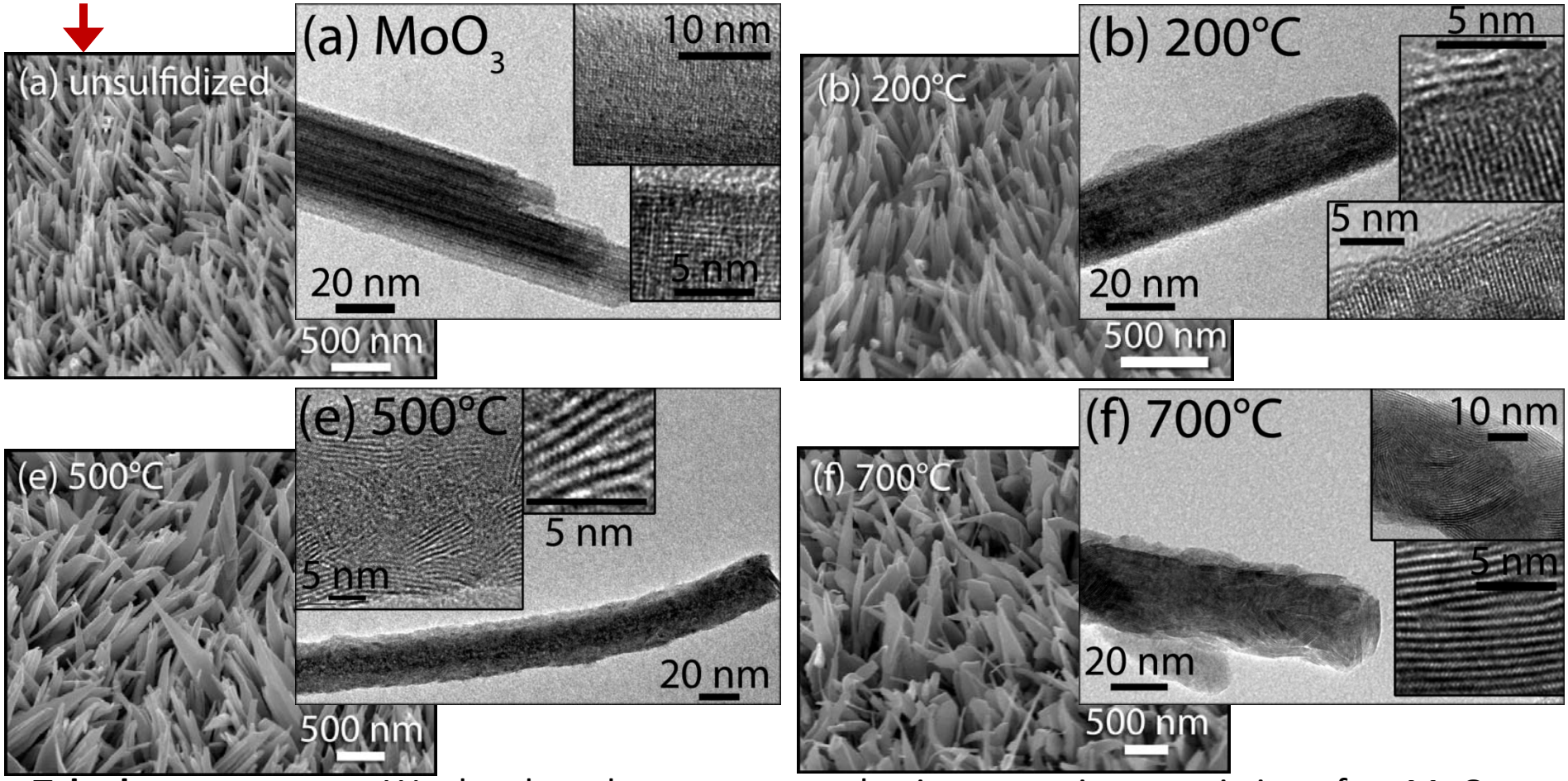
Evaporation induced self assembly (EISA)

- EO_{17}-PO_{14}-C_{12} (DOW) or EO_{19}-PO_{43}-EO_{19} (BASF)
- Tetraethylorthosilicate (TEOS) silica precursor
- Careful control of humidity during synthesis

Take-home message: We developed a route to synthesize a nano-structured double-gyroid film of MoS_2.

Technical Accomplishment: Synthesis of MoO_3-MoS_2 core-shell nanowires

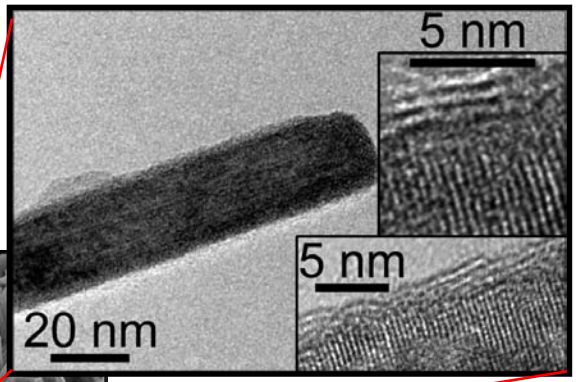
In collaboration with Prof. Mahendra Sunkara, University of Louisville, who grows the pure MoO_3 nanowires by hot wire chemical vapor deposition (CVD).

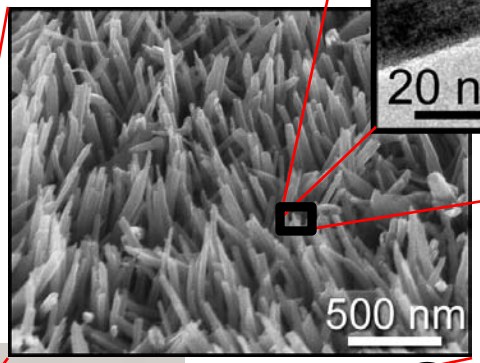


Take-home message: We developed a route to synthesize nanowires consisting of an MoO_3 core and an MoS_2 shell, with exquisite control of the shell thickness via sulfidation temp.

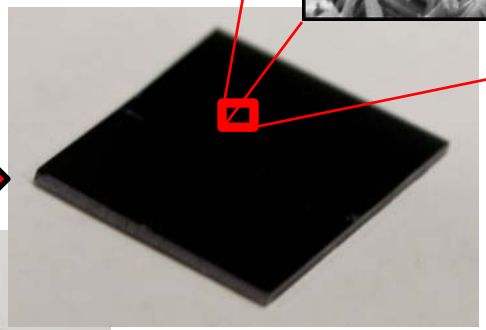
Technical Accomplishment: Excellent Photon Absorption by core-shell MoO_3-MoS_2 Nanowires

Take-home message:
The MoS_2 shell provides for excellent light-trapping, > 90 % of the light is absorbed with a shell only ~ 5 monolayers thick (200 °C sulfidation). The sample is black and opaque.

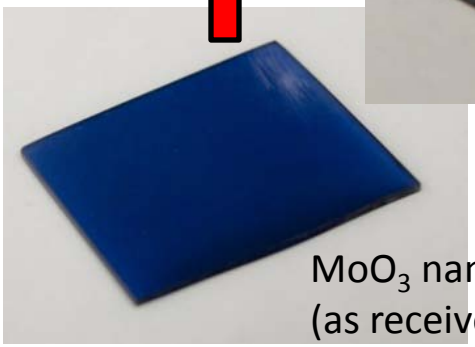




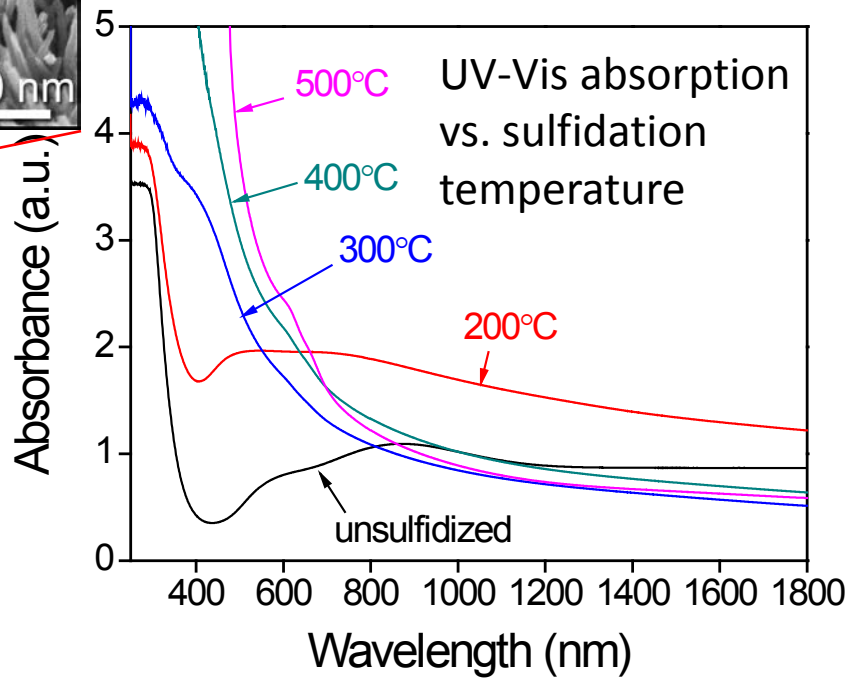
200 °C in
10% H_2S
90 % H_2



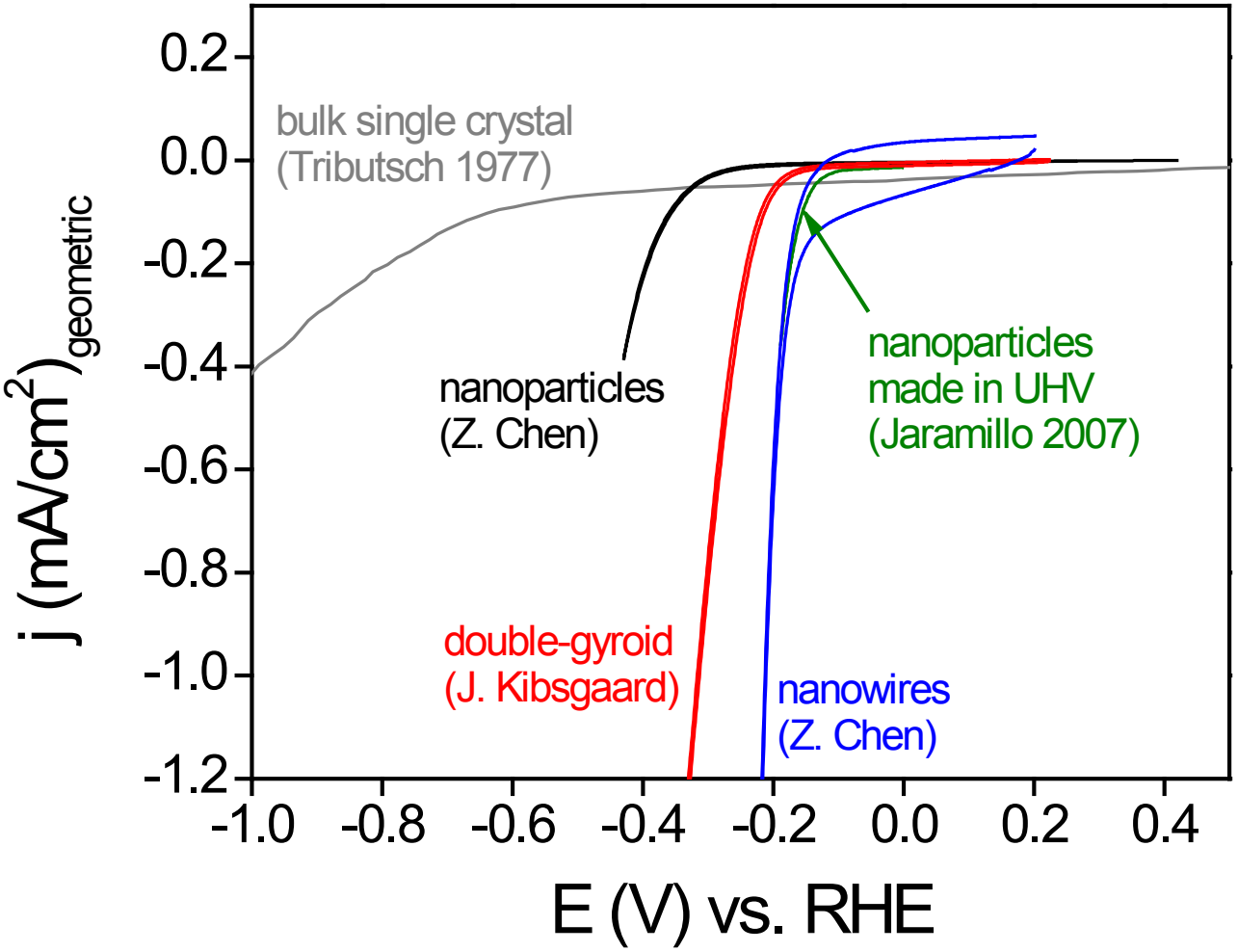
Core-shell MoO_3 –MoS_2 nanowires after sulfidation.



MoO_3 nanowires before sulfidation
(as received from Univ. of Louisville)

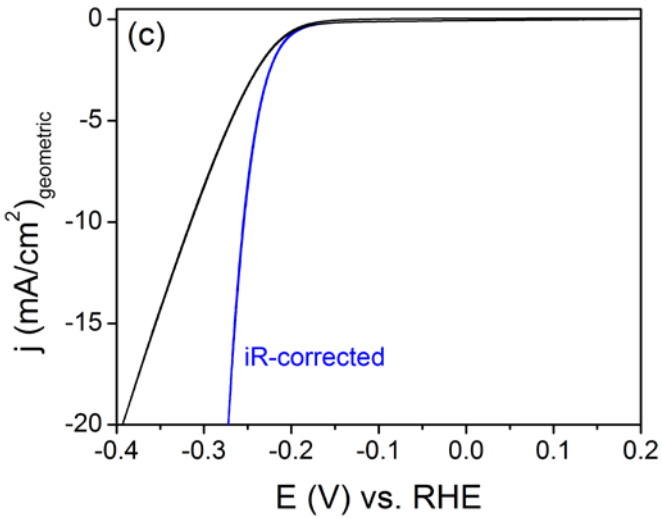


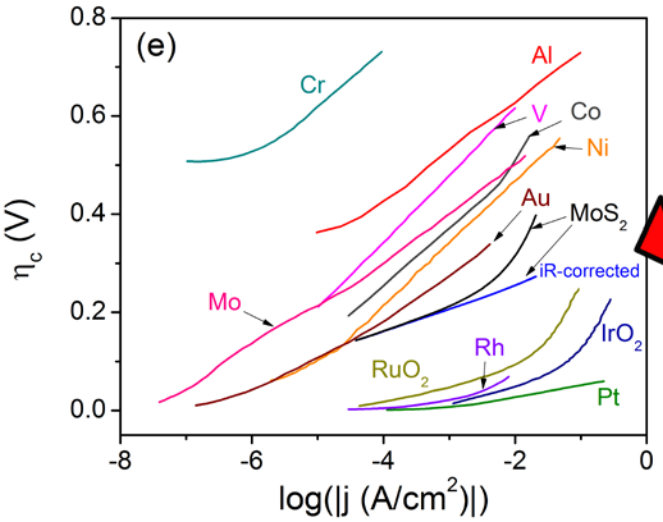
Technical Accomplishment: Excellent electrocatalytic H_2 evolution by nano-MoS_2



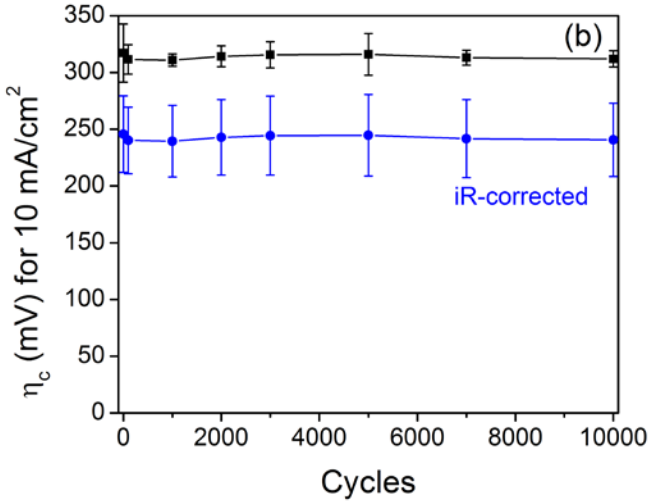
Take-home message: The MoS_2 nanostructures that we have developed are all active H_2 electrocatalysts.

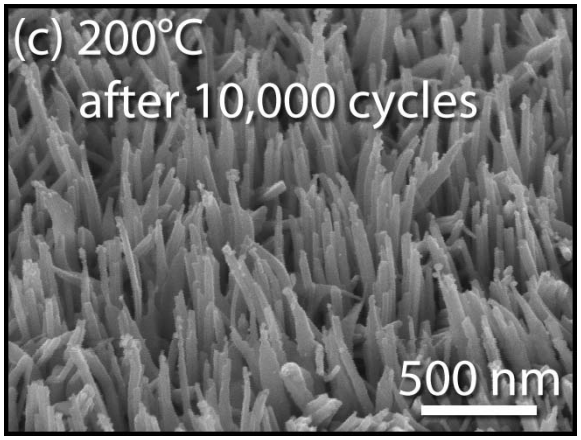
Technical Accomplishment: Highly active, highly stable H_2 evolution electrocatalysis by core-shell MoO_3-MoS_2 Nanowires





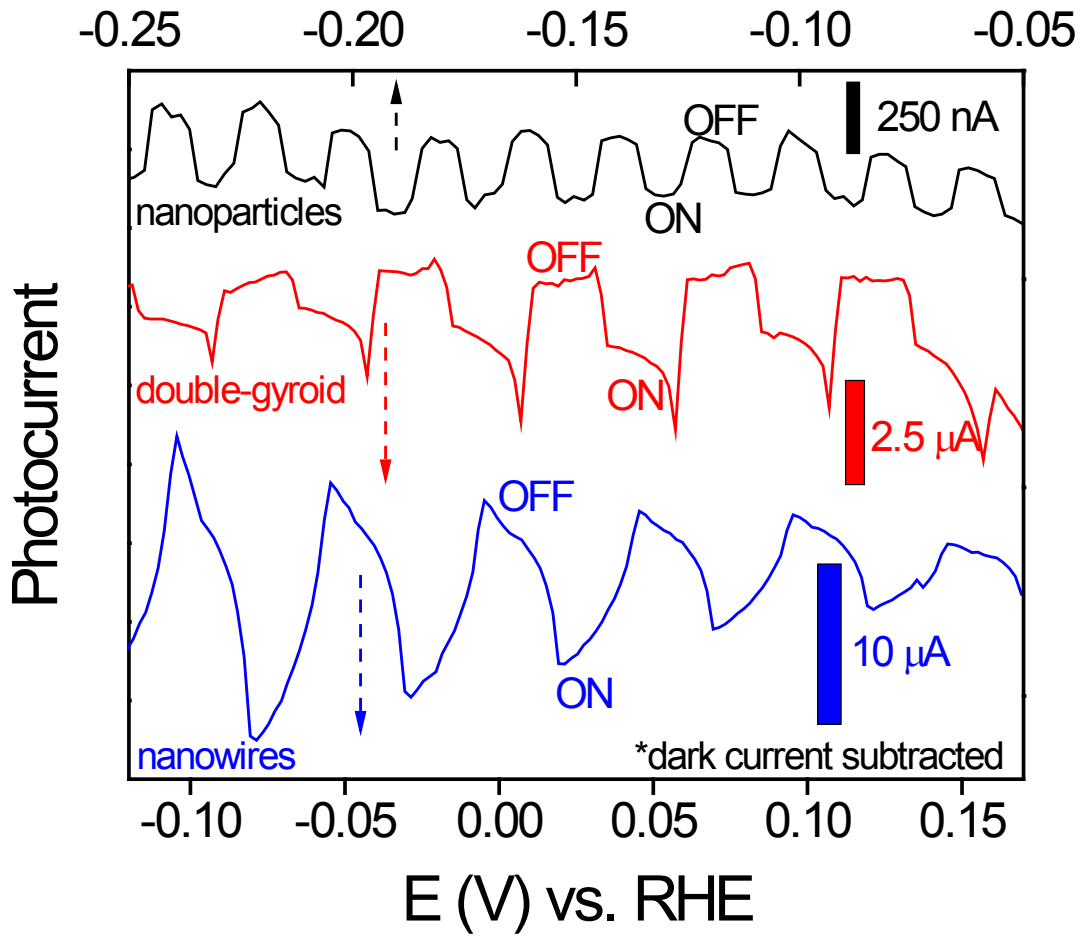
Core-shell MoO_3-MoS_2 Nanowires



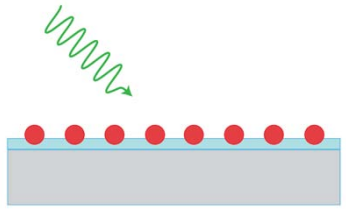


Take-home message: Among non-precious metal catalysts, this is **the most active** H_2 evolution catalyst ever reported in an acidic environment. It is **100% stable** even after 10,000 cycles.

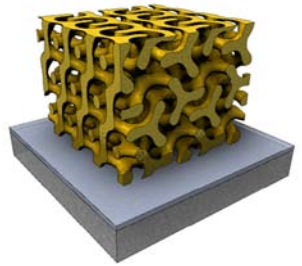
Technical Accomplishments: PEC Characterization of Nanostructured MoS_2



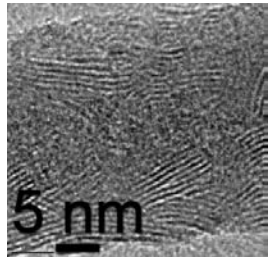
- Absorption limitations in nanoparticle submonlayer



- Charge transport and Diffusion limitations in double-gyroid

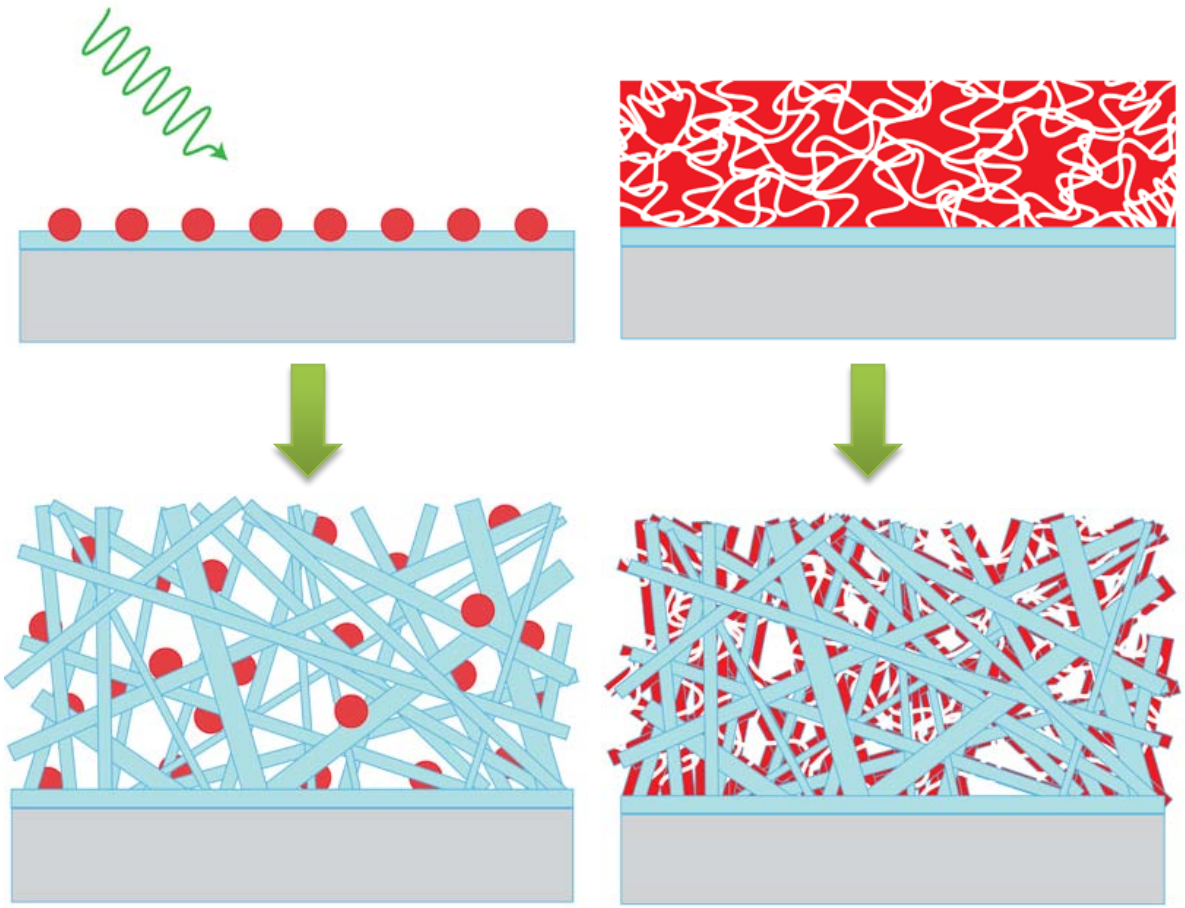


- Hole transport limitations in nanowires



Take-home message: Nano-MoS2 is PEC active, but with low efficiency – there is a need to develop a PEC substrate: a high-surface area, transparent, conducting material upon which nanostructured MoS_2 can be deposited.

Relevance: Photo-electrochemical Substrate Development



Take-home message: A photo-electrochemical substrate that is transparent, conducting, high surface area, and macroporous would be of significant value to the engineering of PEC materials as it allows for effectively long absorption paths through nanomaterials without requiring charge transport over long distances through the semiconductor.

Approach: ITO of different length-scales

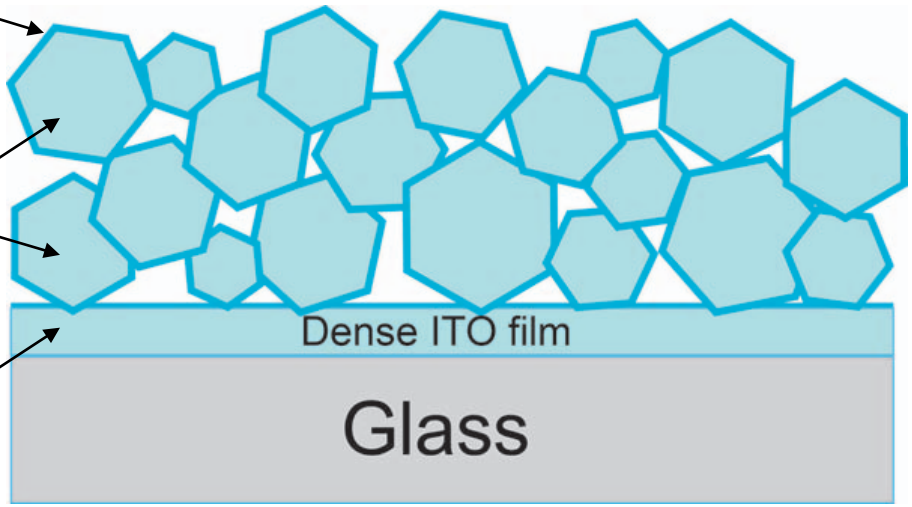
Indium-tin oxide (ITO) is a common transparent conducting oxide (TCO) material that is used extensively in PEC as well as other related fields such as dye-sensitized solar cells (DSSCs).

Three different forms of ITO are employed to produce the desired substrate architecture.

ITO sol-gel coating (~20-100 nm)

Large, commercial ITO particles (microns)

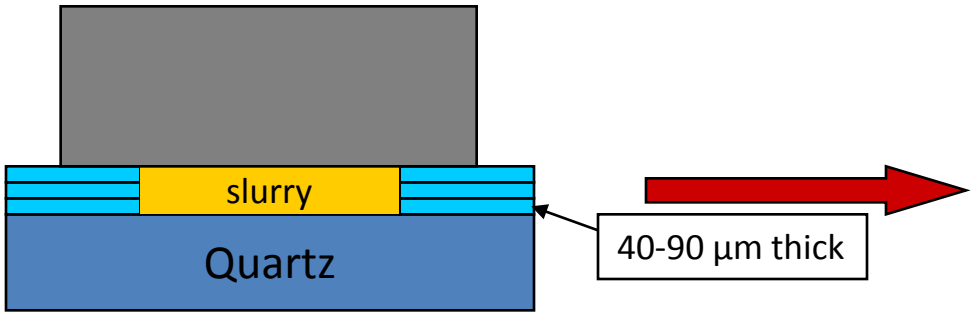
Dense ITO film on Glass



Take-home message: Our approach is to combine two different length scales of ITO to form a 3-Dimensional macroporous film: The large, commercial ITO crystals (microns) allow for high conductivity while the ITO sol-gel coating (which produces 20-100 nm crystals) serves to adhere the large crystals to one another and to the dense, commercial ITO film .

Technical Accomplishment: Synthesis of a photo-electrochemical substrate/scaffold

"Doctor Blade" technique



Precursor slurry:

- ITO powder (9:1, In:Sn)
- Indium (III) acetylacetonate
- Tin (IV) chloride
- Sol precursor ratio, 9:1, In:Sn
- HCl
- EtOH

Heat treatment

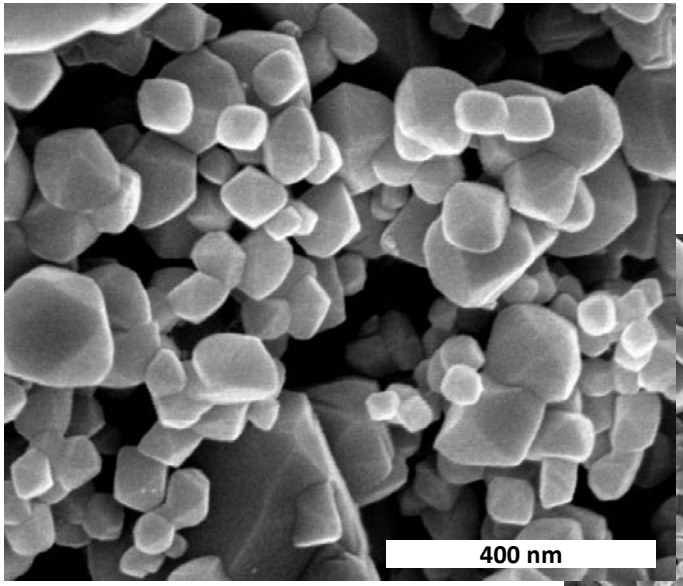
1) 300 C @ 0.3 C/min in air
   - Controlled condensation and dehydration of sol-gel

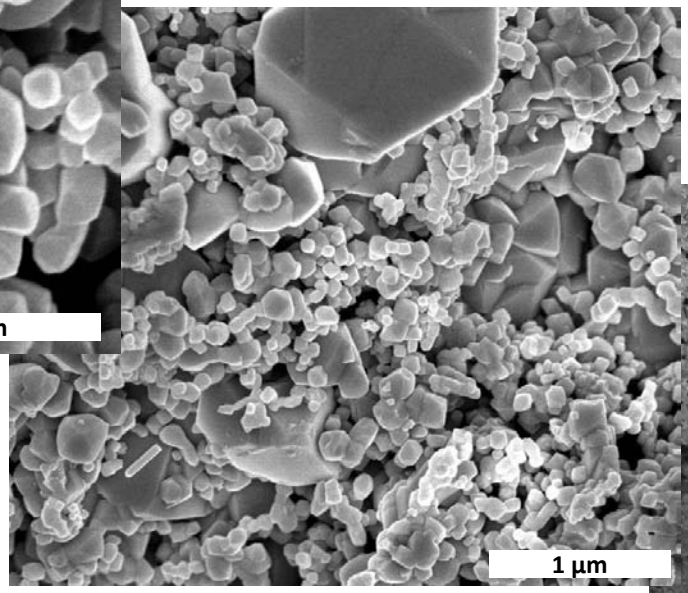
2) 450 °C @ 10 °C/min in air
   - Induce crystallization of gel

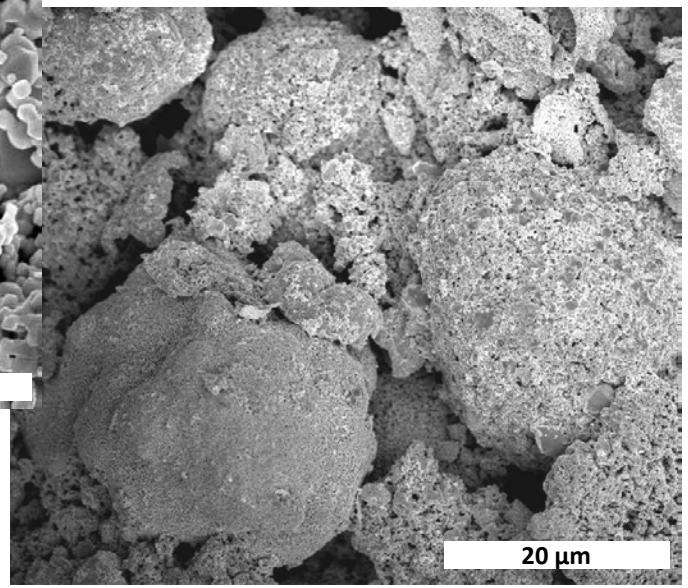
3) 450 °C @ 10 °C/min in N_2
   - Create oxygen defects to increase conductivity

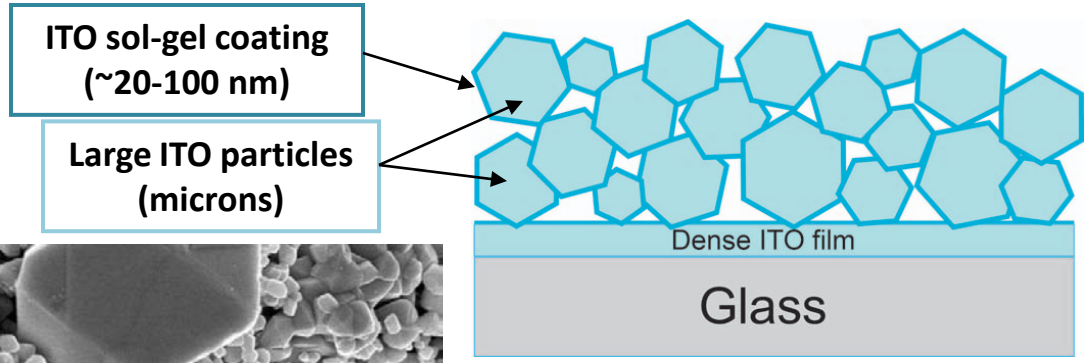
Take-home message: We have developed a scalable synthetic route involving low-cost materials and simple solution processing to produce a thick, macroporous ITO film on top of a thin, dense, commercial ITO film on glass.

Technical Accomplishment: Physical characterization of the Photoelectrochemical Substrate



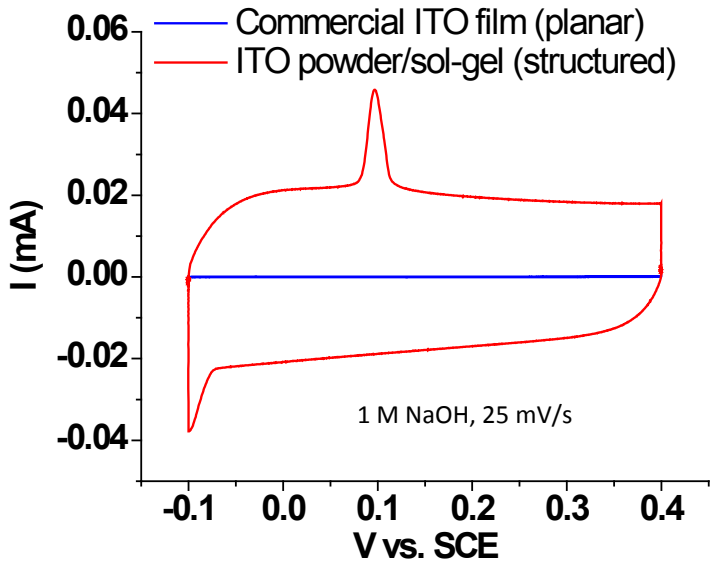


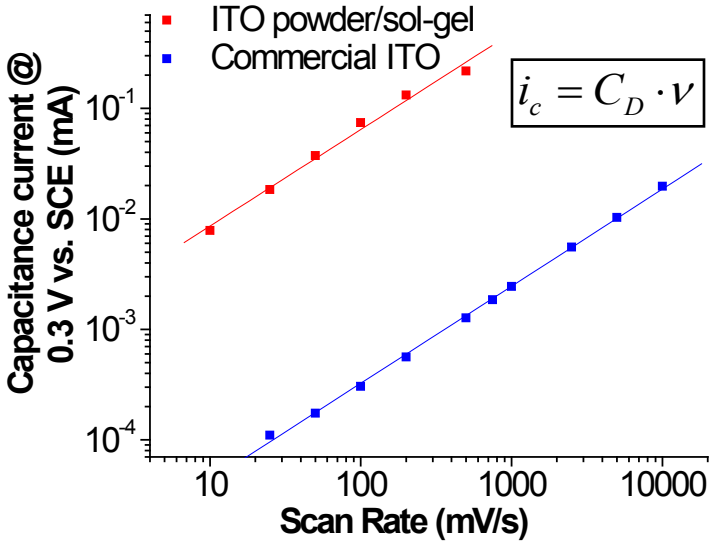




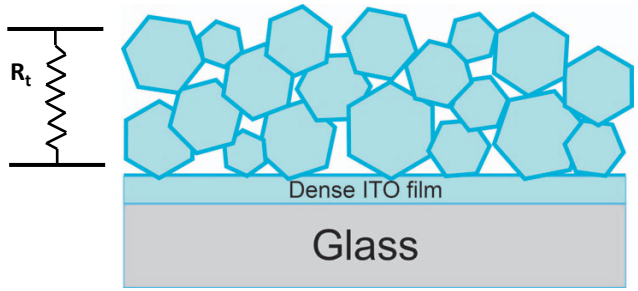
Take-home message: The synthetic route we have developed is a facile solution phase synthesis that combines large crystallites with small crystallites to yield a film with high conductivity, tunable film thickness, tunable surface area, and is scalable to large area PEC device panels

Technical Accomplishment: Achievement of a Milestone for a Photoelectrochemical Substrate





- Sheet resistance on quartz substrate:
  - 0.5 – 2.0 kΩ/□
- Transverse resistance (R_t)
  - ~1 Ω/10 µm



200 fold increase in surface area!

- Thickness (t) = 100 µm… R_t = ~10 Ω

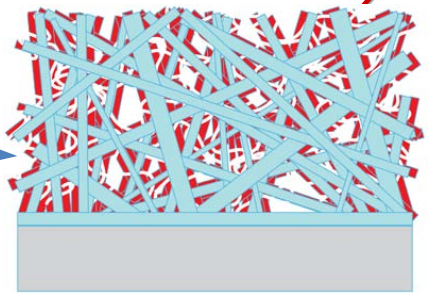
Take-home message: We have hit our target of developing a photo-electrochemical substrate that is transparent, conducting, high surface area, and macroporous.

Proposed Future Work: Enabling performance gains for charge-transport limited materials

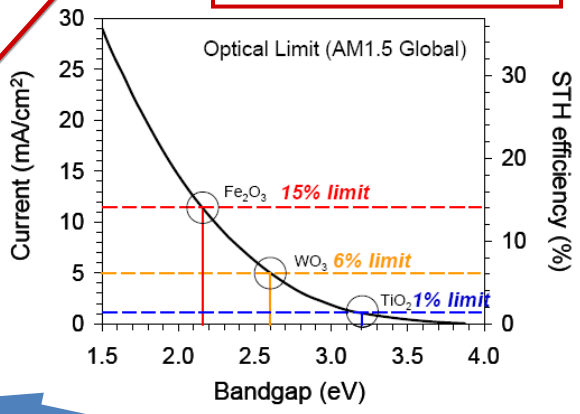
Future Work: To deposit MoS_2 and other PEC materials known to have charge-transport limitations (e.g. Fe_2O_3) onto the recently developed macroporous, high surface area, ITO scaffolds.

MoS_2

Thin MoS_2 film =
high resistivity, low *hv* absorption

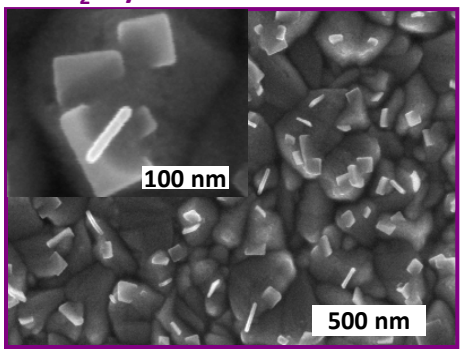


Fe_2O_3 Hematite



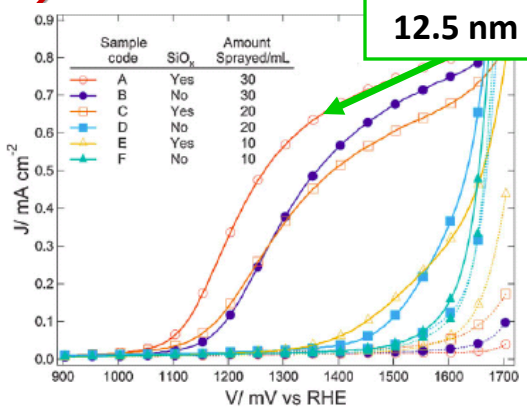
J. Mater. Res, **2010**, 25, 3-16

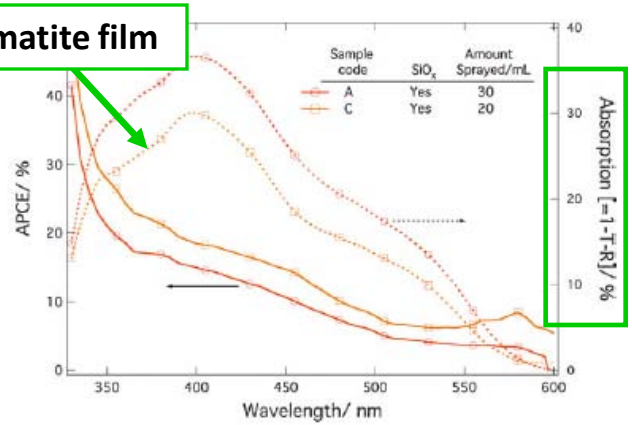
MoS_2 crystals on FTO substrate



Thin hematite film = high performance, low *hv* absorption

12.5 nm hematite film





M. Gratzel, et.al., *Adv. Funct. Mater.* **2010**, 20, 1099-1107

Collaborations

- University of Louisville, Kentucky
  - Collaboration with Prof. Mahendra Sunkara to develop core-shell MoO_3-MoS_2 nanowires for PEC.
    - 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.
- 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 vs. PV-Electrolysis Hydrogen.
    - all supported by DOE H_2 program.
- MV Systems, Inc.
  - Surface modifications of their triple-junction Si-based devices.
    - supported by DOE H_2 program.

Active collaborations take place via frequent (e.g. weekly) conference calls as well as meetings in-person during DOE quarterly working group meetings.

Summary

- **Relevance**

  The **2 objectives** of the project are to:
  #1. Develop new **PEC materials** based on nano-structured MoS_2 that can potentially meet DOE performance targets (2013 and 2018).
  #2. Develop **PEC substrates** consisting of macroporous, high surface area, transparent, conducting oxides upon which PEC materials can be loaded.

- **Approach**

  #1. The approach is to nanostructure MoS_2 in order to tailor its bulk and surface properties for PEC.
  #2. The approach is to use solution-based processing to combine ITO particles with two distinct lengthscales – ~50 nm and ~1 micron.

- **Technical Accomplishments & Progress**

  #1. We have developed MoS_2 nanostructures that are highly active H_2 evolution catalysts, however PEC efficiencies remain low.
  #2. We have developed a macroporous scaffold that is transparent, conducting and high surface area – an ideal PEC substrate for MoS_2 and other materials.

- **Collaborations**

  Collaborations with the U. Louisville, NREL, UCSB, U. Hawaii, UNLV, MV Systems, and Directed Technologies, Inc. have been fruitful in terms of material development and exchange of knowledge/expertise.

- **Future Research**

  To deposit MoS_2 and other PEC materials known to have charge-transport limitations (e.g. Fe_2O_3) onto the recently developed macroporous, high surface area, ITO scaffolds.

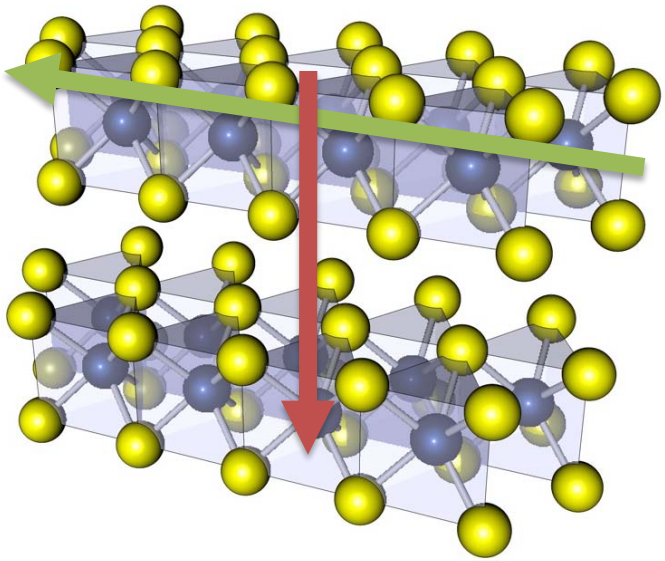
Technical Back-Up Slides

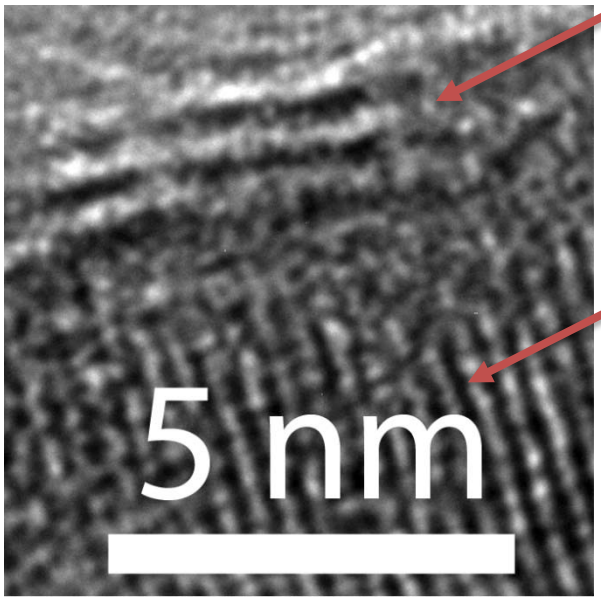
(max of 5)

Charge Transport in Nano-MoS_2

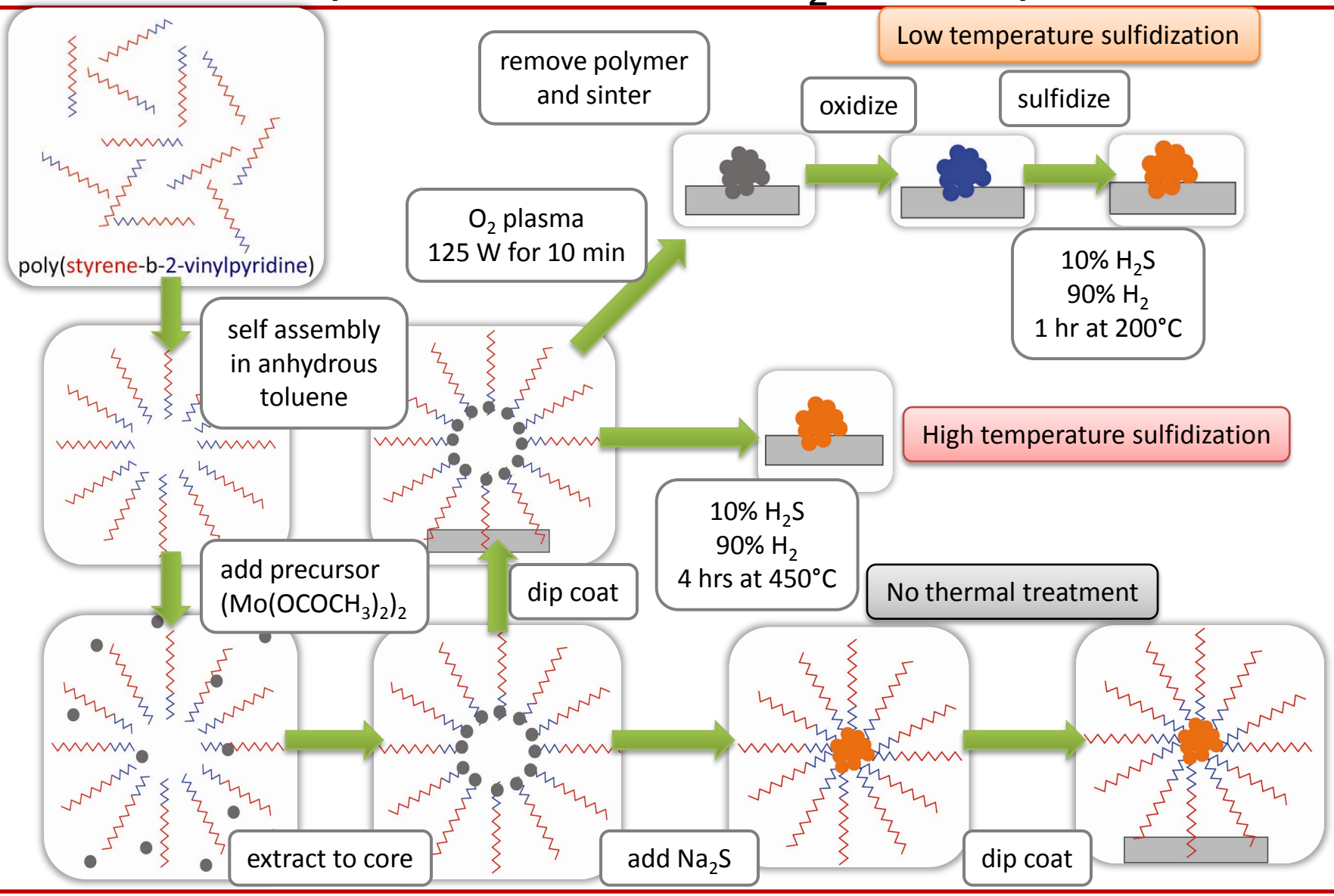
- μ ~ 100-260 cm^2/Vs within layers, ~ 0.1 cm^2/Vs between[1], usually results in R_s ~ 100-200 Ω in bulk
- nanostructuring minimizes distance of e^- and h^+ travel
- R_s < 1 Ω achieved in thin layers!

[1]Tributsch and Bennett, *J. Electroanal. Chem.*, 1977 **81**, 97

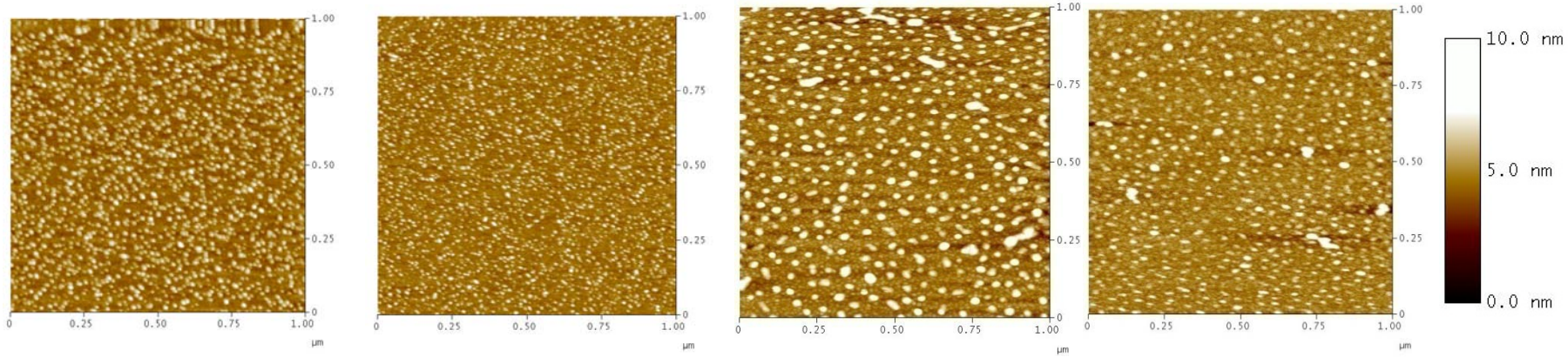




Technical accomplishment: Development of Multiple Routes to MoS_2 Nanoaprticles



Technical accomplishments: Size-control of MoS_2 nanoparticles



27700/4300
PS(266)-*b*-P2VP(41)

32500/7800
PS(313)-*b*-P2VP(74)

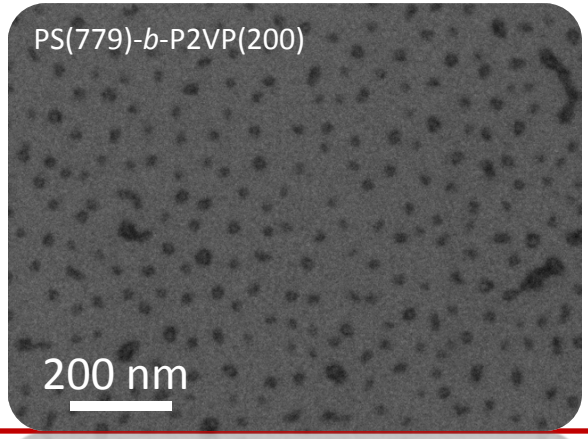
81000/21000
PS(779)-*b*-P2VP(200)

172000/42000
PS(1654)-*b*-P2VP(400)

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

	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

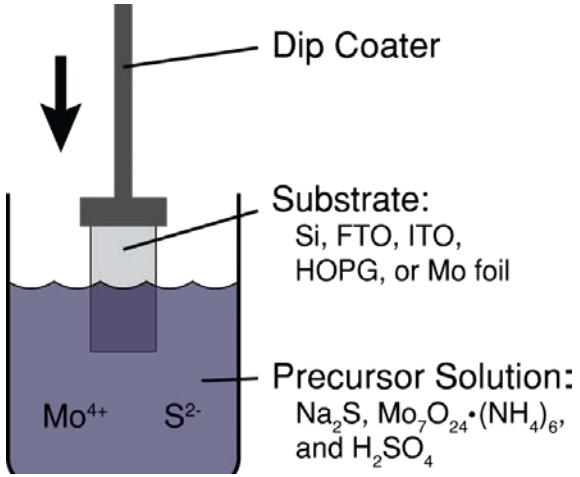
*Measurement limited to microscope resolution

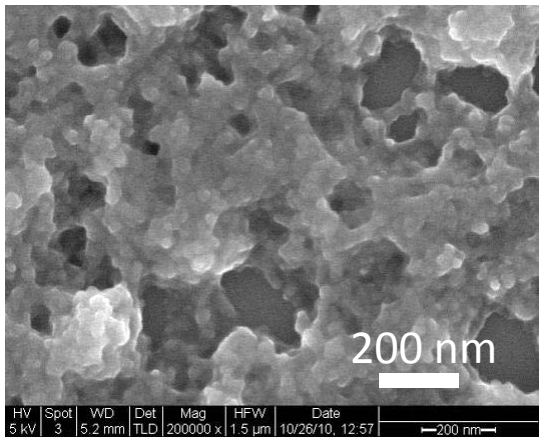


Technical Accomplishment: Development of Ultra-thin MoS_2 films by Chemical Bath Deposition

Synthesis:

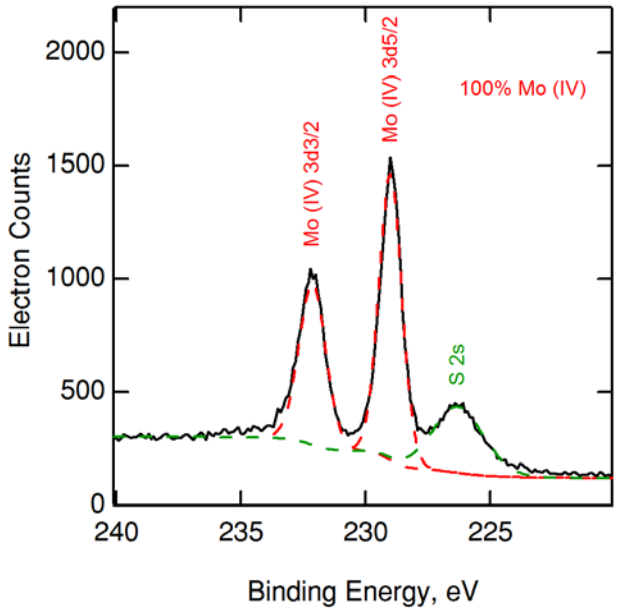
1. Chemical solution deposition
   - Aqueous, room temperature
2. Post-deposition sulfidization
   - 10% H_2S/90% H_2 at 300 C





XPS Characterization:

Peak	Atom %
O 1s	23
C 1s	26
Na 1s	7
Mo 3d	16
S 2p	27

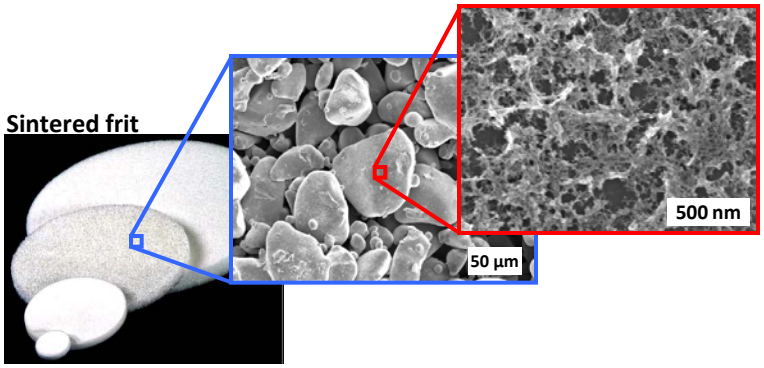


Properties:

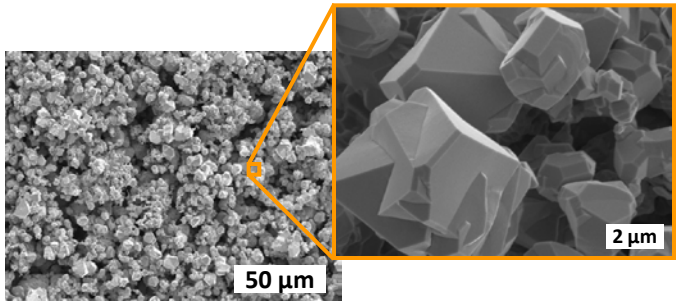
- Conformal coating
- Thickness ~10 nm
- XPS confirms Mo (IV) corresponding to MoS_2

Technical Accomplishment: Alternate Approaches to PEC Substrate Development

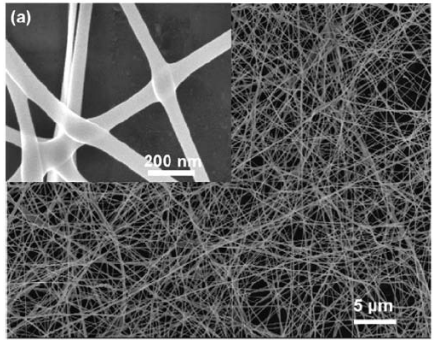
- **ITO Sol-gel on structural glass/quartz frit**
  - Physically robust
  - Poor crystallinity
  - low bulk conductivity
  - MΩ sheet resistance



- **High temp sintering of ITO powder**
  - ~2600 °C, H_2/O_2 torch
  - Superb crystallinity
  - Poor cohesion within film
  - High kΩ – low MΩ sheet resistance



- **ITO nanofiber films**
  - Collaboration with Yi Cui group @ Stanford
  - Flexible films
  - 10-100 kΩ sheet resistance
  - Poor adhesion to substrate
    - Film delamination



Y. Cui *et. al., J. Am. Chem. Soc.*, 2011, 133 (1), pp 27–29